SYMPOSIUM S.CT01

Artificial Intelligence for Material Design, Processing and Characterizations
November 21 - November 30, 2020

Symposium Organizers
Brian Giera, Lawrence Livermore National Laboratory
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Jian Lin, University of Missouri-Columbia
Nav Nidhi Rajput, Stony Brook University

* Invited Paper

SESSION S.CT01.08: Live Lightning/Flash I: Artificial Intelligence for Material Design, Processing and Characterizations
Saturday Morning, November 28, 2020
S.CT01

10:15 AM INTRODUCTORY COMMENTS

10:22 AM DISCUSSION TIME

10:28 AM S.CT01.01.04
De novo Design of Molecules with Low Hole Reorganization Energy Based on a Quarter-Million Molecule DFT Screen (1): DFT Computation and Design Using a Variational Autoencoder/Decoder
Nobuyuki N. Matsuzawa¹, Hiroyuki Maeshima¹, Hideyuki Arai¹, Masaru Sasago¹, Eiji Fujii¹, Karl Leswing², Mathew D. Halls², Tim Robertson², Kyle Marshall², Joshua Staker², Gabriel Marques², Tsubuo Morisato², David Giesen² and Alexander Goldberg²; ¹Panasonic Corporation, Japan; ²Schrödinger Incorporated, United States

Materials exhibiting higher mobilities than conventional organic semiconducting materials (e.g. fullerenes and heteroacenes [1]), are in high demand for applications such as printed electronics. In order to explore new molecules in the heteroacene family that might show improved mobility, a massive theoretical screen of hole-conducting properties of molecules were performed using a cloud computing environment. Over 7,000,000 structures of fused furans, thiophenes and selenophenes were generated, and 250,000 structures were randomly chosen for subsequent DFT (Density Functional Theory) calculations of hole reorganization energies ($\lambda_h$). Utilizing the cloud-computed DFT dataset of a quarter-million reorganization energies, the de novo design method proposed by Gomez-Bombarelli [2] was applied to find further chemical structures with minimal reorganization energy. This method converts molecular structures into continuous variables by applying the variational autoencoder/decoder technique, which enables optimization of chemical structures in a continuous numerical space. Results of the inverse design showed that the method has the ability to generate exotic chemical matter, such as structures with a seven- and eight-membered rings, with reasonably low calculated reorganization energies.


10:34 AM S.CT01.01.05
De novo Design of Molecules with Low Hole Reorganization Energy Based on a Quarter Million Molecule DFT Screen (2)—Application of Deep Reinforcement Learning and Junction Tree Variational Autoencoder
Karl Leswing¹, Mathew D. Halls¹, Tim Robertson¹, Kyle Marshall¹, Joshua Staker¹, Gabriel Marques¹, Tsubuo Morisato¹, David Giesen¹, Alexander Goldberg¹, Nobuyuki N. Matsuzawa², Hiroyuki Maeshima², Hideyuki Arai², Masaru Sasago² and Eiji Fujii²; ¹Schrödinger Incorporated, United States; ²Panasonic Corporation, Japan

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hole reorganization energies ($\lambda_h$). Utilizing the cloud-computed DFT dataset of a quarter-million reorganization energies, inverse materials design methods were applied to find further chemical structures with minimal reorganization energy. The de novo design methods applied were (1) a method based on reinforcement learning of SMILES strings (the REINVENT method [2]), and (2) a junction tree variational autoencoder that directly generates molecular graphs [3]. Both methods succeeded in obtaining chemical structures whose reorganization energy was lower than the lowest energy in the DFT training dataset, suggesting that an extrapolative materials design protocol can be developed by applying two methods. Finally, these results will be compared to the results obtained from the latent-space de novo molecular design method proposed by Gomez-Bombarelli et al. [4].


10:40 AM *S.CT01.01.06
Accelerated Discovery of Metal Oxide Photoanodes for Solar Fuels Applications John M. Gregoire; California Institute of Technology, United States

Solar fuel generation from H$_2$O, CO$_2$ and sunlight comprises a promising renewable energy technology whose future proliferation relies on materials advancements, including identification of a photoanode for the oxygen evolution reaction. A water-oxidizing photoanode can be coupled to a (photo)cathode for scalable generation of H$_2$ and C-containing fuels. Metal oxides are the most extensively studied class of OER photoanode materials due to the availability of a multitude of metal oxide phases that may stably operate in the oxidative electrochemical environment while converting solar to photoelectrochemical (PEC) energy. Solar fuels photoanodes are quite rare due to the combined needs of solar absorption, charge carrier separation and transport, oxidative stability, and catalytic activity for the OER. The compendium of known metal oxide photoanodes that operate in the visible spectrum is being rapidly expanded via theory-guided high throughput experimentation, including our combination of combinatorial materials synthesis coupled with automated UV-vis spectroscopy and PEC experiments. Discovery of dozens of ternary metal oxide photoanodes will be discussed with focus on the lessons learned in terms of the role of theory and the importance of compositionally graded libraries, and a historical analysis of the discovery rate of metal oxide photoanodes reveals increasing chemical diversity, suggesting there may be many more materials to be discovered. The rapidly expanding portfolio of metal oxide photoanodes creates new avenues of inquiry to realize the requisite stability and efficiency for deployment of solar fuels technologies.

10:46 AM *S.CT01.01.07
Probing the Water-Induced Degradation Pathways of Metal-Organic Frameworks (MOFs)—The Potential for Highly Transferrable Surface Passivation Approach Mohamed H. Alkordi$^1$, Mohamed E. Safy$^1$, Muhamed A. Amin$^2$, Rana R. Haikal$^1$, Basma Elshazly$^1$ and Ahmed H. Ibrahim$^3$; $^1$Zewail City of Science and Technology, Egypt; $^2$University of Groningen, Netherlands

A model describing the origin of water-induced degradation of certain Metal-Organic Frameworks (MOFs) is derived, aiming to explain experimental observations of water stability and instability of prototypical MOFs. The proposed model suggests crucial rule of metal-coordinated water molecules, and solution pH, in triggering a cascade of reactions that in several cases results in pronounced irreversible degradation of several MOFs. It is suggested that such degradation pathways can be affected in neutral to basic solution by deprotonation of metal-coordinated water molecules, or bridging hydroxyl species in multinuclear clusters. Calculations of pKa values for the metal-coordinated water molecules, complemented by geometry relaxation calculations, and variable pH infrared spectroscopy techniques were all simultaneously utilized to draw a comprehensive description for the early stages in MOFs degradation in aqueous medium. Mostly dependent on the nature of metal nodes, we propose two distinct mechanisms for structural degradation of carboxylate-based MOFs. The MOFs investigated herein included MOF-5, HKUST-1, UiO-66, and MIL-101-Cr. It is suggested that for each type of MOF, a narrow pH stability range can be described, mostly determined by the pKa of metal-coordinated water molecules and the relative strength of metal-carboxylate interactions. Beyond this fundamental pH range, a relatively wider pH window can exist, where certain MOFs can be kinetically inert. Finally, we present a highly transferrable and facile approach to induce surface passivation of MOFs crystals to effectively extend such aqueous solution stability limits, as proven by the case of appreciably maintained microporosity of HKUST-1 in neutral, acidic and basic aqueous solution.

10:52 AM S.CT01.01.08
Combinatorial Approach for Single Crystalline TaON Growth—Epitaxial β-TaON (100) /α-Al$_2$O$_3$ (012) Narayanachari
The dream of autonomous materials discovery systems will only be realized if the entire design/synthesis/characterization process is described in an unambiguous machine-readable format. Specifying the experiment process in a machine-readable way facilitates both remote operation, algorithmic control of experiments, and enhanced experimental replicability. A significant challenge is that materials experiments often require a combination of instructions for human operators and machines. Furthermore, the variety of materials characterization data and experimental performance metadata during a process often require significant extraction/transformation/loading before machine learning methods can be applied. Existing tools require significant development time that is incompatible with rapidly evolving scientific needs.

In this talk, I will describe ESCALATE (Experiment Specification, Capture and Laboratory Automation Technology) an adaptable open source package for experiment description and data collection. As a specific example, I will describe its application to Robotic-Accelerated Perovskite Investigation and Discovery (RAPID). The first generation of RAPID uses inverse temperature crystallization (ITC) to grow halide perovskite single crystals for x-ray structure determination and bulk characterization using commercial liquid handling robots. Experiment plans are contributed remotely, by either human scientists or algorithms trained on the reaction data. Incoming experimental data collected by ESCALATE is used to automatically train machine learning models, evaluate model performance and feature influence on model predictions to gain human-interpretable scientific insight into the formation process, and quantify experimental reproducibility using this complete dataset of all experimental successes and failures. A live web dashboard communicates these insights to the scientist and management in visual form; furthermore experimental data can be exported in the form of interactive visualizations for use in publications. Collected characterizations includes qualitative measurements of crystal quality (including photographic images of the samples), powder X-Ray diffraction, and spectroscopic measurements along with background laboratory conditions. The second generation of RAPID has been extended to include antisolvent precipitation synthesis of perovskite single crystals and perovskite thin film synthesis and characterization including remote monitoring of long-term environmental stability. We have used the ESCALATE/RAPID platform to perform experimental tests benchmarking a variety of data-driven approaches for discovering new compounds against human-expert and random baselines. The comprehensive data collected from these experiments has also allowed us to ascertain the relative importance
of descriptive physical models for reaction composition relative to raw experimental descriptions when constructing machine learning models for reaction outcome prediction.

11:16 AM *S.CT01.03.03
Autonomous Combinatorial Experimentation Ichiro Takeuchi; University of Maryland, United States

Machine learning has become an integral part of many aspects of materials research. As a branch of machine learning, active learning has attracted much attention which can effectively help navigate experimental sequences in materials research. We are actively incorporating active learning in screening of combinatorial libraries of functional materials. For some physical properties, each characterization/measurement requires time/resources long/large enough that "high"-throughput measurement is not possible. Examples include detection of martensitic transformation and superconducting transitions in thin film libraries. By incorporating active learning into the protocol of combinatorial characterization, we can streamline the measurement and the analysis process substantially. We will present examples of mapping of phase change memory materials as well as others functional materials. This work is performed in collaboration with A. Gilad Kusne and V. Stanev. This work is funded by ONR and AFOSR.

11:22 AM S.CT01.03.04
Machine Learning Assisted Synthesis of Metal-Organic Nanocapsules Yunchao Xie1, Chen Zhang2, Xiangquan Hu1, Chi Zhang1, Steven Kelley1, Jian Lin1 and Jerry L. Atwood1; 1University of Missouri-Columbia, United States; 2North Carolina State University, United States

Herein, we report the successful discovery of a new hierarchical structure of metal-organic nanocapsules (MONCs) by integrating chemical intuition and machine learning algorithms. By training datasets from a set of both succeeded and failed experiments, we studied the crystallization propensity of metal-organic nanocapsules (MONCs). Among four machine learning models, XGBoost model affords the highest prediction accuracy of 91%. The derived chemical feature scores and chemical hypothesis from the XGBoost model assist to identify proper synthesis parameters showing superior performance to a well-trained chemist. This paper will shed light on the discovery of new crystalline inorganic-organic hybrid materials guided by machine learning algorithms.

11:28 AM *S.CT01.03.05
Autonomous Robotic Assembly of Two-Dimensional Crystals to Build van der Waals Superlattices Satoru Masubuchi1, Masataka Morimoto1, Momoko Onodera1, Sei Morikawa1, Takashi Taniguchi2, Kenji Watanabe2 and Tomoki Machida1; 1University of Tokyo, Japan; 2National Institute for Materials Science, Japan

Van der Waals heterostructures are comprised of stacked atomically thin two-dimensional crystals and serve as novel materials providing unprecedented properties. However, the random natures in positions and shapes of exfoliated two-dimensional crystals have required the repetitive manual tasks of optical microscopy-based searching and mechanical transferring, thereby severely limiting the complexity of heterostructures.

To solve the problem, we develop a robotic system, powered by artificial intelligence, that automatically searches exfoliated 2D crystals and assembles them into vdW superlattices inside glovebox [1-3]. The system can automatically scan the surface of silicon substrates, analyze optical microscope images, and detect a variety of atomically thin 2D materials without human intervention. The stacking order, positions, and crystallographic orientations of the 2D crystals are designed using the customized CAD software. The robotic assembly system of two-dimensional crystals enabled stacking four cycles of the designated two-dimensional crystals per hour with few minutes of human intervention for each stack cycle.

The system enabled fabrication of the vdW superlattice structures consisting of 29 alternating layers of the graphite and the hexagonal boron nitride (hBN) flakes. Encapsulated graphene devices exhibited high charge carrier mobilities (>1,000,000 cm²/Vs), demonstrating the applicability of the system for prototyping a variety of high-quality vdW superlattices. The wider material design freedom enabled by our system offers unprecedented opportunities for exploring the potential of vdW heterostructures. By this development, we can reduce the human intervention involved in the vdW heterostructure fabrication by orders. We believe that this work free up researchers from repetitive tasks and letting them focus on more intellectually creative tasks.

The hardware/software designs are available at https://github.com/tdmms/


11:34 AM S.CT01.03.06
Combining Experiment and Theory in a Closed-Loop Learning Cycle to Improve Perovskite Device Stability and Performance Tonio Buonassisi; Massachusetts Institute of Technology, United States

In my annual poster, I'll review the MIT PVLab's recent work combining experiment and theory in a closed-loop, machine-learning (ML) driven framework. Closed-loop experimentation driven by ML enables rapid and efficient convergence on optima, within vast search spaces. A review of scientific insights, as well as our latest machine-learning algorithms, will be presented.

11:40 AM S.CT01.03.07
High Throughput Nanoindentation and Machine Learning Assisted Analysis for Evaluation of Materials under In Operando Conditions Eric Hintsa1, Bernard Becker1, Youxing Chen2, Benjamin Stadnick1, Ude Hangen1, Nathan Mara3 and Douglas D. Stauffer1; 1Bruker Nano Surfaces, United States; 2University of North Carolina at Charlotte, United States; 3University of Minnesota, United States

Meeting current and future demands for advanced structural materials designed to operate in extreme environments requires rigorous mechanical performance evaluation at such conditions. When considering alloy development for such applications, such as nuclear materials, multiple compositions and processing routes create many permutations of material to be evaluated at different temperatures and radiation damage levels. Where traditional bulk scale mechanical testing is relatively time consuming, high speed nanoindentation mapping techniques can provide large (and highly localized) Hardness and Modulus datasets. This allows for analysis of heterogeneous distributions of properties in multi-phase alloys, which can then be correlated to the microstructure through use of supplementary techniques, such as EBSD, which has similar resolution. However, this requires accompanying analysis methods to also be high throughput, for which machine learning based techniques are of interest. Some datasets, as large as one million indentations in a given map, are beyond the limit of reasonable human analysis.

In this study, a high vacuum, high temperature nanoindenter was utilized to produce temperature controlled mapping of three advanced types reactor materials up to 500°C while protecting the sample surface from oxidation. The materials studied were Fe-based HEAs, with varied Al content to give 3 distinct microstructures. Structure-property correlation was quantitatively explored through clustering to partition the hardness and modulus data to individual microstructural elements and evaluate their thermal stability, with irradiation studies to follow. While qualitatively these methods performed comparably to by hand grouping, there is a need to quantitatively understand their systematic uncertainties without making assumptions regarding the underlying probability distribution. This is further explored for this data set by using a parametric bootstrapping method to resample the probability distribution function from the individual data points. Three different machine learning methods, Kernel Density Estimation, Gaussian Mixture and Multi-Normal, are used to generate a probability distribution function. This is then resampled to produce a simulated dataset 1000 times the original dataset in size. This allows K-means, Spectral and Gaussian Mixture clustering techniques to be applied and compared, but in principal, this can be applied to evaluate other properties as well.

11:46 AM *S.CT01.03.08
Autonomous Materials Development for Fun and Profit Kristofer G. Reyes; State University of New York at Buffalo, United States

Closed-loop, sequential learning is a key paradigm in autonomous materials development. Within this framework, aspects of the materials system under study are modeled, and such models are used to decide subsequent experiments to be run, results of which are fed-back to update models. In the past, off-the-shelf solutions and algorithms have been employed to optimize material properties. In this talk, we describe how autonomous materials platforms can be used for problems other than materials property optimization. We will specifically highlight work on autonomous phase mapping and real-time control, and how a common framework can be used to capture problem-specific structure and objectives. Relevant to this is the development of tools to perform autonomous materials characterization. We will describe how rich characterization data such as microscopy images or three-dimensional reconstructions from atom probe tomography can be analyzed without human intervention to encode experimental results for subsequent use within the closed loop. Together, the work described demonstrates the broad applicability of autonomous platforms throughout materials science research.
11:52 AM *S.CT01.03.09
A Bayesian Experimental Autonomous Researcher for Mechanical Design Keith A. Brown1, Aldair Gongora1, Bowen Xu1, Wyatt Perry1, Chika Okoye1, Patrick Riley2, Kristofer G. Reyes3 and Elise Morgan1; 1Boston University, United States; 2Google, United States; 3University at Buffalo, The State University of New York, United States

While additive manufacturing (AM) has facilitated the production of complex structures, it has also highlighted the immense challenge inherent in identifying the optimum structure for a given application. Numerical methods are important tools for optimization, but experiment remains the gold standard for studying non-linear, but critical, mechanical properties such as toughness. To address the vastness of AM design space and the need for experiment, we develop a Bayesian experimental autonomous researcher (BEAR) that combines Bayesian optimization and high-throughput automated experimentation. Using the BEAR, we explore the toughness of a parametric family of structures and observe more rapid, in terms of both experiments and time, convergence towards higher-performing structures than was obtained using a grid-based search. Specifically, we observe that the BEAR matched the performance of a grid-based search in 60 times fewer experiments. In addition to providing a platform to discover mechanical properties of AM-produced metamaterials, the BEAR provides a framework for exploring active learning in an experimental context including multi-agent decision policies, the incorporation of theory in an experimental loop, and the influence of heteroscedasticity. Collectively, these results show the value of machine learning in experimental fields where data are sparse.

11:58 AM *S.CT01.03.10
Interpretable Machine Learning for Materials Design and Characterisation Keith T. Butler; Rutherford Appleton Laboratory, United Kingdom

In this talk I will look at how we can open up the perceived 'black box' of machine learning when designing and characterising materials. I will show how being able to look at and understand the inner workings of deep neural networks increases the value of these approaches for problems in materials science. Understanding the workings is important for (i) debugging and building better models, (ii) building confidence in models that perform well, (iii) learning from models that exceed human performance in certain problem areas. I will take examples of our research where we use graph neural networks to infer and predict dielectric properties of solids and where we use deep convolutional neural networks to interpret data from inelastic neutron scattering. In the former case a mixture of deep and shallow learning allows for extraction of principles as well as construction of robust accurate models. In the latter case understanding the workings of the neural network allows us to develop a method for guiding experiments to sample the most pertinent areas of signal space.

12:04 PM S.CT01.03.11
Inverse Design of Broadband Highly Reflective Metasurfaces using Neural Networks Eric Harper1, Eleanor Coyle2, Jonathan Vernon1 and Matthew Mills1; 1Air Force Research Laboratory, United States; 2Azimuth Corp, United States

The next generation of high performance optical materials require precise engineering to transcend the inherent limitations of bulk materials and achieve desired optical performance. These targeted properties originate from the interactions between inherent optical properties of the constituent materials and meticulously engineered sub-wavelength inhomogeneities. However, the design of such metamaterials poses a significant challenge to researchers due to the near-infinite design space to consider, even for relatively simple metamaterials such as the two-dimensional all-dielectric metasurface. This metasurface has been the subject of intense research interest because of its unprecedented reflective performance resulting from low-loss dielectric materials and shape-dependent optical resonances. Here we employ artificial neural networks (ANNs) to invert the design process, conceiving metasurface designs with targeted reflection and transmission spectra. These ANNs are capable of coordinating the complex interactions of the eigenmodes from which these desired properties arise, delivering device designs demonstrating coefficients of reflection greater than 99% over a range of wavelengths more than 450nm.

12:10 PM S.CT01.03.12
Machine Learning-Aided Design of DNA-Stabilized Silver Clusters with Specific Fluorescence Wavelengths Stacy Copp1, Steven Swasey2, Alexander Gorovits3, Petko Bogdanov3 and Gwinn Elisabeth2; 1University of California, Irvine, United States; 2University of California, Santa Barbara, United States; 3University at Albany, State University of New York, United States

DNA-templated silver clusters (Ag50-DNA) are known to exhibit a wide range of fluorescence colors for different choices of the DNA template sequence [1]. While these clusters are promising biosensors and biomarkers [2], rational design of Ag50-DNA for specific applications is challenged by the huge space of possible DNA template sequences. To understand how DNA sequence selects for silver cluster size and optical properties, we are employing high-throughput experiments and tools
from machine learning and data mining. We previously showed that machine learning methods trained on experimental data can be used to design new DNA templates that select for AgN-DNA color, for the specific and limited case of 10-base DNA oligomers [3]. An important open question is whether such a design process developed for a specific biopolymer template length is applicable at other lengths, with different numbers and diverse configurations of cluster nucleation sites. More broadly within materials informatics, it is important to determine when models learned on limited training data sets are relevant for prediction within expanded input parameter spaces.

Here, we present a newly developed flexible design approach that utilizes color-correlated DNA base motifs learned from data on > 2,000 ten-base DNA oligomers [4]. We test this motif-based design for templates ranging from 8 bases to 16 bases long, for which the sizes of the sequence spaces differ by nearly 5 orders of magnitude. The experimental data show that designed strands of all lengths are selective for AgN-DNA color in the target wavelength band of 600-660 nm, strongly suggesting that color-selective motifs learned for one template length generalize to other lengths. Thus, a motif-based design approach may be broadly suitable for future AgN-DNA applications.

The development of a hydrogen economy has potentially immense benefits for addressing the crisis of global heating. However, storage remains a problem and decades of research have left us empty-handed: no known materials can satisfy all of the DOE targets for vehicular storage. Metal hydrides are among the most promising solid-state storage materials, but their complex chemistry is a major impediment to discovery of game-changing materials. Specifically, their thermodynamics are often ill-matched to hydrogen release at temperatures compatible with fuel cells. This limitation requires an equilibrium H₂ pressure of at least 5 bar at the maximum delivery temperature of 80 °C. Empirical discovery approaches using, for example, high-throughput synthesis, are largely ineffective because measurement of the equilibrium H₂ pressure can take days or even weeks. Machine learning (ML) methods have already shown promise for accelerating the discovery of new hydrogen sorbents and identifying key features that influence their properties. In recent application to metal hydrides, however, the use of “black-box” algorithms prohibited development of crucial vital scientific insight needed to go beyond existing compositions. We employed a gradient-boosting tree regressor, an “explainable” ML that can reveal the feature dependence of material properties. In particular, we find that the equilibrium H₂ pressure of intermetallic metal hydrides strongly depends on a volume-based feature that requires only the elemental composition to be computed. Remarkably, this simple structure-property relationship is valid across a wide range of compositions, metal substitutions, and structural classes found in intermetallic metal hydrides. This result provides a rational basis for targeting novel hydrogen storage materials with thermodynamic properties appropriate for specific applications. As an illustration, we identified a known intermetallic that forms a hydride with very low stability. Although not yet validated by experiment, this result was confirmed by density functional theory modeling.

7:28 PM S.CT01.02.03
De Novo Discovery of Nanoporous Structures by Machine Learning Mathieu Bauchy; University of California, Los Angeles, United States

Nanoporous materials (e.g., zeolite, activated carbon, metal-organic framework, polymeric membranes, etc.) have various technological applications, including gas separation, gas storage, catalytic transformations, etc. The functionalities of nanoporous materials strongly depend on their pore size and shape distribution—which present virtually limitless degrees of freedom. Here, based on high-throughput simulations and a convolutional neural network (CNN) predictor, we present a model allowing us to predict the water sorption isotherm of hydrophilic and hydrophobic nanoporous materials. The training of a CNN generator then enables the inverse design of optimal porous microstructures featuring tailored/unusual sorption isotherms.

7:46 PM *S.CT01.02.06
Machine-Based Discovery of Energetic Materials Peter W. Chung; University of Maryland, United States

Recent successes demonstrated by machine learning (ML) approaches have created great enthusiasm for their potential translational contributions to other fields. Among these are efforts to demonstrate the feasibility of using machine-based approaches to study and speculate on new energetic materials. This talk will discuss the performance of ML models developed to predict the detonation properties of energetic materials. A comprehensive comparison of approaches reveals that models are highly sensitive to feature selection as well as algorithm differences. But using a relatively limited volume of data and careful problem definitions, surprisingly strong cross validation scores suggest that there is promise to both improve and ultimately use ML methods widely in this field. The talk will conclude with an overview and some perspectives of other recent efforts including generative modeling and natural language processing techniques at their intersections with energetics research.

7:52 PM *S.CT01.02.07
A Machine-Learning-Based Strategy for Accelerated Discovery of Novel Scintillator Chemistries Anjana Talapatra, Christopher R. Stanek, Blas P. Uberuaga and Ghanshyam Pilania; Los Alamos National Laboratory, United States

Inorganic scintillator-based detector materials find a wide variety of applications, ranging from medical imaging to radiation detection for global security and high energy physics experiments. These materials essentially convert a fraction of the total energy deposited by incident gamma rays or X-rays into visible or near-visible range of the spectrum. In many applications a scintillator with high light output, fast response time, and emission at suitable wavelengths, is generally required, among many other application-specific desired characteristics. However, owing to several conflicting relationships between the desired properties (e.g., brightness versus speed), no single scintillator is ideal for all uses; there is a need to design custom scintillators optimized for each application. Traditionally, the discovery and design of new detector materials have relied on a laborious, time-intensive, trial-and-error approach; yielding little physical insight and leaving a vast space of potentially...
revolutionary materials unexplored. To accelerate the discovery of optimal scintillator materials with targeted properties and performance, efforts are ongoing to develop a closed-loop machine learning driven adaptive design framework based on data from literature, in-house experiments and quantum mechanical calculations. This talk will present an overview of this framework, focusing on the screening of complex wide band gaps chemistries with an aim of identifying promising materials that are amenable to band-gap/band-edge engineering to yield custom scintillation properties. The developed framework is general and is expected to prove useful for applications beyond scintillator discovery such as photovoltaics and catalysis.

8:04 PM S.CT01.02.09
Machine-Learning Guided Discovery of MOFs for Enhanced Hydrogen Storage Capacity **Samrendra Singh, Abhishek Sose, Karteek Bejagam and Sanket A. Deshmukh;** Virginia Tech, United States

In recent years the use of various machine-learning (ML) methods to discover new materials with desired properties have emerged as a powerful tool. In this research, we have designed a stacked ensemble model (SEM) by combining several supervised ML models to predict the adsorption of hydrogen in metal-organic frameworks (MOFs). The SEM model was trained by using the hydrogen adsorption data generated by screening of 1000s of MOFs by performing grand canonical monte carlo (GCMC) simulations at 1 atm and 77 K. This SEM was integrated with optimization algorithms and in-house MOF structure generation code to design MOFs with high adsorption of hydrogen. Overall, this new approach of integrating SEM with optimization algorithms accelerated the new MOF discovery process, resulting in a MOF with enhanced hydrogen storage capacity. This new ML framework is transferable and can be used to discover other porous (e.g. zeolites), soft (e.g. polymers), and hard (e.g. alloys) materials for desired applications.

8:10 PM *S.CT01.04.01
Multiscale Machine Learning for Quantum Many Particle Physics with Wavelet Scattering Transforms **Matthew Hirn;** Michigan State University, United States

Computing the ground state energy of quantum many particle systems is of fundamental importance in a variety of fields, including chemistry, physics and materials science, amongst others. However, the complexity of such quantum mechanical computations grows rapidly with the number of particles. Machine learning algorithms do not simulate the physical system, but instead estimate solutions by interpolating values provided by a training set of known examples. However, precise interpolations may require a number of examples that is exponential in the system dimension, and are thus intractable. Tractable algorithms compute interpolations in low dimensional approximation spaces, which leverage the underlying physical properties of the system.

In this talk I will give an overview of machine learning algorithms for computing the ground state energy of quantum many particle systems, describing the core principles of such algorithms and illustrating the common themes that emerge. I will then present in more detail our approach to the problem, which is based on a type of multiscale, multilayer convolutional neural network, called a wavelet scattering transform. Through a cascade of multiscale wavelet transforms and nonlinearities, the scattering transform encodes the appropriate invariants and regularity properties of the physical system. Wavelet scattering regressions, computed over databases of organic molecules and amorphous materials, achieve errors on the order of quantum mechanical simulations, but at a fraction of the computational cost.

8:22 PM S.CT01.04.03
Putting Scientists’ Eyes on Glass-Box Physics Rule Learner for Unraveling Nano-Scale Tribocharging Phenomena **In Ho Cho1, Qiang Li1, Rana Biswas1,2 and Jaeyoun Kim1;** 1Iowa State University, United States; 2Ames Laboratory, United States

This multi-disciplinary research proposes a new framework that can infuse scientists' experience and knowledge (named as scientists' eyes) into a constantly evolving, glass-box physics rule learner that can essentially extract hidden physics rules behind complex nano-scale phenomena. Recently, physics principles are gradually integrated into machine learning (ML) methods, but it is at its infancy to discover hidden physics rules. Such pursuits for hidden rules face formidable challenges when the physical experiments involve multifaceted measurements across three-dimensional (3D) specimens or objects. These remaining challenges render even advanced ML methods such as deep learning secondary, not as a primary explorer, in the broad science and engineering domains. Therefore, there exists a deep chasm still remains between materials science
and ML community.
To overcome this challenge and unravel hidden physics rule behind nano-scale complex phenomena, we reinterpreted the deep learning’s successful notion of multi-layered convolutions and gave rise to a new notion of "convolved information index." The convolved information index can facilely handle physical measurements over 3D nano-scale specimens and measurements without losing experienced perspectives of scientists in the materials science. Also, the framework proposes "link function" as a generator of mathematical expressions about the identified nano-scale physics rules, thereby pursuing "glass-box" (as opposed to the black-box) learning and prediction. Consistent evolution capability is realized by integrating Bayesian update and evolutionary algorithms.

The framework is applied to nano-scale contact electrification (CE) phenomena, which are difficult to elucidate due to length scales and complex physical interactions [1,2]. Three experimental data sets are used. Tribocharged PDMS nanocup array is fabricated by the sequence of (1) prepare a PET mold with a 750 nm-pitch triangular array of nanocones, (2) pour the liquid phase PDMS, Sylgard 184, Dow Corning, mixed with the curing agent, (3) solidify the specimen, and (4) peel off the PDMS from the PET mold (for more details see [1,2]). Atomic force microscopy (AFM) in the tapping mode is used to measure the surface topography and potential. The charge values were measured by Kelvin probe force microscopy over patterned nanocups represented by 3D point cloud. The experimental data consist of a variety of conditions regarding geometries, demolding directions, and nano-scale patterns (3000 nm by 3000 nm square area with an interval of 5.86 nm; 4000 nm by 4000 nm, with 7.8125 nm). The nano-cup's average heights are 154 nm, 93.5 nm, and 117 nm. The proposed glass-box learning begins from horizontal-demolding test data, and then the best-so-far identified rules are inherited to the next learning with new specimens in a chained way.

The feasibility tests show promising performances of the proposed framework in unraveling transparent, reasonable “expressions” of hidden physics rule along with reasonable reproduction of complex patterned distributions of electric potentials over the 3D point cloud. The proposed framework is believed to establish a promising partnership of scientists’ eyes and the advanced ML methods, thereby enabling data and ML-driven discovery of groundbreaking physics laws in the nano-world and beyond. This presentation will cover how this new framework can facilitate materials scientists’ discovery with actual nano applications.


8:28 PM S.CT01.04.04
Materials By Design Using Artificial Intelligence—Modeling, Manufacturing and Testing Markus J. Buehler, Chi-Hua Yu and Yu-Chuan Hsu; Massachusetts Institute of Technology, United States

In this talk we will review recent studies of applying atomistic-level modeling to describe fracture processes at different scales, from molecular to macroscale levels, and to use artificial intelligence and machine learning to design fracture resistant materials. Molecular and related multiscale modeling methods can be an effective method to better understand elementary fracture processes, ranging from brittle to ductile fracture and other materials failure phenomena such as creep, and provides the basis for expansive training sets. To illustrate this framework, we report a design approach for optimizing the toughness of nanocomposite materials using artificial intelligence, implemented in a novel “AutoComp Designer” algorithm. The algorithm consists of a machine learning predictor combined with an AI improved genetic algorithm, which is capable of discovering de novo materials designs in a vast space of possible solutions. Facilitated by a deep convolutional neural network that is trained with a dataset of hundreds of thousands of combinations of soft and brittle materials originating from multiscale models. Through the algorithm, we extend the capability of physical simulations beyond property predictions to optimize the fracture toughness by altering the material distribution. The solutions are generated by our AI model at a dramatically lower computational cost compared to brute-force searching methods. We further investigate the physical mechanism for improving material performance behind the AI approach, and demonstrate the ability of AI to search for optimal designs with very limited sampling. Brute-force molecular dynamics simulations of the nanocomposite designs confirm that our AI design improves the performance by effectively decreasing the stress concentration at crack tip. This AI approach can be easily applied to other nanocomposites, biomaterials and other material classes, and provides a transferrable and reliable rapid design approach expanding current capabilities.

8:34 PM S.CT01.04.05
Fast and Accurate Interatomic Potentials by Symbolic Regression Alberto Hernandez, Adarsh Balasubramanian, Fenglin Yuan, Simon Mason and Tim Mueller; Johns Hopkins University, United States

In recent years there has been great progress in the use of machine learning algorithms to develop interatomic potential
models. Machine-learned potential models are typically orders of magnitude faster than density functional theory but also orders of magnitude slower than physics-derived models such as the embedded atom method. We demonstrate that machine learning, in the form of genetic programming, can be used to develop accurate and transferable many-body potential models that are as fast as the embedded atom method, making them suitable to model materials on extreme time and length scales. The key to our approach is to explore a hypothesis space of models based on fundamental physical principles and to select models from this hypothesis space based on their accuracy, speed, and simplicity. We demonstrate our approach by developing fast and accurate interatomic potential models for copper that generalize well to properties they were not trained on, and we discuss additional applications. Our approach requires relatively small sets of training data, making it possible to generate training data using highly accurate methods at a reasonable computational cost.

8:46 PM *S.CT01.04.07
**Describing Materials for Machine Learning** Shyue Ping Ong, Chi Chen, Yunxing Zuo, Xiangguo Li, Zhi Deng and Wei Ke Ye; University of California, San Diego, United States

Machine learning (ML) has emerged as a powerful tool in the study and design of materials. In this talk, I will discuss the different ways in which materials can be described and their relative merits and limitations. In particular, I will highlight the importance of choosing representations that not only satisfy known physical invariances (e.g., rotation, translation, etc.), but also incorporate known physics and chemistry in a hierarchy of knowledge. I will provide an overview of leading ML models and applications, and discuss how the problems of data scarcity and bias in materials science can be addressed using multifidelity, transfer learning and other approaches.

8:58 PM S.CT01.04.09
**A General Machine Learning Framework for Impurity Level Prediction in Semiconductors** Arun Kumar Mannodi Kanakkithodi and Maria K. Chan; Argonne National Laboratory, United States

Electronic levels introduced by impurities and defects in the middle of the band gap are critically important in semiconductors for optoelectronic, photovoltaic (PV) and quantum sensing applications. While “deep” defect levels can prove catastrophic for PV performance by causing non-radiative carrier recombination, impurity levels in the band gap could also be entangled for quantum sensing or lead to increased absorption of sub-gap photons which can enhance efficiencies. Predicting formation energies and charge transition levels for defects in semiconductors is thus paramount; density functional theory (DFT) has been widely applied for such studies to overcome experimental bottlenecks and confirm measured defect levels. However, the requirement of large supercells, advanced levels of theory, and inclusion of charge corrections make DFT computation of defect properties very expensive, and trends and knowledge from previous calculations are not exploited in subsequent ones.

In this work, we combine high-throughput DFT and machine learning (ML) to develop general predictive models for the formation enthalpy and charge transition levels of impurities in two broad semiconductor classes: (a) ABX₃ halide perovskites, and (b) group IV, III-V and II-VI semiconductors. DFT data is generated for impurity atoms selected from across the periodic table and simulated in various possible cation, anion or interstitial sites. Any “semiconductor + impurity” combination is converted into a unique feature vector based on the defect site coordination environment, the tabulated elemental properties (e.g. ionization energy, electronegativity, etc.) of the impurity atom, and electronic and energetic properties computed using low cost unit cell defect calculations. State-of-the-art neural networks (NN), random forest regression (RFR) and kernel ridge regression (KRR) are applied to train models for (a) impurity formation enthalpy, and (b) impurity charge transition levels, based on the input feature vector. Model performance is evaluated for different ML techniques, ML parameters such as number of hidden layers and network weights in NN, subsets of features, and size and nature of training dataset; the best predictive models thus obtained are deployed for comprehensive prediction and design purposes. It is seen that models trained on defects and impurities in pure cation/anion composition semiconductors are applicable to mixed or alloyed compositions as well: for instance, by training on data from pure canonical AB semiconductors like CdTe, ZnO, GaAs and SiC, the ML models can make accurate predictions for impurities in alloyed compositions of the same compounds, such as CdTe₁₋ₓSeₓ, Cd₁₋ₓZnₓO, Al₁₋ₓGaₓAs₁₋𝙬Sb₂, etc. This versatility of the machine-learned models provides an avenue to access the optoelectronic impact of any atomic impurity in any possible pure or mixed composition semiconductor belonging to the same chemical space, which is useful for compositions that are expensive to model. We use the predictive models to efficiently screen for dominating impurities, that is impurities that shift the equilibrium Fermi level in the semiconductor as determined by dominant native defects, in hundreds of possible compositions in the halide perovskite and groups IV, III-V and II-VI semiconductor spaces. ML-based screening of impurities was tested against DFT screening for CdTe and seen to have an accuracy of 95%. The quick and accurate
estimation of interesting dopants/impurities in semiconductors is made possible by this materials design framework powered by quantum mechanical computations and machine learning, which can be easily expanded to other semiconductor classes and improved by the infusion of fresh data, new descriptors and more advanced ML techniques.

References
1. A. Mannodi-Kanakkithodi et al., Chemistry of Materials 31 (10), 3599–3612 (2019).

9:04 PM S.CT01.04.10
Optimization Thermal Conductivity at Interfaces Using Learning Algorithms Malachi Schram1, Anne Chaka1, Zexi Lu1, Sabiha Rustam1 and Eric Harper2; 1Pacific Northwest National Laboratory, United States; 2Air Force Research Laboratory, United States

In material science, we are frequently interested in understanding the properties and design implication of material at interfaces. These interfaces can be manipulated to improve the desired characteristics of the bulk material. In this study, we are interested in understanding and optimize the impact of interfacial atomic defects on the thermal transport across a Cu/Si junction. To that end, we developed a reinforcement learning based framework to optimize over a potentially large parameter search. Using this technique allows us to accumulate knowledge of the system of a given type of atoms and store this information into a neural network. In this study, we present our results on optimizing the thermal transport by varying the fraction and length of the interfacial atomic defects using molecular dynamics (MD) simulations with normal mode analysis (NMA) to investigate thermal transport.

9:10 PM S.CT01.04.11
Physics-Informed Machine Learning for Deep Elastic Strain Engineering of Electronic Properties of Materials Zhe Shi1, Evgenii Tsymbolov2, Ming Dao1, Subra Suresh1, Alexander Shapeev2 and Ju Li1; 1Massachusetts Institute of Technology, United States; 2Skolkovo Institute of Science and Technology, Russian Federation; 3Nanyang Technological University, Singapore

Deforming a material to a large extent without inelastic relaxation can result in unprecedented properties. However, the optimal deformation state is buried within the vast continua of choices available in the strain space. Motivated by this challenge, we hereby advance a powerful strategy to circumvent conventional trial-and-error methods and adopt a unique type of machine learning framework for rationally designing the most energy-efficient pathway to achieve a desirable material property such as the electronic bandgap. This method invokes recent advances in the field of convolutional neural networks and active learning by utilizing a limited amount of ab initio data for the training of a surrogate model, predicting electronic bandgap within an accuracy of sub-10 meV. Our model is capable of discovering the indirect-to-direct bandgap transition and semiconductor-to-metal transition in silicon by scanning the entire strain space [1]. It is also able to identify the most energy-efficient strain pathways that would transform diamond from an ultrawide-bandgap material to a narrow-bandgap semiconductor or even semimetal [2]. A broad framework is presented to tailor any target figure of merit by recourse to deep elastic strain engineering and machine learning for a variety of applications in microelectronics, optoelectronics, photonics, and energy technologies.

Autonomous Research Systems like ARES™ are disrupting the research process by using AI and Machine Learning to drive closed-loop iterative research. ARES™ is our autonomous research robot capable of designing, executing and evaluating its own experiments at a rate of up to 100 iterations per day. Previously ARES taught itself to grow carbon nanotubes at controlled rates (NPJ Comp Mat 2016). Here we discuss recent research campaigns on maximizing carbon nanotube growth rates using a Bayesian optimization planner. We also use HOLMES and knowledge gradient descent to introduce advanced decision policies with local parametric models to control nanotube diameter. Implications for nanotube materials development will be discussed. Finally, we have developed a new research robot for additive manufacturing, AM ARES™, which is at the early stages of teaching itself to print structures with unknown inks. We plan to make the AM ARES™ Robot available online so that a broad community of researchers can test concepts and approaches for AI/ML and experimental design as applied to 3D printing, thus building to the larger goal of enhancing citizen science.

8:07 AM S.CT01.05.02
Automated Construction of Materials Imaging Datasets Eric Schwenker1,2, Weixin Jiang1,2, Trevor Spreadbury1,3, E. J. Beard4, Jacqueline M. Cole4, Nicola Ferrier1 and Maria K. Chan1; 1Argonne National Laboratory, United States; 2Northwestern University, United States; 3Massachusetts Institute of Technology, United States; 4University of Cambridge, United Kingdom

Due to recent improvements in image resolution and acquisition speed, materials microscopy is experiencing an explosion of published imaging data. Intensive human efforts, however, are required to digest such published images. In this talk, we will discuss the MaterialEyes project, in which deep learning and natural language processing tools are used to extract microscopy images from scientific literature. The process is accomplished via a suite of scientifically-informed software tools in the EXSCLAIM python package (automatic EXtraction, Separation, and Caption-based natural Language Annotation of Images from scientific figures), which is ultimately focused on the acceleration of inductive materials insights by collecting, structuring, and interpreting an aggregate of materials microscopy imaging data. In this talk, we will discuss how deep learning and NLP is used in EXSCLAIM to: (1) extract figures and caption data from open source scientific documents, (2) automate the construction of self-annotated materials imaging datasets, and then (3) leverage literature-based insights to assist in image classification and segmentation tasks. In addition, we will discuss a new pipeline for crowdsourced image labeling that was used for training some of the deep learning models.

8:13 AM S.CT01.05.03
Deep Learning Accelerated Optical Characterization System for Two-Dimensional Material Research Yuxuan Lin1, Bingnan Han1,2, Yafang Yang1, Pablo Jarillo-Herrero1, Jihao Yin2, Jing Kong1 and Tomás Palacios1; 1Massachusetts Institute of Technology, United States; 2Beihang University, China

Characterization of nanomaterial morphologies with advanced microscopy and/or spectroscopy tools plays an indispensable role in nanoscience and nanotechnology research, as rich information about the chemical compositions, crystallography, other physical and chemical properties, as well as the growth mechanism can be extracted from morphology analysis. However, the interpretation of imaging data heavily relies on the “intuition” of experienced researchers. As a result, many of the deep graphical features are often unused because of difficulties in processing the data and finding the correlations. Such difficulties can be well addressed by deep learning. In this work, we use the optical characterization of two-dimensional (2D) materials as a case study.

Currently, the most widely used approach to obtain high-quality 2D crystals in laboratories is mechanical exfoliation, followed by 2D crystal “hunting” under an optical microscope. This task is time-consuming and difficult especially for inexperienced researchers. Very recently, there has been growing interest in automating such a process. However, existing optical contrast based identification methods could not satisfy the needs for a general-use, fully automatic optical identification and/or characterization system, as they are often very specific to types of 2D crystals, conditions and configurations of the microscopes being used, image qualities, etc. In addition, optical contrast based methods would fail for harder problems in which the classes to be differentiated are not separable in the color space, such as identifying the materials or even predicting their physical properties from unlabeled optical images. In reality, optical microscopic (OM) images contain rich, often unused information other than optical contrast. These deep
graphical features can be extracted through deep learning, especially semantic segmentation methods based on convolutional neural networks (CNNs). In this work, an encoder-decoder semantic segmentation network called “SegNet” is configured for pixel-wise identification of OM images of 2D materials, in real time, and regardless of variations in optical setups. A fully automated system utilizing this algorithm can be used to free up tremendous amount of time for researchers. Additionally, we find that the algorithm finds correlations between the OM images and physical properties of the 2D materials and can thereby be used to anticipate the properties of new, as-yet uncharacterized 2D crystals. Finally, a transfer learning technique is applied to adapt the pretrained network to more optical characterization applications such as identifying layer numbers of chemically synthesized graphene domains. The proposed methodology can potentially be extended for identification and understanding other morphological or spectroscopic data of diverse nanomaterials.

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8:19 AM S.CT01.05.04
Density Functional Theory and Deep-Learning to Accelerate Scanning Tunneling Microscopy Analysis Kamal Choudhary; National Institute of Standards and Technology, United States

We introduce the first systematic database of scanning tunneling microscope (STM) images obtained using density functional theory (DFT) for two-dimensional (2D) materials. Specifically, the database is constructed using the Tersoff-Hamann method. It currently contains data for 681 exfoliable 2D from the JARVIS-DFT database. These computational STM images can directly aid the experimental analysis of experimental STM results as they provide ideal reference images. Examples of the five possible Bravais lattice types for 2D materials are discussed and the images for all the materials are made available on the website. We validated the computational STM technique by comparing our results to a few experimental images. As the analysis of multiple STM images during an experiment could be tedious, we used our DFT-STM image database to train a high-accuracy convolution neural network (CNN) model to accelerate the characterization process.

8:25 AM *S.CT01.05.05
Measurements in Machine Learning Gerald Friedland; University of California, Berkeley, United States

A major obstacle in applying machine learning to scientific and engineering tasks is the lack of engineering rules for the design of machine learning systems that allow to make these system reproducible and the limits of the systems known. Based on joint research with physicists and material engineers, this talk presents engineering principles and measurement processes[1] that aim at structured engineering of machine learning systems. While the focus of this talk is on neural networks, the principles and presented measurements are universal and applicable to a variety of machine learning systems.

https://dl.acm.org/citation.cfm?id=3350545

8:31 AM S.CT01.05.06
Machine Learning the Magnetostriction of Polycrystalline Tb$_x$Dy$_{1-x}$Fe$_2$ Alloys—A Graph Neural Network Approach Minyi Dai, Mehmet F. Demirel, Yingyu Liang and Jiamian Hu; University of Wisconsin-Madison, United States

Predicting the magnetostriction of a large-scale (mm-mm) polycrystalline Tb$_x$Dy$_{1-x}$Fe$_2$ (Terfenol-D) alloy by direct numerical simulations is mathematically tedious and computationally expensive, because it requires solving a set of partial differential equations which describe the mutual coupling between local magnetization dynamics and polycrystal elasticity, and because it requires a large number of simulation cells (tens of millions and more). For accelerating the prediction of magnetostriction, we apply a graph-based deep learning method, namely, the Graph Neural Network (GNN), to discover the correlation between a microstructure dataset of 350 different polygrain structures and a property dataset describing the magnetic-field-induced deformation of each polygrain structure (viz., magnetostriction). In the GNN based approach, each grain is represented as a node, in which all important physical features (e.g., Euler angle, magnetization direction) inside a grain are stored. As a result, the polygrain structure is represented as a network of nodes, in which the identity information of each grain(node)’s neighboring grains(nodes) is also preserved. This in turn allows us to consider the grain-grain interaction which
critically influences the magnetostriction of the entire alloy and interpret the contribution of each node (grain) to the magnetostriction. A >90% prediction accuracy has so far been achieved with ample space for improvement. Our results demonstrate the exciting potential of applying GNN to accelerate the discovery of microstructure-property linkage in polycrystalline materials.

8:37 AM S.CT01.05.07
Data-Driven Characterization of Structural Dynamics in Nanoparticles Peter A. Crozier¹, Ramon Manzorro¹, Carlos Fernandez-Granda², Qiang Zhu³, Mahmoud Moradi⁴, David Matteson⁵ and Roberto Rivera⁶; ¹Arizona State University, United States; ²New York University, United States; ³University of Nevada Las Vegas, United States; ⁴University of Arkansas–Fayetteville, United States; ⁵Cornell University, United States; ⁶University of Puerto Rico-Mayaguez, United States

Materials are ubiquitous in society and lie at the heart of many technologies including energy, communication, buildings, transportation, the environment and medicine. The constant need to develop new materials with properties that are matched to applications is a major driver of materials research. Understanding how atoms come together, self-assemble, dissociate and undergo phase transformations under different stimuli is a critical question in materials science. Transmission electron microscopy can routinely achieve a spatial resolution of better than 1 Å allowing the projected spatial distribution of atoms to be observed. In situ methodologies allow these signals to be mapped both spatially and temporally in the presence of different stimuli. Rapid advances in detector and spectrometer technology now allow local imaging, diffraction and spectroscopic signals to be acquired at unprecedented rates, generating terabytes of data in relatively short times.

The availability of large spatially and temporally resolved datasets offers unprecedented potential to transform our understanding of the fundamental atomic level dynamic processes taking place in materials. The rate at which atomic resolution data can be generated in experiments has now outstripped our ability to process and mine scientifically important information. The complex nature of atomic resolution images necessitates intense supervision and input in most quantitative image processing operations. Such an approach is possible for a few hundred images but becomes completely impractical when millions of data frames are available. This has become a serious bottle-neck to extracting the new knowledge potentially available from advanced characterization systems. We need approaches that can recognize recurring motifs in noisy data sets, provide statistical confidence levels for detection of real structural features, track dynamic changes within the sample, and flag events which are likely to be scientifically significant.

We are focused on applying emerging data-driven techniques based on statistics and machine learning to characterize structural dynamics in nanomaterials with an initial focus on metal and oxide nanoparticles 1 – 3 nm in size. Nanoparticles have wide applications in many areas of materials science and are an ideal system for developing and benchmarking novel data-driven processing techniques because they only contain a few thousand atoms. The datasets are acquired using in situ electron microscopy and structural dynamic processes are stimulated using heat, gas or electron irradiation. We compare and contrast the performance of automated image processing algorithms designed to determine atomic coordinates and structural evolution with more conventional manual methods. The importance of understanding the confidence level that can be associated with derived structural models is critical to assess the reliability of the scientific information extracted from large data sets.

Acknowledgements
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8:43 AM S.CT01.05.08
Deep Learning Based Characterization of Nanoindentation Induced Acoustic Events Antanas Daugela¹ and David W. Peterson²; ¹Nanometronix LLC, United States; ²University of St. Thomas, United States

Developed as a Baushinger effect monitoring technique in polycrystalline metallic materials, passive acoustic wave monitoring has been a critical health monitoring technique in: Atomic energy pressurized tank; Power and structure monitoring in aeronautics; Automotive; As well as recent applications in spinning disk data storage (HDD) health monitoring applications [1]. Passive monitoring of acoustic waves generated during the initial contact point has been attracting the attention of material scientists since the inception of nanomechanical test instruments for nanoindentation and nanoscratch applications. The conventional acoustic wave signal treatment via RMS or integrated energy values proves that quantitative acoustic wave properties correlate well with the local contact materials phenomena such as: Yield point initiation for W(100)
Sapphire [4], phase transformation for SMA [2]; and differentiating of thin film fracture modes [5]. Several attempts have been made to look at the differentiative properties of the acoustic signatures via signal decomposition techniques such as wavelets [2, 6]. Even though acoustic wave signatures were reconstructed, the true potential of the method was not investigated from the machine learning perspective.

In this work a deep learning based signal processing of nanoindentation induced acoustic events was investigated. The synergy of wavelet signal decomposition and information theory based signal presorting prepared data for the deep learning step. In the deep learning step convolutive neural networks sort wavelet coefficients by their statistical significance via provided 2D signal topographies. This creates acoustic signature libraries that are typical for the specific materials phenomena during the indent. The hardware consists of a newly developed ultrasonic probe integrated into the nanoindentation tip, thus eliminating boundary effects and ensuring that only waves that pass via the contact are being recorded. Appropriate signal conditioning and fast data acquisition hardware is synchronized with a quasi-static nanoindentation process. The machine learning routine together with wavelet decomposition and presorting algorithms are implemented into the dedicated acoustic data evaluation kernel which resides in the fast access memory of the designated controller.

REFERENCES:

8:49 AM S.CT01.05.09
Thermal Diffusivity Characterization of High-Temperature Solids Using Bayesian Statistics Yuan Hu, Bryce Boyer, Alex Pagano and Timothy S. Fisher; University of California, Los Angeles, United States

Thermal characterization in high-temperature environments is difficult because of high radiation losses and significant temperature measurement noise and inaccuracy. Ångström’s method can accurately measure thermal diffusivity in the presence of heat losses by observing the propagation of temperature perturbations through a material sample. This work applies a modified Ångström’s method to measure thermal properties at extreme temperatures (>1000 °C). Previous studies employing Ångström’s method at high temperatures typically have employed evenly spaced thermocouples on samples for thermal diffusivity measurements. We have recently demonstrated in preliminary room-temperature testing (copper - 1.13 x 10^(-4) m2/s, 1% uncertainty) that the uncertainty in thermal diffusivity within a Bayesian statistical framework is inversely proportional to the square root of the number of concurrent temperature measurements. In this work, we employ IR thermography for non-contact temperature measurement to greatly increase the number of measurements that can be resolved on a sample compared to the conventional thermocouple approach. To subject materials to extreme temperatures, samples are mounted vertically in a vacuum chamber and heated by concentrated thermal radiation from a 10 kW Xenon bulb. A controller is used to precisely modulate power output to produce the periodic temperature oscillation required for Ångström’s method. Transient temperature measurements are made along the length of the sample using both an infrared camera and optical spectroscopy. Bayesian statistics then quantify the measurement uncertainty associated with the noisy high temperature environment, and this approach is shown to substantially reduce measurement uncertainty for high-temperature material characterization.

8:55 AM S.CT01.05.10
Beyond Expert-Level Performance Prediction for Rechargeable Batteries by Unsupervised Machine Learning Xin Li; Harvard University, United States

Predicting the performance of rechargeable batteries in real time is of great importance to battery research and industrial production, and hence has been a long pursuit. In this talk, a novel end-to-end unsupervised machine learning approach is shown for the battery performance prediction, which is free from feature engineering and uses only the raw images of the charge–discharge voltage profiles [1]. This model enables unsupervised real-time automatic extraction of latent physical factors that control the performance of Na-ion batteries to classify good or bad cycling performance by using only the voltage profile of the first cycle. This model can also monitor the safety of Li-metal battery systems by giving warnings when the
battery is approaching a failure. With the beyond expert-level prediction ability, the abovementioned framework can be a promising prototype to further develop and enable high accuracy predictions of battery performance for real-world applications in the future.


9:01 AM *S.CT01.06.01
Causal Learning from Structural Electron and Scanning Probe Microscopy Data Sergei V. Kalinin, Rama Vasudevan, Chris T. Nelson, Ondrej Dyck, Andrew Lupini and Maxim Ziatdinov; Oak Ridge National Laboratory, United States

Machine learning has emerged as a powerful tool for the analysis of mesoscopic and atomically resolved images and spectroscopy in electron and scanning probe microscopy. The applications ranging from feature extraction to information compression and elucidation of relevant order parameters to inversion of imaging data to reconstruct structural models have been demonstrated. However, the fundamental limitation of the vast majority of machine learning methods is their correlative nature, leading to extreme susceptibility to confounding factors. While in classical statistical methods the methodology to address phenomena such as Simpson paradox are established, the complex and often non-transparent nature of modern DL tools renders them extremely prone to misinterpretation. We argue that correlative machine learning provides a reliable and powerful tool in cases when the causal links are well established, and discuss several examples of atom finding in SPM and STEM and analysis of 4D STEM data when this condition is satisfied. Notably, ML applications in theory generally fall under this category. Alternatively, ML methods work well when the confounding factors are effectively frozen via the narrowness of experimental conditions or experimental system. However, both these conditions are violated for experimental studies, when causal relationships are known only partially (and are in fact often the target of study) and confounding factors (composition uncertainty, microscope tuning, contaminations) are abundant. In this presentation, I will discuss the several examples of extending machine learning methods towards the analysis of causative physical mechanisms. One such approach is based on the Bayesian methods that allow to take into consideration the prior knowledge the system and evaluate the changes in understanding of the behaviors given new experimental data. The second pathway explores the parsimony of physical laws and aims to extract these from the set of real-world observations. Finally, the Bayesian networks can be used to explore the causative relationships in the multimodal data sets. These concepts will be illustrated using several examples of causal machine learning, including analysis of phase transitions on a single atom level in 2D materials and interplay between physical and chemical effects in the ferroelectric perovskites. Ultimately, we seek to answer the questions such as whether electronic instability due to the average Fermi level guides the development of the local atomic structure, or frozen atomic disorder drives the emergence of the local structural distortions, whether the nucleation spot of phase transition can be predicted based on observations before the transition, and what is the driving forces controlling the emergence of unique functionalities of morphotropic materials and ferroelectric relaxors.

This research is supported by the by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division and the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, BES DOE.

9:07 AM S.CT01.06.02
Accelerated Discovery of Efficient Solar Cell Materials Using Quantum and Machine-Learning Methods Kamal Choudhary; National Institute of Standards and Technology, United States

Solar energy plays an important role in solving serious environmental problems and meeting the high energy demand. However, the lack of suitable materials hinders further progress of this technology. Here, we present the largest inorganic solar cell material search till date using density functional theory (DFT) and machine-learning approaches. We calculated the spectroscopic limited maximum efficiency (SLME) using the Tran–Blaha-modified Becke–Johnson potential for 5097 nonmetallic materials and identified 1997 candidates with an SLME higher than 10%, including 934 candidates with a suitable convex-hull stability and an effective carrier mass. Screening for two-dimensional-layered cases, we found 58 potential materials and performed G0W0 calculations on a subset to estimate the prediction uncertainty. As the above DFT methods are still computationally expensive, we developed a high accuracy machine-learning model to prescreen efficient materials and applied it to over a million materials. Our results provide a general framework and universal strategy for the design of high-efficiency solar cell materials. The data and tools are publicly distributed at:
9:13 AM S.CT01.06.03
Autonomous Thin-Film Growth System for Materials Discovery

Ryota Shimizu1,2, Shigeru Kobayashi1, Yasunobu Ando3 and Taro Hitosugi1; 1Tokyo Institute of Technology, Japan; 2JST-PRESTO, Japan; 3National Institute of Advanced Industrial Science and Technology, Japan

The integration of knowledge, experience, and intuition of researchers with artificial intelligence (AI) and robotics is the new direction to accelerate progress in materials research [1]. Strategies combining high-throughput synthesis with machine learning have already been producing new small organic molecules and bio-materials at ever faster rates. However, the application of the techniques to inorganic materials research is still in its infancy. Therefore, to drastically accelerate inorganic materials science research, establishing the AI and robotics inclusion into inorganic materials research is an urgent issue.

In this study, we demonstrate the autonomous synthesis of inorganic compounds using robotics and Bayesian optimization. This system fully automates sample transfer, thin film deposition, physical-property characterization, and growth condition optimization. The apparatus is equipped with a robot arm that can access each satellite chamber for growth and characterization. Based on the values obtained from the physical-property characterization, the Bayesian-optimization algorithm predicts the next growth condition (closed-loop). Here, we show the process of reducing the resistivity of Nb-doped TiO2 transparent conducting thin films [2]. The autonomous synthesis can be applied to a wide variety of functional materials including magnetic, optical, electronic, and ionic properties.

References


9:19 AM S.CT01.06.04
Gr-ResQ—a Database for Graphene Synthesis Recipes

Aagam Shah, Joshua Schiller, Matthew Robertson, Kristina Miller, Kevin J. Cruse, Kaihao Zhang, Mitisha Surana, Chae Seol, Darren Adams, Elif Ertekin and Sameh Tawfick; University of Illinois at Urbana-Champaign, United States

This presentation introduces Graphene Recipes for Synthesis of High Quality Materials (Gr-ResQ) (https://nanohub.org/tools/gresq). Gr-ResQ is designed to be a one stop solution for analysis of graphene synthesis by Chemical Vapor Deposition (CVD). Gr-ResQ consists of a comprehensive crowd-sourced database of synthesis recipes and results as well as a suite of software tools to analyze the database. It offers tools to analyze scanning electron microscope images and Raman spectra of graphene. It was developed as part of NSF’s nanoMFG node within nanoHUB.

Advancing the manufacturing of graphene by CVD requires the ability to make CVD more cost-effective, including synthesizing low-defect density graphene directly on relevant substrates at reasonable costs. This is currently difficult mainly due to the multi-physics nature and the multi-time, and multi-length scales of the synthesis reaction. CVD processes can have over 200 variables, many of which are difficult to precisely control. This leads to poor repeatability and lack of a quantitative distribution of the parameter space. Characterization of synthesized graphene with electron microscopy and Raman spectroscopy gives useful information about the crystallinity, coverage, nucleation density and other such physical and chemical properties. The challenge of making interpretations and correlations from this data can be met by constructing a database that ties together the variables used in a process (the recipe) with the characterization of the synthesized graphene, which allows the application of data science and machine learning techniques to graphene and other 2D materials. One such use is in the estimation of graphene coverage from SEM images, which is generally a manual and time consuming task. We are trying to replace that by training a deep neural network (DNN) image segmentation algorithm with our manual coverage data to produce high quality, automated graphene coverage metrics.

In this presentation, we will discuss the database and the various tools, showing a number of examples that uniquely take advantage of the functionality of the database.

9:25 AM S.CT01.06.05
Bridging the Gap Between Literature Data Extraction and Domain-Specific Materials Informatics
Zachary Jensen, Haihao Liu, Rubayyat Mahbub, Kevin J. Huang and Elsa Olivetti; Massachusetts Institute of Technology, United States

Advances in applying natural language processing (NLP) to material science text has greatly increased the size and acquisition speed of materials science synthesis data. These methods have been successfully applied to well-studied material systems with large amounts of data. However, we need ways to leverage literature data in materials domains without thousands of papers. Applying NLP pipelines to these types of materials science systems can be challenging due to the general schema and the noisiness of automatically extraction data. In this presentation, we demonstrate how to leverage domain knowledge to build upon existing data extraction techniques and improve extraction accuracy using examples in the zeolite, alternative cement, and solid-state electrolyte fields. We present data engineering techniques and discuss an optimal balance between automatic and manual data extraction.

9:37 AM S.CT01.06.07
CAMD: An AI-Accelerated End-to-End Materials Discovery Platform
Joseph H. Montoya and Muratahan Aykol; Toyota Research Institute, United States

We present an end-to-end system for computational autonomy in materials discovery (CAMD). This system is designed to sequentially augment a given dataset according to user-specified strategies for choosing new experiments and experimental procedures. The decision-making entities, called "agents," can make use of past knowledge, surrogate models, logic, thermodynamic or other physical constructs, heuristic rules, and different exploration-exploitation strategies. We show a series of examples for how discovery campaigns for finding materials satisfying a phase stability objective can be simulated to design new agents, and how those agents can be deployed in real discovery campaigns to control experiments run externally, such as the cloud-based density functional theory simulations in this work. Lastly, we present results from the cloud-based deployment of our tool that have resulted in over 2000 new inorganic crystalline materials in various crystal symmetries and compositions predicted to be within 200 meV of the phase diagram's convex hull.

9:43 AM S.CT01.06.08
Improved Structure-Informed Prediction of Formation Energy Based on the Voronoi Tessellation—New Neural Network-Based Model and Applications
Adam M. Krajewski, Jonathan Siegel, Zhengqi Liu, Jinchao Xu and Zi-Kui Liu; The Pennsylvania State University, United States

Recently, machine learning (ML) is becoming an increasingly important tool for material discovery, thanks to its ability to quickly predict results of time and power-intensive calculations. Fundamentally, each ML model predicts some property and is composed of three essential elements: a database, a descriptor, and an ML algorithm. In this work, we have created and assessed a new tool for predicting formation enthalpies (ΔHf). We take an open DFT database (OQMD), Voronoi tessellation-based descriptor developed by the Wolverton group[1], and then design new neural networks that allow us to significantly improve the accuracy of predictions and reduce the computation time down to the order of 100 microseconds per prediction.

During the neural network design process, we created and tested around 50 networks belonging to 19 architectures. We used cross-validation on a randomly selected test set comprising 5% of the OQMD database (21,800 test entries) to compare with competing models. We found that our best network achieved a ΔHf mean average error of 35 meV/atom, compared with ≈70 meV/atom for a model based on the Random Forest algorithm[1]. In addition to simple cross-validation against a subset of the data for comparison with other models, the performance was also evaluated on more challenging systems. These included Special Quasirandom Structures (SQS) and 243 endmembers of a ternary σ phase (topologically close packed). Using such an approach during design, allowed us to improve accuracy for structures that are significantly different from those in the original dataset, and thus require extrapolation.

In this presentation, we show not only the new model but also new applications. Most notably, we take advantage of the improved prediction speed to screen whole databases for entries that do not fit the discovered patterns, and then automatically compare flagged entries to other sources. This, in turn, combined with more in-depth analysis, allows us to pinpoint entries that are likely to contain poor quality data, as well as those at risk of having a systematic error in the DFT calculation.

References:
[1] L. Ward et al., "Including crystal structure attributes in machine learning models of formation energies via Voronoi...
9:49 AM S.CT01.06.09
Supervised and Unsupervised Machine Learning of EELS Data for Oxidation State Determination and Phase Analysis Cassandra Pate, Mitra Taheri and Jamie Hart; Johns Hopkins University, United States

Advances in electron imaging and spectroscopy instrumentation now allow for time-resolved data acquisition at rates over 1000 frames per second. However, this acquisition speed comes at the expense of the signal-to-noise ratio. At high frame rates, the low signal-to-noise (SNR) ratio can causes datasets to be too noisy for analysis with the naked eye without significant post-processing. Another challenge (often times exacerbated by poor SNR) is quantification of oxidation state. For example, in transition metal oxides, many methods exist for valence determination, e.g. L3/L2 ratio, chemical shift, or O K-edge pre-peak analysis. Unfortunately, these different methods can yield contradictory results, particularly in the presence of noisy data. Here, we seek to address both of these challenges through the application of machine learning techniques. First, we will discuss supervised learning of oxidation state in SrFeOx thin films. With a convolutional neural network trained on >10,000 spectra, we obtain ~70% classification accuracy in differentiating SrFeO3 (Fe4+) from SrFeO2.5 (Fe3+) during an in situ experiment with very noisy data collected at 400 frames / second. Next, we will discuss ongoing efforts in unsupervised learning of EELS data. Unsupervised learning makes it possible to analyze different materials without needing a comprehensive database of labelled EELS data to compare with. Because unsupervised learning works by finding its own patterns or structures within the data, via techniques such as feature extraction or clustering, applying it to real-time in-situ data could help better understand phase morphology of the materials and could expose if unintentional or incomplete transformations of the sample occurred and in turn, the ability to more precisely and predictively tune complex materials. Unsupervised learning will be applied to various in situ EELS experiments.
A model describing the origin of water-induced degradation of certain Metal-Organic Frameworks (MOFs) is derived, aiming to explain experimental observations of water stability and instability of prototypal MOFs. The proposed model suggests crucial role of metal-coordinated water molecules, and solution pH, in triggering a cascade of reactions that in several cases results in pronounced irreversible degradation of several MOFs. It is suggested that such degradation pathways can be affected in neutral to basic solution by deprotonation of metal-coordinated water molecules, or bridging hydroxyl species in multilayered clusters. Calculations of pKa values for the metal-coordinated water molecules, complemented by geometry relaxation calculations, and variable pH infrared spectroscopy techniques were all simultaneously utilized to draw a comprehensive description for the early stages in MOFs degradation in aqueous medium. Mostly dependent on the nature of metal nodes, we propose two distinct mechanisms for structural degradation of carboxylate-based MOFs. The MOFs investigated herein included MOF-5, HKUST-1, UiO-66, and MIL-101-Cr.  

It is suggested that for each type of MOF, a comprehensive description for the early stages in MOFs degradation in aqueous medium. Mostly dependent on the nature of metal nodes, we propose two distinct mechanisms for structural degradation of carboxylate-based MOFs. The MOFs investigated herein included MOF-5, HKUST-1, UiO-66, and MIL-101-Cr. It is suggested that for each type of MOF, a narrow pH stability range can be described, mostly determined by the pKa of metal-coordinated water molecules and the relaxation calculations, and variable pH infrared spectroscopy techniques were all simultaneously utilized to draw a comprehensive description for the early stages in MOFs degradation in aqueous medium. Mostly dependent on the nature of metal nodes, we propose two distinct mechanisms for structural degradation of carboxylate-based MOFs. The MOFs investigated herein included MOF-5, HKUST-1, UiO-66, and MIL-101-Cr. It is suggested that for each type of MOF, a narrow pH stability range can be described, mostly determined by the pKa of metal-coordinated water molecules and the

5:00 AM S.CT01.01.06
Accelerated Discovery of Metal Oxide Photoanodes for Solar Fuels Applications John M. Gregoire; California Institute of Technology, United States

Solar fuel generation from H$_2$O, CO$_2$ and sunlight comprises a promising renewable energy technology whose future proliferation relies on materials advancements, including identification of a photoanode for the oxygen evolution reaction. A water-oxidizing photoanode can be coupled to a (photo)cathode for scalable generation of H$_2$ and C-containing fuels. Metal oxides are the most extensively studied class of OER photoanode materials due to the availability of a multitude of metal oxide phases that may stably operate in the oxidative electrochemical environment while converting solar to photoelectrochemical (PEC) energy. Solar fuels photoanodes are quite rare due to the combined needs of solar absorption, charge carrier separation and transport, oxidative stability, and catalytic activity for the OER. The compendium of known metal oxide photoanodes that operate in the visible spectrum is being rapidly expanded via theory-guided high throughput experimentation, including our combination of combinatorial materials synthesis coupled with automated UV-vis spectroscopy and PEC experiments. Discovery of dozens of ternary metal oxide photoanodes will be discussed with focus on the lessons learned in terms of the role of theory and the importance of compositionally graded libraries, and a historical analysis of the discovery rate of metal oxide photoanodes reveals increasing chemical diversity, suggesting there may be many more materials to be discovered. The rapidly expanding portfolio of metal oxide photoanodes creates new avenues of inquiry to realize the requisite stability and efficiency for deployment of solar fuels technologies.

5:00 AM S.CT01.01.07
Probing the Water-Induced Degradation Pathways of Metal-Organic Frameworks (MOFs)—The Potential for Highly Transferrable Surface Passivation Approach Mohamed H. Alkordi$^1$, Mohamed E. Safy$^1$, Muhamed A. Amin$^2$, Rana R. Haikal$^1$, Basma Elshazly$^1$ and Ahmed H. Ibrahim$^1$; 1Zewail City of Science and Technology, Egypt; 2University of Groningen, Netherlands

A model describing the origin of water-induced degradation of certain Metal-Organic Frameworks (MOFs) is derived, aiming to explain experimental observations of water stability and instability of prototypal MOFs. The proposed model suggests crucial role of metal-coordinated water molecules, and solution pH, in triggering a cascade of reactions that in several cases results in pronounced irreversible degradation of several MOFs. It is suggested that such degradation pathways can be affected in neutral to basic solution by deprotonation of metal-coordinated water molecules, or bridging hydroxyl species in multilayered clusters. Calculations of pKa values for the metal-coordinated water molecules, complemented by geometry relaxation calculations, and variable pH infrared spectroscopy techniques were all simultaneously utilized to draw a comprehensive description for the early stages in MOFs degradation in aqueous medium. Mostly dependent on the nature of metal nodes, we propose two distinct mechanisms for structural degradation of carboxylate-based MOFs. The MOFs investigated herein included MOF-5, HKUST-1, UiO-66, and MIL-101-Cr. It is suggested that for each type of MOF, a narrow pH stability range can be described, mostly determined by the pKa of metal-coordinated water molecules and the
relative strength of metal-carboxylate interactions. Beyond this fundamental pH range, a relatively wider pH window can exist, where certain MOFs can be kinetically inert. Finally, we present a highly transferrable and facile approach to induce surface passivation of MOFs crystals to effectively extend such aqueous solution stability limits, as proven by the case of appreciably maintained microporosity of HKUST-1 in neutral, acidic and basic aqueous solution.

5:00 AM S.CT01.01.08

**Combinatorial Approach for Single Crystalline TaON Growth—Epitaxial β-TaON (100) /α-Al₂O₃ (012)**

Narayanachari Kondapalli, D. Bruce Buchholz, Elise Goldfine, Sossina M. Haile and Michael J. Bedzyk; Northwestern University, United States

The semiconductor photocatalyst β-TaON used for water splitting is of interest due to its promising properties, such as stability, suitable band gap for visible light photocatalysis and carrier mobility. We have implemented a combinatorial, materials discovery approach using pulse-laser deposition (PLD) for thin film growth, X-ray diffraction (XRD) for phase determination and machine learning for data reduction. A lateral compositional gradient of TaOₓNₓ was grown across the surface of a α-Al₂O₃ (012) 25-mm-wide wafer by PLD at 675°C in 10 mTorr of N₂. After annealing in N₂ at 1000°C, small-area XRD scattering patterns were collected for 71 positions across the lateral gradient. Unsupervised machine learning separated the XRD data into 4 clusters (phases); one of which turned out to be the desired β-TaON phase. Using high-resolution XRD we determined that the β-TaON region of the film to be single crystal epitaxy with out-of-plane β-TaON (100) // α-Al₂O₃ (012) and in-plane β-TaON (010) // α-Al₂O₃ (2-10). X-ray reflectivity (XRR) analysis of the β-TaON region of the film determined the film thickness to be 260 Å with an electron density matching that expected for β-TaON. Ta 4f7/2 XPS measurements across the graded film showed Ta⁵⁺ valence state at the β-TaON region of the film. In comparison to the standard method of growing many uniform films at different compositions, this combinatorial method that produces a library of phases on a single wafer is much more efficient for materials discovery.

5:00 AM S.CT01.01.09

**The Energy Landscape Governs Plasticity in Glasses**

Longwen Tang and Mathieu Bauchy; University of California, Los Angeles, United States

Based on their structure, non-crystalline phases can fail in a brittle or ductile fashion. However, the nature of the linkages between structure and propensity for ductility in disordered materials has remained elusive. Here, based on molecular dynamics simulations, we investigate the fracture of several disordered phases (metallic glass, glassy silica, colloidal gel, etc.) with varying degrees of disorder. We find that that, in general, structural disorder results in an increase in ductility. By applying the activation-relaxation technique (an accelerated sampling method to identify transition states), we show that the degree of plasticity is controlled by the topography of the energy landscape.

SESSION S.CT01.02: Functional Material Design and Discovery by Machine Learning

Session Chairs: Ross King and Nav Nidhi Rajput

On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

S-CT01

5:00 AM *S.CT01.02.01

**Data-Driven Materials Discovery for Functional Applications**

Jacqueline M. Cole¹²³; ¹University of Cambridge, United Kingdom; ²STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, United Kingdom; ³Argonne National Laboratory, United States

Large-scale data-mining workflows are increasingly able to predict successfully new materials that possess a targeted functionality. The success of such materials discovery approaches is nonetheless contingent upon having the right data source to mine, adequate supercomputing facilities and workflows to enable this mining, and algorithms that suitably encode structure-function relationships as data-mining workflows which progressively short list data toward the prediction of a lead material for experimental validation.

This talk describes how to meet these data science requirements by showing how to auto-generate large material databases of experimental information from documents, using natural language processing and machine learning, via our
ChemDataExtractor tool [1-3]. The resulting large databases of chemical structures and their cognate properties are then mined for materials discovery using custom-built algorithms that are encoded forms of structure-function relationships. These molecular design rules progressively filter the parent set of chemicals until a lead candidate appears, which is experimentally validated. Case studies are demonstrated to illustrate the power of data-driven materials discovery for several functional applications.

References
[1] www.chemdataextractor.org

5:30 AM S.CT01.02.02
Discovering New Hydrogen Storage Materials Using an Empirical Design Principle for Metal Hydrides Matthew Witman¹, Sanliang Ling², David Grant², Gavin Walker², Sapan Agarwal¹, Vitalie Stavila¹ and Mark D. Allendorf³; ¹Sandia National Laboratories, United States; ²The University of Nottingham, United Kingdom

The development of a hydrogen economy has potentially immense benefits for addressing the crisis of global heating. However, storage remains a problem and decades of research have left us empty-handed: no known materials can satisfy all of the DOE targets for vehicular storage. Metal hydrides are among the most promising solid-state storage materials, but their complex chemistry is a major impediment to discovery of game-changing materials. Specifically, their thermodynamics are often ill-matched to hydrogen release at temperatures compatible with fuel cells. This limitation requires an equilibrium H₂ pressure of at least 5 bar at the maximum delivery temperature of 80 °C. Empirical discovery approaches using, for example, high-throughput synthesis, are largely ineffective because measurement of the equilibrium H₂ pressure can take days or even weeks. Machine learning (ML) methods have already shown promise for accelerating the discovery of new hydrogen sorbents and identifying key features that influence their properties. In recent application to metal hydrides, however, the use of “black-box” algorithms prohibited development of crucial vital scientific insight needed to go beyond existing compositions. We employed a gradient-boosting tree regressor, an “explainable” ML that can reveal the feature dependence of material properties. In particular, we find that the equilibrium H₂ pressure of intermetallic metal hydrides strongly depends on a volume-based feature that requires only the elemental composition to be computed. Remarkably, this simple structure-property relationship is valid across a wide range of compositions, metal substitutions, and structural classes found in intermetallic metal hydrides. This result provides a rational basis for targeting novel hydrogen storage materials with thermodynamic properties appropriate for specific applications. As an illustration, we identified a known intermetallic that forms a hydride with very low stability. Although not yet validated by experiment, this result was confirmed by density functional theory modeling.

5:45 AM S.CT01.02.03
De Novo Discovery of Nanoporous Structures by Machine Learning Mathieu Bauchy; University of California, Los Angeles, United States

Nanoporous materials (e.g., zeolite, activated carbon, metal-organic framework, polymeric membranes, etc.) have various technological applications, including gas separation, gas storage, catalytic transformations, etc. The functionalities of nanoporous materials strongly depend on their pore size and shape distribution—which present virtually limitless degrees of freedom. Here, based on high-throughput simulations and a convolutional neural network (CNN) predictor, we present a model allowing us to predict the water sorption isotherm of hydrophilic and hydrophobic nanoporous materials. The training of a CNN generator then enables the inverse design of optimal porous microstructures featuring tailored/unusual sorption isotherms.

6:00 AM *S.CT01.02.06
Machine-Based Discovery of Energetic Materials Peter W. Chung; University of Maryland, United States

Recent successes demonstrated by machine learning (ML) approaches have created great enthusiasm for their potential translational contributions to other fields. Among these are efforts to demonstrate the feasibility of using machine-based approaches to study and speculate on new energetic materials. This talk will discuss the performance of ML models developed to predict the detonation properties of energetic materials. A comprehensive comparison of approaches reveals that models are highly sensitive to feature selection as well as algorithm differences. But using a relatively limited volume of data and careful problem definitions, surprisingly strong cross validation scores suggest that there is promise to both improve and ultimately use ML methods widely in this field. The talk will conclude with an overview and some perspectives of other
recent efforts including generative modeling and natural language processing techniques at their intersections with energetics research.

6:30 AM *S.CT01.02.07
A Machine-Learning-Based Strategy for Accelerated Discovery of Novel Scintillator Chemistries Anjana Talapatra, Christopher R. Stanek, Blas P. Uberuaga and Ghanshyam Pilania; Los Alamos National Laboratory, United States

Inorganic scintillator-based detector materials find a wide variety of applications, ranging from medical imaging to radiation detection for global security and high energy physics experiments. These materials essentially convert a fraction of the total energy deposited by incident gamma rays or X-rays into visible or near-visible range of the spectrum. In many applications a scintillator with high light output, fast response time, and emission at suitable wavelengths, is generally required, among many other application-specific desired characteristics. However, owing to several conflicting relationships between the desired properties (e.g., brightness versus speed), no single scintillator is ideal for all uses; there is a need to design custom scintillators optimized for each application. Traditionally, the discovery and design of new detector materials have relied on a laborious, time-intensive, trial-and-error approach; yielding little physical insight and leaving a vast space of potentially revolutionary materials unexplored. To accelerate the discovery of optimal scintillator materials with targeted properties and performance, efforts are ongoing to develop a closed-loop machine learning driven adaptive design framework based on data from literature, in-house experiments and quantum mechanical calculations. This talk will present an overview of this framework, focusing on the screening of complex wide band gaps chemistries with an aim of identifying promising materials that are amenable to band-gap/band-edge engineering to yield custom scintillation properties. The developed framework is general and is expected to prove useful for applications beyond scintillator discovery such as photovoltaics and catalysis.

7:00 AM S.CT01.02.09
Machine-Learning Guided Discovery of MOFs for Enhanced Hydrogen Storage Capacity Samrendra Singh, Abhishek Sose, Karteeck Bejagam and Sanket A. Deshmukh; Virginia Tech, United States

In recent years the use of various machine-learning (ML) methods to discover new materials with desired properties have emerged as a powerful tool. In this research, we have designed a stacked ensemble model (SEM) by combining several supervised ML models to predict the adsorption of hydrogen in metal-organic frameworks (MOFs). The SEM model was trained by using the hydrogen adsorption data generated by screening of 1000s of MOFs by performing grand canonical monte carlo (GCMC) simulations at 1 atm and 77 K. This SEM was integrated with optimization algorithms and in-house MOF structure generation code to design MOFs with high adsorption of hydrogen. Overall, this new approach of integrating SEM with optimization algorithms accelerated the new MOF discovery process, resulting in a MOF with enhanced hydrogen storage capacity. This new ML framework is transferable and can be used to discover other porous (e.g. zeolites), soft (e.g. polymers), and hard (e.g. alloys) materials for desired applications.

SESSION S.CT01.03: Toward Autonomous Lab
Session Chairs: Ross King and Jian Lin
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-CT01

5:00 AM *S.CT01.03.02
Progress towards Autonomous Perovskite Discovery, Synthesis and Characterization Using ESCALATE+RAPID Joshua Schrier; Fordham University, United States

The dream of autonomous materials discovery systems will only be realized if the entire design/synthesis/characterization process is described in an unambiguous machine-readable format. Specifying the experiment process in a machine-readable way facilitates both remote operation, algorithmic control of experiments, and enhanced experimental replicability. A significant challenge is that materials experiments often require a combination of instructions for human operators and machines. Furthermore, the variety of materials characterization data and experimental performance metadata during a process often require significant extraction/transformation/loading before machine learning methods can be applied. Existing
tools require significant development time that is incompatible with rapidly evolving scientific needs.

In this talk, I will describe ESCALATE (Experiment Specification, Capture and Laboratory Automation Technology) an adaptable open source package for experiment description and data collection. As a specific example, I will describe its application to Robotic-Accelerated Perovskite Investigation and Discovery (RAPID). The first generation of RAPID uses inverse temperature crystallization (ITC) to grow halide perovskite single crystals for x-ray structure determination and bulk characterization using commercial liquid handling robots. Experiment plans are contributed remotely, by either human scientists or algorithms trained on the reaction data. Incoming experimental data collected by ESCALATE is used to automatically train machine learning models, evaluate model performance and feature influence on model predictions to gain human-interpretable scientific insight into the formation process, and quantify experimental reproducibility using this complete dataset of all experimental successes and failures. A live web dashboard communicates these insights to the scientist and management in visual form; furthermore experimental data can be exported in the form of interactive visualizations for use in publications. Collected characterizations includes qualitative measurements of crystal quality (including photographic images of the samples), powder X-Ray diffraction, and spectroscopic measurements along with background laboratory conditions. The second generation of RAPID has been extended to include antisolvent precipitation synthesis of perovskite single crystals and perovskite thin film synthesis and characterization including remote monitoring of long-term environmental stability. We have used the ESCALATE/RAPID platform to perform experimental tests benchmarking a variety of data-driven approaches for discovering new compounds against human-expert and random baselines. The comprehensive data collected from these experiments has also allowed us to ascertain the relative importance of descriptive physical models for reaction composition relative to raw experimental descriptions when constructing machine learning models for reaction outcome prediction.

5:30 AM *S.CT01.03.03
Autonomous Combinatorial Experimentation Ichiro Takeuchi; University of Maryland, United States

Machine learning has become an integral part of many aspects of materials research. As a branch of machine learning, active learning has attracted much attention which can effectively help navigate experimental sequences in materials research. We are actively incorporating active learning in screening of combinatorial libraries of functional materials. For some physical properties, each characterization/measurement requires time/resources long/large enough that "high"-throughput measurement is not possible. Examples include detection of martensitic transformation and superconducting transitions in thin film libraries. By incorporating active learning into the protocol of combinatorial characterization, we can streamline the measurement and the analysis process substantially. We will present examples of mapping of phase change memory materials as well as others functional materials. This work is performed in collaboration with A. Gilad Kusne and V. Stanev. This work is funded by ONR and AFOSR.

6:00 AM S.CT01.03.04
Machine Learning Assisted Synthesis of Metal-Organic Nanocapsules Yunchao Xie¹, Chen Zhang², Xiangquan Hu¹, Chi Zhang¹, Steven Kelley¹, Jian Lin¹ and Jerry L. Atwood¹; ¹University of Missouri-Columbia, United States; ²North Carolina State University, United States

Herein, we report the successful discovery of a new hierarchical structure of metal-organic nanocapsules (MONCs) by integrating chemical intuition and machine learning algorithms. By training datasets from a set of both succeeded and failed experiments, we studied the crystallization propensity of metal-organic nanocapsules (MONCs). Among four machine learning models, XGBoost model affords the highest prediction accuracy of 91%. The derived chemical feature scores and chemical hypothesis from the XGBoost model assist to identify proper synthesis parameters showing superior performance to a well-trained chemist. This paper will shed light on the discovery of new crystalline inorganic-organic hybrid materials guided by machine learning algorithms.

6:15 AM *S.CT01.03.05
Autonomous Robotic Assembly of Two-Dimensional Crystals to Build van der Waals Superlattices Satoru Masubuchi¹, Masataka Morimoto¹, Momoko Onodera¹, Sei Morikawa¹, Takashi Taniguchi², Kenji Watanabe² and Tomoki Machida¹; ¹University of Tokyo, Japan; ²National Institute for Materials Science, Japan

Van der Waals heterostructures are comprised of stacked atomically thin two-dimensional crystals and serve as novel materials providing unprecedented properties. However, the random natures in positions and shapes of exfoliated two-dimensional crystals have required the repetitive manual tasks of optical microscopy-based searching and mechanical transferring, thereby severely limiting the complexity of heterostructures.
To solve the problem, we develop a robotic system, powered by artificial intelligence, that automatically searches exfoliated 2D crystals and assembles them into vdW superlattices inside glovebox [1-3]. The system can automatically scan the surface of silicon substrates, analyze optical microscope images, and detect a variety of atomically thin 2D materials without human intervention. The stacking order, positions, and crystallographic orientations of the 2D crystals are designed using the customized CAD software. The robotic assembly system of two-dimensional crystals enabled stacking four cycles of the designated two-dimensional crystals per hour with few minutes of human intervention for each stack cycle.

The system enabled fabrication of the vdW superlattice structures consisting of 29 alternating layers of the graphite and the hexagonal boron nitride (hBN) flakes. Encapsulated graphene devices exhibited high charge carrier mobilities (>1,000,000 cm²/Vs), demonstrating the applicability of the system for prototyping a variety of high-quality vdW superlattices. The wider material design freedom enabled by our system offers unprecedented opportunities for exploring the potential of vdW heterostructures. By this development, we can reduce the human intervention involved in the vdW heterostructure fabrication by orders. We believe that this work free up researchers from repetitive tasks and letting them focus on more intellectually creative tasks.

The hardware/software designs are available at https://github.com/tdmms/


6:45 AM S.CT01.03.06
Combining Experiment and Theory in a Closed-Loop Learning Cycle to Improve Perovskite Device Stability and Performance Tonio Buonassisi; Massachusetts Institute of Technology, United States

In my annual poster, I'll review the MIT PVLab's recent work combining experiment and theory in a closed-loop, machine-learning (ML) driven framework. Closed-loop experimentation driven by ML enables rapid and efficient convergence on optima, within vast search spaces. A review of scientific insights, as well as our latest machine-learning algorithms, will be presented.

7:00 AM S.CT01.03.07
High Throughput Nanoindentation and Machine Learning Assisted Analysis for Evaluation of Materials under In Operando Conditions Eric Hintsala¹, Bernard Becker¹, Youxing Chen², Benjamin Stadnick¹, Ude Hangen¹, Nathan Mara³ and Douglas D. Stauffer¹; ¹Bruker Nano Surfaces, United States; ²University of North Carolina at Charlotte, United States; ³University of Minnesota, United States

Meeting current and future demands for advanced structural materials designed to operate in extreme environments requires rigorous mechanical performance evaluation at such conditions. When considering alloy development for such applications, such as nuclear materials, multiple compositions and processing routes create many permutations of material to be evaluated at different temperatures and radiation damage levels. Where traditional bulk scale mechanical testing is relatively time consuming, high speed nanoindentation mapping techniques can provide large (and highly localized) Hardness and Modulus datasets. This allows for analysis of heterogeneous distributions of properties in multi-phase alloys, which can then be correlated to the microstructure through use of supplementary techniques, such as EBSD, which has similar resolution. However, this requires accompanying analysis methods to also be high throughput, for which machine learning based techniques are of interest. Some datasets, as large as one million indentations in a given map, are beyond the limit of reasonable human analysis.

In this study, a high vacuum, high temperature nanoindenter was utilized to produce temperature controlled mapping of three advanced types reactor materials up to 500°C while protecting the sample surface from oxidation. The materials studied were Fe-based HEAs, with varied Al content to give 3 distinct microstructures. Structure-property correlation was quantitatively explored through clustering to partition the hardness and modulus data to individual microstructural elements and evaluate their thermal stability, with irradiation studies to follow. While qualitatively these methods performed comparably to by hand grouping, there is a need to quantitatively understand their systematic uncertainties without making assumptions regarding the underlying probability distribution. This is further explored for this data set by using a parametric bootstrapping method to resample the probability distribution function from the individual data points. Three different machine learning methods, Kernel Density Estimation, Gaussian Mixture and Multi-Normal, are used to generate a probability distribution function. This is then resampled to produce a simulated dataset 1000 times the original dataset in size. This allows K-means, Spectral and
Gaussian Mixture clustering techniques to be applied and compared, but in principal, this can be applied to evaluate other properties as well.

7:15 AM *S.CT01.03.08
Autonomous Materials Development for Fun and Profit Kristofer G. Reyes; State University of New York at Buffalo, United States

Closed-loop, sequential learning is a key paradigm in autonomous materials development. Within this framework, aspects of the materials system under study are modeled, and such models are used to decide subsequent experiments to be run, results of which are fed-back to update models. In the past, off-the-shelf solutions and algorithms have been employed to optimize material properties. In this talk, we describe how autonomous materials platforms can be used for problems other than materials property optimization. We will specifically highlight work on autonomous phase mapping and real-time control, and how a common framework can be used to capture problem-specific structure and objectives. Relevant to this is the development of tools to perform autonomous materials characterization. We will describe how rich characterization data such as microscopy images or three-dimensional reconstructions from atom probe tomography can be analyzed without human intervention to encode experimental results for subsequent use within the closed loop. Together, the work described demonstrates the broad applicability of autonomous platforms throughout materials science research.

7:45 AM *S.CT01.03.09
A Bayesian Experimental Autonomous Researcher for Mechanical Design Keith A. Brown1, Aldair Gongora1, Bowen Xu1, Wyatt Perry1, Chika Okoye1, Patrick Riley2, Kristofer G. Reyes3 and Elise Morgan3; 1Boston University, United States; 2Google, United States; 3University at Buffalo, The State University of New York, United States

While additive manufacturing (AM) has facilitated the production of complex structures, it has also highlighted the immense challenge inherent in identifying the optimum structure for a given application. Numerical methods are important tools for optimization, but experiment remains the gold standard for studying non-linear, but critical, mechanical properties such as toughness. To address the vastness of AM design space and the need for experiment, we develop a Bayesian experimental autonomous researcher (BEAR) that combines Bayesian optimization and high-throughput automated experimentation. Using the BEAR, we explore the toughness of a parametric family of structures and observe more rapid, in terms of both experiments and time, convergence towards higher-performing structures than was obtained using a grid-based search. Specifically, we observe that the BEAR matched the performance of a grid-based search in 60 times fewer experiments. In addition to providing a platform to discover mechanical properties of AM-produced metamaterials, the BEAR provides a framework for exploring active learning in an experimental context including multi-agent decision policies, the incorporation of theory in an experimental loop, and the influence of heteroscedasticity. Collectively, these results show the value of machine learning in experimental fields where data are sparse.

8:15 AM *S.CT01.03.10
Interpretable Machine Learning for Materials Design and Characterisation Keith T. Butler; Rutherford Appleton Laboratory, United Kingdom

In this talk I will look at how we can open up the perceived 'black box' of machine learning when designing and characterising materials. I will show how being able to look at and understand the inner workings of deep neural networks increases the value of these approaches for problems in materials science. Understanding the workings is important for (i) debugging and building better models, (ii) building confidence in models that perform well, (iii) learning from models that exceed human performance in certain problem areas. I will take examples of our research where we use graph neural networks to infer and predict dielectric properties of solids and where we use deep convolutional neural networks to interpret data from inelastic neutron scattering. In the former case a mixture of deep and shallow learning allows for extraction of principles as well as construction of robust accurate models. In the latter case understanding the workings of the neural network allows us to develop a method for guiding experiments to sample the most pertinent areas of signal space.

8:45 AM S.CT01.03.11
Inverse Design of Broadband Highly Reflective Metasurfaces using Neural Networks Eric Harper1, Eleanor Coyle2,1, Jonathan Vernon1 and Matthew Mills1; 1Air Force Research Laboratory, United States; 2Azimuth Corp, United States

The next generation of high performance optical materials require precise engineering to transcend the inherent limitations of bulk materials and achieve desired optical performance. These targeted properties originate from the interactions between inherent optical properties of the constituent materials and meticulously engineered sub-wavelength inhomogeneities.
However, the design of such metamaterials poses a significant challenge to researchers due to the near-infinite design space to consider, even for relatively simple metamaterials such as the two-dimensional all-dielectric metasurface. This metasurface has been the subject of intense research interest because of its unprecedented reflective performance resulting from low-loss dielectric materials and shape-dependent optical resonances. Here we employ artificial neural networks (ANNs) to invert the design process, conceiving metasurface designs with targeted reflection and transmission spectra. These ANNs are capable of coordinating the complex interactions of the eigenmodes from which these desired properties arise, delivering device designs demonstrating coefficients of reflection greater than 99% over a range of wavelengths more than 450nm.

9:00 AM S.CT01.03.12

Machine Learning-Aided Design of DNA-Stabilized Silver Clusters with Specific Fluorescence Wavelengths  
Stacy Copp1,2, Steven Swasey2, Alexander Gorovits1, Petko Bogdanov1 and Gwinn Elisabeth2; 1University of California, Irvine, United States; 2University of California, Santa Barbara, United States; 3University at Albany, State University of New York, United States

DNA-templated silver clusters (AgN-DNA) are known to exhibit a wide range of fluorescence colors for different choices of the DNA template sequence [1]. While these clusters are promising biosensors and biomarkers [2], rational design of AgN-DNA for specific applications is challenged by the huge space of possible DNA template sequences. To understand how DNA sequence selects for silver cluster size and optical properties, we are employing high-throughput experiments and tools from machine learning and data mining. We previously showed that machine learning methods trained on experimental data can be used to design new DNA templates that select for AgN-DNA color, for the specific and limited case of 10-base DNA oligomers [3]. An important open question is whether such a design process developed for a specific biopolymer template length is applicable at other lengths, with different numbers and diverse configurations of cluster nucleation sites. More broadly within materials informatics, it is important to determine when models learned on limited training data sets are relevant for prediction within expanded input parameter spaces.

Here, we present a newly developed flexible design approach that utilizes color-correlated DNA base motifs learned from data on > 2,000 ten-base DNA oligomers [4]. We test this motif-based design for templates ranging from 8 bases to 16 bases long, for which the sizes of the sequence spaces differ by nearly 5 orders of magnitude. The experimental data show that designed strands of all lengths are selective for AgN-DNA color in the target wavelength band of 600-660 nm, strongly suggesting that color-selective motifs learned for one template length generalize to other lengths. Thus, a motif-based design approach may be broadly suitable for future AgN-DNA applications.


SESSION S.CT01.04: Cognitive Materials Design and Discovery

Session Chairs: Jian Lin and Nav Nidhi Rajput

On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

S-CT01

5:00 AM *S.CT01.04.01

Multiscale Machine Learning for Quantum Many Particle Physics with Wavelet Scattering Transforms Matthew Hirn; 
Michigan State University, United States

Computing the ground state energy of quantum many particle systems is of fundamental importance in a variety of fields, including chemistry, physics and materials science, amongst others. However, the complexity of such quantum mechanical computations grows rapidly with the number of particles. Machine learning algorithms do not simulate the physical system, but instead estimate solutions by interpolating values provided by a training set of known examples. However, precise interpolations may require a number of examples that is exponential in the system dimension, and are thus intractable. Tractable algorithms compute interpolations in low dimensional approximation spaces, which leverage the underlying physical properties of the system.
In this talk I will give an overview of machine learning algorithms for computing the ground state energy of quantum many particle systems, describing the core principles of such algorithms and illustrating the common themes that emerge. I will then present in more detail our approach to the problem, which is based on a type of multiscale, multilayer convolutional neural network, called a wavelet scattering transform. Through a cascade of multiscale wavelet transforms and nonlinearities, the scattering transform encodes the appropriate invariants and regularity properties of the physical system. Wavelet scattering regressions, computed over databases of organic molecules and amorphous materials, achieve errors on the order of quantum mechanical simulations, but at a fraction of the computational cost.

5:15 AM S.CT01.04.03
Putting Scientists’ Eyes on Glass-Box Physics Rule Learner for Unraveling Nano-Scale Tribocharging Phenomena

In Ho Cho1, Qiang Li1, Rana Biswas1,2 and Jaeyoun Kim1; 1Iowa State University, United States; 2Ames Laboratory, United States

This multi-disciplinary research proposes a new framework that can infuse scientists’ experience and knowledge (named as scientists' eyes) into a constantly evolving, glass-box physics rule learner that can essentially extract hidden physics rules behind complex nano-scale phenomena. Recently, physics principles are gradually integrated into machine learning (ML) methods, but it is at its infancy to discover hidden physics rules. Such pursuits for hidden rules face formidable challenges when the physical experiments involve multifaceted measurements across three-dimensional (3D) specimens or objects. These remaining challenges render even advanced ML methods such as deep learning secondary, not as a primary explorer, in the broad science and engineering domains. Therefore, there exists a deep chasm still remains between materials science and ML community.

To overcome this challenge and unravel hidden physics rule behind nano-scale complex phenomena, we reinterpreted the deep learning's successful notion of multi-layered convolutions and gave rise to a new notion of "convolved information index." The convolved information index can facilitate handle physical measurements over 3D nano-scale specimens and measurements without losing experienced perspectives of scientists in the materials science. Also, the framework proposes "link function" as a generator of mathematical expressions about the identified nano-scale physics rules, thereby pursuing "glass-box" (as opposed to the black-box) learning and prediction. Consistent evolution capability is realized by integrating Bayesian update and evolutionary algorithms.

The framework is applied to nano-scale contact electrification (CE) phenomena, which are difficult to elucidate due to length scales and complex physical interactions [1,2]. Three experimental data sets are used. Tribocharged PDMS nanocup array is fabricated by the sequence of (1) prepare a PET mold with a 750 nm-pitch triangular array of nanocones, (2) pour the liquid phase PDMS, Sylgard 184, Dow Corning, mixed with the curing agent, (3) solidify the specimen, and (4) peel off the PDMS from the PET mold (for more details see [1,2]). Atomic force microscopy (AFM) in the tapping mode is used to measure the surface topography and potential. The charge values were measured by Kelvin probe force microscopy over patterned nano-cups represented by 3D point cloud. The experimental data consist of a variety of conditions regarding geometries, demolding directions, and nano-scale patterns (3000 nm by 3000 nm square area with an interval of 5.86 nm; 4000 nm by 4000 nm, with 7.8125 nm). The nano-cup's average heights are 154 nm, 93.5 nm, and 117 nm. The proposed glass-box learning begins from horizontal-demolding test data, and then the best-so-far identified rules are inherited to the next learning with new specimens in a chained way.

The feasibility tests show promising performances of the proposed framework in unraveling transparent, reasonable "expressions" of hidden physics rule along with reasonable reproduction of complex patterned distributions of electric potentials over the 3D point cloud. The proposed framework is believed to establish a promising partnership of scientists’ eyes and the advanced ML methods, thereby enabling data and ML-driven discovery of groundbreaking physics laws in the nano-world and beyond. This presentation will cover how this new framework can facilitate materials scientists' discovery with actual nano applications.


5:25 AM S.CT01.04.04
Materials By Design Using Artificial Intelligence—Modeling, Manufacturing and Testing

Markus J. Buehler, Chi-Hua Yu and Yu-Chuan Hsu; Massachusetts Institute of Technology, United States

In this talk we will review recent studies of applying atomistic-level modeling to describe fracture processes at different scales, from molecular to macroscale levels, and to use artificial intelligence and machine learning to design fracture resistant materials. Molecular and related multiscale modeling methods can be an effective method to better understand elementary fracture processes, ranging from brittle to ductile fracture and other materials failure phenomena such as creep, and provides
the basis for expansive training sets. To illustrate this framework, we report a design approach for optimizing the toughness of nanocomposite materials using artificial intelligence, implemented in a novel “AutoComp Designer” algorithm. The algorithm consists of a machine learning predictor combined with an AI improved genetic algorithm, which is capable of discovering de novo materials designs in a vast space of possible solutions. Facilitated by a deep convolutional neural network that is trained with a dataset of hundreds of thousands of combinations of soft and brittle materials originating from multiscale models. Through the algorithm, we extend the capability of physical simulations beyond property predictions to optimize the fracture toughness by altering the material distribution. The solutions are generated by our AI model at a dramatically lower computational cost compared to brute-force searching methods. We further investigate the physical mechanism for improving material performance behind the AI approach, and demonstrate the ability of AI to search for optimal designs with very limited sampling. Brute-force molecular dynamics simulations of the nanocomposite designs confirm that our AI design improves the performance by effectively decreasing the stress concentration at crack tip. This AI approach can be easily applied to other nanocomposites, biomaterials and other material classes, and provides a transferrable and reliable rapid design approach expanding current capabilities.

5:35 AM S.CT01.04.05
**Fast and Accurate Intertatomic Potentials by Symbolic Regression** Alberto Hernandez, Adarsh Balasubramanian, Fenglin Yuan, Simon Mason and Tim Mueller; Johns Hopkins University, United States

In recent years there has been great progress in the use of machine learning algorithms to develop interatomic potential models. Machine-learned potential models are typically orders of magnitude faster than density functional theory but also orders of magnitude slower than physics-derived models such as the embedded atom method. We demonstrate that machine learning, in the form of genetic programming, can be used to develop accurate and transferable many-body potential models that are as fast as the embedded atom method, making them suitable to model materials on extreme time and length scales. The key to our approach is to explore a hypothesis space of models based on fundamental physical principles and to select models from this hypothesis space based on their accuracy, speed, and simplicity. We demonstrate our approach by developing fast and accurate interatomic potential models for copper that generalize well to properties they were not trained on, and we discuss additional applications. Our approach requires relatively small sets of training data, making it possible to generate training data using highly accurate methods at a reasonable computational cost.

5:45 AM S.CT01.04.07
**Describing Materials for Machine Learning** Shyue Ping Ong, Chi Chen, Yunxing Zuo, Xiangguo Li, Zhi Deng and Weike Ye; University of California, San Diego, United States

Machine learning (ML) has emerged as a powerful tool in the study and design of materials. In this talk, I will discuss the different ways in which materials can be described and their relative merits and limitations. In particular, I will highlight the importance of choosing representations that not only satisfy known physical invariances (e.g., rotation, translation, etc.), but also incorporate known physics and chemistry in a hierarchy of knowledge. I will provide an overview of leading ML models and applications, and discuss how the problems of data scarcity and bias in materials science can be addressed using multi-fidelity, transfer learning and other approaches.

6:00 AM S.CT01.04.09
**A General Machine Learning Framework for Impurity Level Prediction in Semiconductors** Arun Kumar Mannodi Kanakkithodi and Maria K. Chan; Argonne National Laboratory, United States

Electronic levels introduced by impurities and defects in the middle of the band gap are critically important in semiconductors for optoelectronic, photovoltaic (PV) and quantum sensing applications. While “deep” defect levels can prove catastrophic for PV performance by causing non-radiative carrier recombination, impurity levels in the band gap could also be entangled for quantum sensing or lead to increased absorption of sub-gap photons which can enhance efficiencies. Predicting formation energies and charge transition levels for defects in semiconductors is thus paramount; density functional theory (DFT) has been widely applied for such studies to overcome experimental bottlenecks and confirm measured defect levels. However, the requirement of large supercells, advanced levels of theory, and inclusion of charge corrections make DFT computation of defect properties very expensive, and trends and knowledge from previous calculations are not exploited in subsequent ones.

In this work, we combine high-throughput DFT and machine learning (ML) to develop general predictive models for the formation enthalpy and charge transition levels of impurities in two broad semiconductor classes: (a) ABX₃ halide perovskites, and (b) group IV, III-V and II-VI semiconductors. DFT data is generated for impurity atoms selected from
across the periodic table and simulated in various possible cation, anion or interstitial sites. Any “semiconductor + impurity” combination is converted into a unique feature vector based on the defect site coordination environment, the tabulated elemental properties (eg. ionization energy, electronegativity, etc.) of the impurity atom, and electronic and energetic properties computed using low cost unit cell defect calculations. State-of-the-art neural networks (NN), random forest regression (RFR) and kernel ridge regression (KRR) are applied to train models for (a) impurity formation enthalpy, and (b) impurity charge transition levels, based on the input feature vector. Model performance is evaluated for different ML techniques, ML parameters such as number of hidden layers and network weights in NN, subsets of features, and size and nature of training dataset; the best predictive models thus obtained are deployed for comprehensive prediction and design purposes. It is seen that models trained on defects and impurities in pure cation/anion composition semiconductors are applicable to mixed or alloyed compositions as well: for instance, by training on data from pure canonical AB semiconductors like CdTe, ZnO, GaAs and SiC, the ML models can make accurate predictions for impurities in alloyed compositions of the same compounds, such as CdTe$_{1-x}$Se$_x$, Cd$_{1-x}$Zn$_x$O, Al$_{1-x}$Ga$_x$As$_{1-y}$Sb$_y$, etc. This versatility of the machine-learned models provides an avenue to access the optoelectronic impact of any atomic impurity in any possible pure or mixed composition semiconductor belonging to the same chemical space, which is useful for compositions that are expensive to model. We use the predictive models to efficiently screen for dominating impurities, that is impurities that shift the equilibrium Fermi level in the semiconductor as determined by dominant native defects, in hundreds of possible compositions in the halide perovskite and groups IV, III-V and II-VI semiconductor spaces. ML-based screening of impurities was tested against DFT screening for CdTe and seen to have an accuracy of 95%. The quick and accurate estimation of interesting dopants/impurities in semiconductors is made possible by this materials design framework powered by quantum mechanical computations and machine learning, which can be easily expanded to other semiconductor classes and improved by the infusion of fresh data, new descriptors and more advanced ML techniques.

References

1. A. Mannodi-Kanakkithodi et al., Chemistry of Materials 31 (10), 3599–3612 (2019).

6:10 AM S.CT01.04.10
Optimization Thermal Conductivity at Interfaces Using Learning Algorithms Malachi Schram$^1$, Anne Chaka$^1$, Zexi Lu$^1$, Sabiha Rustam$^1$ and Eric Harper$^2$; $^1$Pacific Northwest National Laboratory, United States; $^2$Air Force Research Laboratory, United States

In material science, we are frequently interested in understanding the properties and design implication of material at interfaces. These interfaces can be manipulated to improve the desired characteristics of the bulk material. In this study, we are interested in understanding and optimize the impact of interfacial atomic defects on the thermal transport across a Cu/Si junction. To that end, we developed a reinforcement learning based framework to optimize over a potentially large parameter search. Using this technique allows us to accumulate knowledge of the system of a given type of atoms and store this information into a neural network. In this study, we present our results on optimizing the thermal transport by varying the fraction and length of the interfacial atomic defects using molecular dynamics (MD) simulations with normal mode analysis (NMA) to investigate thermal transport.

6:20 AM S.CT01.04.11
Physics-Informed Machine Learning for Deep Elastic Strain Engineering of Electronic Properties of Materials Zhe Shi$^1$, Evgenii Tsymbalov$^2$, Ming Dao$^1$, Subra Suresh$^3$, Alexander Shapeev$^2$ and Ju Li$^1$; $^1$Massachusetts Institute of Technology, United States; $^2$Skolkovo Institute of Science and Technology, Russian Federation; $^3$Nanyang Technological University, Singapore

Deforming a material to a large extent without inelastic relaxation can result in unprecedented properties. However, the optimal deformation state is buried within the vast continua of choices available in the strain space. Motivated by this challenge, we hereby advance a powerful strategy to circumvent conventional trial-and-error methods and adopt a unique type of machine learning framework for rationally designing the most energy-efficient pathway to achieve a desirable material property such as the electronic bandgap. This method invokes recent advances in the field of convolutional neural networks and active learning by utilizing a limited amount of \textit{ab initio} data for the training of a surrogate model, predicting electronic bandgap within an accuracy of sub-10 meV. Our model is capable of discovering the indirect-to-direct bandgap transition and semiconductor-to-metal transition in silicon by scanning the entire strain space [1]. It is also able to identify the most energy-efficient strain pathways that would transform diamond from an ultrawide-bandgap material to a narrow-bandgap semiconductor or even semimetal [2]. A broad framework is presented to tailor any target figure of merit by recourse to deep elastic strain engineering and machine learning for a variety of applications in microelectronics,
Autonomous Research Systems like ARES™ are disrupting the research process by using AI and Machine Learning to drive closed-loop iterative research. ARES™ is our autonomous research robot capable of designing, executing and evaluating its own experiments at a rate of up to 100 iterations per day. Previously ARES taught itself to grow carbon nanotubes at controlled rates (NPJ Comp Mat 2016). Here we discuss recent research campaigns on maximizing carbon nanotube growth rates using a Bayesian optimization planner. We also use HOLMES and knowledge gradient descent to introduce advanced decision policies with local parametric models to control nanotube diameter. Implications for nanotube materials development will be discussed. Finally, we have developed a new research robot for additive manufacturing, AM ARES™, which is at the early stages of teaching itself to print structures with unknown inks. We plan to make the AM ARES™ Robot available online so that a broad community of researchers can test concepts and approaches for AI/ML and experimental design as applied to 3D printing, thus building to the larger goal of enhancing citizen science.

Due to recent improvements in image resolution and acquisition speed, materials microscopy is experiencing an explosion of published imaging data. Intensive human efforts, however, are required to digest such published images. In this talk, we will discuss the MaterialEyes project, in which deep learning and natural language processing tools are used to extract microscopy images from scientific literature. The process is accomplished via a suite of scientifically-informed software tools in the EXSCLAIM python package (automatic EXtraction, Separation, and Caption-based natural Language Annotation of Images from scientific figures), which is ultimately focused on the acceleration of inductive materials insights by collecting, structuring, and interpreting an aggregate of materials microscopy imaging data. In this talk, we will discuss how deep learning and NLP is used in EXSCLAIM to: (1) extract figures and caption data from open source scientific documents, (2) automate the construction of self-annotated materials imaging datasets, and then (3) leverage literature-based insights to assist in image classification and segmentation tasks. In addition, we will discuss a new pipeline for crowdsourced image labeling that was used for training some of the deep learning models.

Characterization of nanomaterial morphologies with advanced microscopy and/or spectroscopy tools plays an indispensable
role in nanoscience and nanotechnology research, as rich information about the chemical compositions, crystallography, other physical and chemical properties, as well as the growth mechanism can be extracted from morphology analysis. However, the interpretation of imaging data heavily relies on the “intuition” of experienced researchers. As a result, many of the deep graphical features are often unused because of difficulties in processing the data and finding the correlations. Such difficulties can be well addressed by deep learning. In this work, we use the optical characterization of two-dimensional (2D) materials as a case study.

Currently, the most widely used approach to obtain high-quality 2D crystals in laboratories is mechanical exfoliation, followed by 2D crystal “hunting” under an optical microscope. This task is time-consuming and difficult especially for inexperienced researchers. Very recently, there has been growing interest in automating such a process. However, existing optical contrast based identification methods could not satisfy the needs for a general-use, fully automatic optical identification and/or characterization system, as they are often very specific to types of 2D crystals, conditions and configurations of the microscopes being used, image qualities, etc. In addition, optical contrast based methods would fail for harder problems in which the classes to be differentiated are not separable in the color space, such as identifying the materials or even predicting their physical properties from unlabeled optical images.

In reality, optical microscopic (OM) images contain rich, often unused information other than optical contrast. These deep graphical features can be extracted through deep learning, especially semantic segmentation methods based on convolutional neural networks (CNNs). In this work, an encoder-decoder semantic segmentation network called “SegNet” is configured for pixel-wise identification of OM images of 2D materials, in real time, and regardless of variations in optical setups. A fully automated system utilizing this algorithm can be used to free up tremendous amount of time for researchers. Additionally, we find that the algorithm finds correlations between the OM images and physical properties of the 2D materials and can thereby be used to anticipate the properties of new, as-yet uncharacterized 2D crystals. Finally, a transfer learning technique is applied to adapt the pretrained network to more optical characterization applications such as identifying layer numbers of chemically synthesized graphene domains. The proposed methodology can potentially be extended for identification and understanding other morphological or spectroscopic data of diverse nanomaterials.

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6:00 AM S.CT01.05.04
Density Functional Theory and Deep-Learning to Accelerate Scanning Tunneling Microscopy Analysis Kamal Choudhary; National Institute of Standards and Technology, United States

We introduce the first systematic database of scanning tunneling microscope (STM) images obtained using density functional theory (DFT) for two-dimensional (2D) materials. Specifically, the database is constructed using the Tersoff-Hamann method. It currently contains data for 681 exfoliable 2D from the JARVIS-DFT database. These computational STM images can directly aid the experimental analysis of experimental STM results as they provide ideal reference images. Examples of the five possible Bravais lattice types for 2D materials are discussed and the images for all the materials are made available on the website. We validated the computational STM technique by comparing our results to a few experimental images. As the analysis of multiple STM images during an experiment could be tedious, we used our DFT-STM image database to train a high-accuracy convolution neural network (CNN) model to accelerate the characterization process.

6:15 AM *S.CT01.05.05
Measurements in Machine Learning Gerald Friedland; University of California, Berkeley, United States

A major obstacle in applying machine learning to scientific and engineering tasks is the lack of engineering rules for the design of machine learning systems that allow to make these system reproducible and the limits of the systems known. Based on joint research with physicists and material engineers, this talk presents engineering principles and measurement processes[1] that aim at structured engineering of machine learning systems. While the focus of this talk is on neural networks, the principles and presented measurements are universal and applicable to a variety of machine learning systems.


6:45 AM S.CT01.05.06
Machine Learning the Magnetostriction of Polycrystalline Tb,Dy1-x,Fe2 Alloys—A Graph Neural Network
**Approach** Minyi Dai, Mehmet F. Demirel, Yingyu Liang and Jiamian Hu; University of Wisconsin-Madison, United States

Predicting the magnetostriction of a large-scale (mm-mm) polycrystalline Tb\textsubscript{x}Dy\textsubscript{1-x}Fe\textsubscript{2} (Terfenol-D) alloy by direct numerical simulations is mathematically tedious and computationally expensive, because it requires solving a set of partial differential equations which describe the mutual coupling between local magnetization dynamics and polycrystal elasticity, and because it requires a large number of simulation cells (tens of millions and more). For accelerating the prediction of magnetostriction, we apply a graph-based deep learning method, namely, the Graph Neural Network (GNN), to discover the correlation between a microstructure dataset of 350 different polygrain structures and a property dataset describing the magnetic-field-induced deformation of each polygrain structure (viz., magnetostriction). In the GNN based approach, each grain is represented as a node, in which all important physical features (e.g., Euler angle, magnetization direction) inside a grain are stored. As a result, the polygrain structure is represented as a network of nodes, in which the identity information of each grain(node)’s neighboring grains(nodes) is also preserved. This in turn allows us to consider the grain-grain interaction which critically influences the magnetostriction of the entire alloy and interpret the contribution of each node(grain) to the magnetostriction. A >90% prediction accuracy has so far been achieved with ample space for improvement. Our results demonstrate the exciting potential of applying GNN to accelerate the discovery of microstructure-property linkage in polycrystalline materials.

**Data-Driven Characterization of Structural Dynamics in Nanoparticles** Peter A. Crozier\textsuperscript{1}, Ramon Manzorro\textsuperscript{1}, Carlos Fernandez-Granda\textsuperscript{2}, Qiang Zhu\textsuperscript{3}, Mahmoud Moradi\textsuperscript{4}, David Matteison\textsuperscript{2} and Roberto Rivera\textsuperscript{5}; \textsuperscript{1}Arizona State University, United States; \textsuperscript{2}New York University, United States; \textsuperscript{3}University of Nevada Las Vegas, United States; \textsuperscript{4}University of Arkansas–Fayetteville, United States; \textsuperscript{5}Cornell University, United States; \textsuperscript{6}University of Puerto Rico-Mayaguez, United States

Materials are ubiquitous in society and lie at the heart of many technologies including energy, communication, buildings, transportation, the environment and medicine. The constant need to develop new materials with properties that are matched to applications is a major driver of materials research. Understanding how atoms come together, self-assemble, dissociate and undergo phase transformations under different stimuli is a critical question in materials science. Transmission electron microscopy can now routinely achieve a spatial resolution of better than 1 Å allowing the projected spatial distribution of atoms to be observed. In situ methodologies allow these signals to be mapped both spatially and temporally in the presence of different stimuli. Rapid advances in detector and spectrometer technology now allow local imaging, diffraction and spectroscopic signals to be acquired at unprecedented rates, generating terabytes of data in relatively short times.

The availability of large spatially and temporally resolved datasets offers unprecedented potential to transform our understanding of the fundamental atomic level dynamic processes taking place in materials. The rate at which atomic resolution data can be generated in experiments has now outstripped our ability to process and mine scientifically important information. The complex nature of atomic resolution images necessitates intense supervision and input in most quantitative image processing operations. Such an approach is possible for a few hundred images but becomes completely impractical when millions of data frames are available. This has become a serious bottle-neck to extracting the new knowledge potentially available from advanced characterization systems. We need approaches that can recognize recurring motifs in noisy data sets, provide statistical confidence levels for detection of real structural features, track dynamic changes within the sample, and flag events which are likely to be scientifically significant.

We are focused on applying emerging data-driven techniques based on statistics and machine learning to characterize structural dynamics in nanomaterials with an initial focus on metal and oxide nanoparticles 1 – 3 nm in size. Nanoparticles have wide applications in many areas of materials science and are an ideal system for developing and benchmarking novel data-driven processing techniques because they only contain a few thousand atoms. The datasets are acquired using in situ electron microscopy and structural dynamic processes are stimulated using heat, gas or electron irradiation. We compare and contrast the performance of automated image processing algorithms designed to determine atomic coordinates and structural evolution with more conventional manual methods. The importance of understanding the confidence level that can be associated with derived structural models is critical to assess the reliability of the scientific information extracted from large data sets.

**Acknowledgements**
We gratefully acknowledge support of NSF OAC-1940263, and the use of facilities at Arizona State University’s John M. Cowley Center for High Resolution Electron Microscopy.
Deep Learning Based Characterization of Nanoindentation Induced Acoustic Events

Antanas Daugela1 and David W. Peterson2; 1Nanometrix LLC, United States; 2University of St. Thomas, United States

Developed as a Baushinger effect monitoring technique in polycrystalline metallic materials, passive acoustic wave monitoring has been a critical health monitoring technique in: Atomic energy pressurized tank; Power and structure monitoring in aeronautics; Automotive; As well as recent applications in spinning disk data storage (HDD) health monitoring applications [1]. Passive monitoring of acoustic waves generated during the initial contact point has been attracting the attention of material scientists since the inception of nanomechanical test instruments for nanoindentation and nanoscratch applications. The conventional acoustic wave signal treatment via RMS or integrated energy values proves that quantitative acoustic wave properties correlate well with the local contact materials phenomena such as: Yield point initiation for W(100) [2, 3]; Sapphire [4], phase transformation for SMA [2]; and differentiating of thin film fracture modes [5]. Several attempts have been made to look at the differentiative properties of the acoustic signatures via signal decomposition techniques such as wavelets [2, 6]. Even though acoustic wave signatures were reconstructed, the true potential of the method was not investigated from the machine learning perspective.

In this work a deep learning based signal processing of nanoindentation induced acoustic events was investigated. The synergy of wavelet signal decomposition and information theory based signal presorting prepared data for the deep learning step. In the deep learning step convolutive neural networks sort wavelet coefficients by their statistical significance via provided 2D signal topographies. This creates acoustic signature libraries that are typical for the specific materials phenomena during the indent. The hardware consists of a newly developed ultrasonic probe integrated into the nanoindentation tip, thus eliminating boundary effects and ensuring that only waves that pass via the contact are being recorded. Appropriate signal conditioning and fast data acquisition hardware is synchronized with a quasi-static nanoindentation process. The machine learning routine together with wavelet decomposition and presorting algorithms are implemented into the dedicated acoustic data evaluation kernel which resides in the fast access memory of the designated controller.

REFERENCES:
Beyond Expert-Level Performance Prediction for Rechargeable Batteries by Unsupervised Machine Learning Xin Li; Harvard University, United States

Predicting the performance of rechargeable batteries in real time is of great importance to battery research and industrial production, and hence has been a long pursuit. In this talk, a novel end-to-end unsupervised machine learning approach is shown for the battery performance prediction, which is free from feature engineering and uses only the raw images of the charge–discharge voltage profiles [1]. This model enables unsupervised real-time automatic extraction of latent physical factors that control the performance of Na-ion batteries to classify good or bad cycling performance by using only the voltage profile of the first cycle. This model can also monitor the safety of Li-metal battery systems by giving warnings when the battery is approaching a failure. With the beyond expert-level prediction ability, the above-mentioned framework can be a promising prototype to further develop and enable high accuracy predictions of battery performance for real-world applications in the future.

Accelerated Discovery of Efficient Solar Cell Materials Using Quantum and Machine-Learning Methods

Kamal Choudhary; National Institute of Standards and Technology, United States

Solar energy plays an important role in solving serious environmental problems and meeting the high energy demand. However, the lack of suitable materials hinders further progress of this technology. Here, we present the largest inorganic solar cell material search till date using density functional theory (DFT) and machine-learning approaches. We calculated the spectroscopic limited maximum efficiency (SLME) using the Tran–Blaha-modified Becke–Johnson potential for 5097 nonmetallic materials and identified 1997 candidates with an SLME higher than 10%, including 934 candidates with a suitable convex-hull stability and an effective carrier mass. Screening for two-dimensional-layered cases, we found 58 potential materials and performed G0W0 calculations on a subset to estimate the prediction uncertainty. As the above DFT methods are still computationally expensive, we developed a high accuracy machine-learning model to prescreen efficient materials and applied it to over a million materials. Our results provide a general framework and universal strategy for the design of high-efficiency solar cell materials. The data and tools are publicly distributed at:

Autonomous Thin-Film Growth System for Materials Discovery

Ryota Shimizu1,2, Shigeru Kobayashi1, Yasunobu Ando3 and Taro Hitosugi1; 1Tokyo Institute of Technology, Japan; 2JST-PRESTO, Japan; 3National Institute of Advanced Industrial Science and Technology, Japan

The integration of knowledge, experience, and intuition of researchers with artificial intelligence (AI) and robotics is the new direction to accelerate progress in materials research [1]. Strategies combining high-throughput synthesis with machine learning have already been producing new small organic molecules and bio-materials at ever faster rates. However, the application of the techniques to inorganic materials research is still in its infancy. Therefore, to drastically accelerate inorganic materials science research, establishing the AI and robotics inclusion into inorganic materials research is an urgent issue.

In this study, we demonstrate the autonomous synthesis of inorganic compounds using robotics and Bayesian optimization. This system fully automates sample transfer, thin film deposition, physical-property characterization, and growth condition optimization. The apparatus is equipped with a robot arm that can access each satellite chamber for growth and characterization. Based on the values obtained from the physical-property characterization, the Bayesian-optimization algorithm predicts the next growth condition (closed-loop). Here, we show the process of reducing the resistivity of Nb-doped TiO2 transparent conducting thin films [2]. The autonomous synthesis can be applied to a wide variety of functional materials including magnetic, optical, electronic, and ionic properties.

References


Gr-ResQ—A Database for Graphene Synthesis Recipes

Aagam Shah, Joshua Schiller, Matthew Robertson, Kristina Miller, Kevin J. Cruse, Kaifao Zhang, Mitisha Surana, Chae Seol, Darren Adams, Elif Ertekin and Sameh Tawfick; University of Illinois at Urbana-Champaign, United States

This presentation introduces Graphene Recipes for Synthesis of High Quality Materials (Gr-ResQ) (https://nanohub.org/tools/gresq). Gr-ResQ is designed to be a one stop solution for analysis of graphene synthesis by Chemical Vapor Deposition (CVD). Gr-ResQ consists of a comprehensive crowd-sourced database of synthesis recipes and results as well as a suite of software tools to analyze the database. It offers tools to analyze scanning electron microscope images and Raman spectra of graphene. It was developed as part of NSF’s nanoMFG node within nanoHUB.

Advancing the manufacturing of graphene by CVD requires the ability to make CVD more cost-effective, including synthesizing low-defect density graphene directly on relevant substrates at reasonable costs. This is currently difficult mainly due to the multi-physics nature and the multi-time, and multi-length scales of the synthesis reaction. CVD processes can have...
over 200 variables, many of which are difficult to precisely control. This leads to poor repeatability and lack of a quantitative
distribution of the parameter space. Characterization of synthesized graphene with electron microscopy and Raman
spectroscopy gives useful information about the crystallinity, coverage, nucleation density and other such physical and
chemical properties. The challenge of making interpretations and correlations from this data can be met by constructing a
database that ties together the variables used in a process (the recipe) with the characterization of the synthesized graphene,
which allows the application of data science and machine learning techniques to graphene and other 2D materials. One such
use is in the estimation of graphene coverage from SEM images, which is generally a manual and time consuming task. We
are trying to replace that by training a deep neural network (DNN) image segmentation algorithm with our manual coverage
data to produce high quality, automated graphene coverage metrics.

In this presentation, we will discuss the database and the various tools, showing a number of examples that uniquely take
advantage of the functionality of the database.

6:15 AM S.CT01.06.05
Bridging the Gap Between Literature Data Extraction and Domain-Specific Materials Informatics Zachary Jensen,
Haihao Liu, Rubayyat Mahbub, Kevin J. Huang and Elsa Olivetti; Massachusetts Institute of Technology, United States

Advances in applying natural language processing (NLP) to material science text has greatly increased the size and
acquisition speed of materials science synthesis data. These methods have been successfully applied to well-studied material
systems with large amounts of data. However, we need ways to leverage literature data in materials domains without
thousands of papers. Applying NLP pipelines to these types of materials science systems can be challenging due to the
general schema and the noisiness of automatically extraction data. In this presentation, we demonstrate how to leverage
domain knowledge to build upon existing data extraction techniques and improve extraction accuracy using examples in the
zeolite, alternative cement, and solid-state electrolyte fields. We present data engineering techniques and discuss an optimal
balance between automatic and manual data extraction.

6:30 AM S.CT01.06.07
CAMD: An AI-Accelerated End-to-End Materials Discovery Platform Joseph H. Montoya and Muratahan Aykol; Toyota
Research Institute, United States

We present an end-to-end system for computational autonomy in materials discovery (CAMD). This system is designed to
sequentially augment a given dataset according to user-specified strategies for choosing new experiments and experimental
procedures. The decision-making entities, called "agents," can make use of past knowledge, surrogate models, logic,
thermodynamic or other physical constructs, heuristic rules, and different exploration-exploitation strategies. We show a
series of examples for how discovery campaigns for finding materials satisfying a phase stability objective can be simulated
to design new agents, and how those agents can be deployed in real discovery campaigns to control experiments run
externally, such as the cloud-based density functional theory simulations in this work. Lastly, we present results from the
cloud-based deployment of our tool that have resulted in over 2000 new inorganic crystalline materials in various crystal
symmetries and compositions predicted to be within 200 meV of the phase diagram's convex hull.

6:45 AM S.CT01.06.08
Improved Structure-Informed Prediction of Formation Energy Based on the Voronoi Tessellation—New Neural
Network-Based Model and Applications Adam M. Krajewski, Jonathan Siegel, Zhengqi Liu, Jinchao Xu and Zi-Kui Liu;
The Pennsylvania State University, United States

Recently, machine learning (ML) is becoming an increasingly important tool for material discovery, thanks to its ability to
quickly predict results of time and power-intensive calculations. Fundamentally, each ML model predicts some property and
is composed of three essential elements: a database, a descriptor, and an ML algorithm. In this work, we have created and
assessed a new tool for predicting formation enthalpies (ΔHf). We take an open DFT database (OQMD), Voronoi tesselation-
based descriptor developed by the Wolverton group[1], and then design new neural networks that allow us to significantly
improve the accuracy of predictions and reduce the computation time down to the order of 100 microseconds per prediction.

During the neural network design process, we created and tested around 50 networks belonging to 19 architectures. We used
cross-validation on a randomly selected test set comprising 5% of the OQMD database (21,800 test entries) to compare with
competing models. We found that our best network achieved a ΔHf mean average error of 35 meV/atom, compared with ≈70
meV/atom for a model based on the Random Forest algorithm[1]. In addition to simple cross-validation against a subset of the
data for comparison with other models, the performance was also evaluated on more challenging systems. These included
Special Quasirandom Structures (SQS) and 243 endmembers of a ternary σ phase (topologically close packed). Using such an approach during design, allowed us to improve accuracy for structures that are significantly different from those in the original dataset, and thus require extrapolation.

In this presentation, we show not only the new model but also new applications. Most notably, we take advantage of the improved prediction speed to screen whole databases for entries that do not fit the discovered patterns, and then automatically compare flagged entries to other sources. This, in turn, combined with more in-depth analysis, allows us to pinpoint entries that are likely to contain poor quality data, as well as those at risk of having a systematic error in the DFT calculation.

References:

7:00 AM S.CT01.06.09
Supervised and Unsupervised Machine Learning of EELS Data for Oxidation State Determination and Phase Analysis Cassandra Pate, Mitra Taheri and Jamie Hart; Johns Hopkins University, United States

Advances in electron imaging and spectroscopy instrumentation now allow for time-resolved data acquisition at rates over 1000 frames per second. However, this acquisition speed comes at the expense of the signal-to-noise ratio. At high frame rates, the low signal-to-noise (SNR) ratio can causes datasets to be too noisy for analysis with the naked eye without significant post-processing. Another challenge (often times exacerbated by poor SNR) is quantification of oxidation state. For example, in transition metal oxides, many methods exist for valence determination, e.g. L3/L2 ratio, chemical shift, or O K-edge pre-peak analysis. Unfortunately, these different methods can yield contradictory results, particularly in the presence of noisy data. Here, we seek to address both of these challenges through the application of machine learning techniques. First, we will discuss supervised learning of oxidation state in SrFeO\textsubscript{x} thin films. With a convolutional neural network trained on >10,000 spectra, we obtain ~70% classification accuracy in differentiating SrFeO\textsubscript{3} (Fe\textsuperscript{4+}) from SrFeO\textsubscript{2.5} (Fe\textsuperscript{3+}) during an in situ experiment with very noisy data collected at 400 frames / second. Next, we will discuss ongoing efforts in unsupervised learning of EELS data. Unsupervised learning makes it possible to analyze different materials without needing a comprehensive database of labelled EELS data to compare with. Because unsupervised learning works by finding its own patterns or structures within the data, via techniques such as feature extraction or clustering, applying it to real-time in-situ data could help better understand phase morphology of the materials and could expose if unintentional or incomplete transformations of the sample occurred and in turn, the ability to more precisely and predictively tune complex materials. Unsupervised learning will be applied to various in situ EELS experiments.
propellant materials. Since the molecules in this category mostly have SOx / NOx groups, their chemical differentiation becomes difficult for sensing. We have already shown that metamaterial-inspired ring resonator works on the principle of sensing the changes in the dielectric media in its vicinity, thereby generating a change in the resonant frequency. In this work we further discuss the approach towards sensor optimization for sensing fixed library of propellant molecules by first. Machine learning algorithms like, Linear Discriminant analysis, Random Forrest and so on, would be optimized to achieve maximum selectivity and accuracy in the sensor. The data would be collected for the sensor operating at 430 MHz, and Vector Network Analyser is used to measure the sensor response. Sensing time, power shift, frequency shift and the recovery time are the basic parameters which would be measured. Sensor output is calibrated for the ppm concentration varying from 10 ppm to 1000 ppm. The data is submitted to the machine learning algorithm and the algorithm is subsequently trained for the unknown sample of the propellant material with unknown concentration, to establish the correctness of the device developed. The emerging data-driven techniques based on statistics collected from the actual sensor testing, and use of machine learning, and artificial intelligence (AI) to unlock predictions of the performance of resonator-based sensor, will be discussed elaborately in this presentation.

S.CT01.07.04
PLIM—Phosphorescence Lifetime Imaging Microscopy with Adapted Excitation Christian Oelsner, Volker Buschmann, Felix Koberling, Matthias Patting and Rainer Erdmann; PicoQuant GmbH, Germany

The combination of microscopic techniques with time-resolved luminescence detection is a valuable and powerful toolbox to investigate photophysical properties not only of different classes molecular systems, but also semiconductors, nanoparticles and QDs, polymers, solid-states as well as nano structures. Understanding of both photophysical processes as well as structure-property relationships are important steps toward optimization of properties and efficiencies in practical applications.

Investigating fast processes with short lifetimes as well as really long lived excited states (in the µs to ms range) do impose vastly different requirements. On one hand, monitoring fast dynamic processes necessitate high time resolution that can be achieved by using picosecond pulsed lasers and fast detectors along with appropriate time-correlated single photon counting (TCSPC) units. On the other hand, studying long-lived excited states normally require pulsed lasers with low repetition rates, detectors with good efficiency and sensitivity up to NIR, and counting electronics capable of multi-channel scaling mode for acquiring signal on the µs / ms time scale.

Here we demonstrate another way to investigate long lifetime decays (e.g., phosphorescence or delayed fluorescence) of samples by using adapted excitation in combination with a microscope for good spatial resolution, better signal quality, and faster measurement time. This PLIM setup uses a special laser driver with appropriate laser heads and suited photon counting electronics which enables experiments with higher photon flux, even with low laser repetition rates. Resulting intensity images clearly show an almost 7 fold higher intensity using the adapted excitation instead of excitation with a low repetition rate. Therefore we can reduce the acquisition time significantly because of the increased emission intensities and by recording lifetime images with a focus on detecting of photons with longer lifetimes in combination with fast electronics, that are not limited by dead-time effects.

S.CT01.07.06
Rapid Identification of X-Ray Diffraction Spectra Based on Very Limited Data by Convolutional Neural Networks Hong Wang, Yunchao Xie, Dawei Li, Heng Deng, Ming Xin and Jian Lin; University of Missouri-Columbia, United States

Large volumes of data generated during high-throughput synthesis and rapid characterizations call for rapid and automatic data analysis to accelerate material discovery. Herein, we report a convolution neural network (CNN) that was trained based on theoretic data and very limited experimental data for fast identification of experimental X-ray diffraction (XRD) spectra of metal-organic frameworks (MOFs). To augment the theoretical spectra as the training datasets, noise extracted from experimental spectra was applied to the theoretic spectra. The optimized CNN model can successfully identify all individual spectrum within Top 2 choice. Data dimension reduction analysis on the experimental XRD spectra by the local linear embedding (LLE) shows that the spectra from the same material are clustered in groups in the LLE component map. Some groups are highly distinguishable, while others are very close or overlapped. The reported CNN model together with the data-augmentation technique and procedure for interpreting the black box would not only open the numerous potential applications for identifying XRD spectra for different materials, but also pave avenues to autonomously analyze data by other characterization tools such as FTIR, Raman, and NMR.

S.CT01.07.07
Estimating Sound-Induced Piezoelectric Voltage—PDE and Machine Learning Approach Jason J. Kim; Korea
We suggest a practical and scientific method to select the optimal piezoelectric material to generate electricity from vibration induced by sound. The proposed method begins by modeling deflections caused by given voltages using partial differential equations (PDE), then implementing machine learning (shallow neural network) to estimate the generated electricity from varying deflections. During the PDE computations, while the geometry such as width and length is fixed, material properties such as the Poisson’s Ratio, Shear Modulus, and Elastic modulus are changed according to the selected piezoelectric material. By running a machine learning simulation trained by these data, we obtain the relationship between voltage changes and deflections which provides the way to select optimal materials. Among the 33 easily accessible, mostly commercialized piezoelectric materials, the trained learning model predicts voltage from given sound/deflection. Upon analysis, it is observed that the Steel Stainless Austenitic 304, Nickel Alloys, and Cork performed highest for our application by showing higher sensitivity between induced voltage to the deflections. This result demonstrates the versatile applicability of our scheme. It shows its transferability and, in other words, how readily the simulation can be applied to other materials with different properties and deflection variations.

S.CT01.07.09
Big Data-Driven and Machine Learning Approaches to Processing Large Atomic-Resolution In Situ TEM Image Datasets of Structural Reconfigurations in Catalytic Nanomaterials Joshua L. Vincent, Barnaby D. Levin and Peter A. Crozier; Arizona State University, United States

Heterogenous catalysts are an important class of materials that receive considerable research attention due to their large impact on energy and the environment. Aberration-corrected in situ environmental transmission electron microscopy (ETEM) is a powerful catalyst characterization tool capable of providing atomic-scale structural information from active catalysts under reaction conditions. Recent advancements in the realization of highly efficient direct electron detectors now enable atomically-resolved ETEM images to be acquired with a temporal resolution in the millisecond or sub-millisecond regime where catalytically relevant structural reconfigurations are thought to occur [1,2,3]. While there is potentially much to be gained from applying these new detectors to catalytic nanomaterials characterization, acquiring ETEM image series with high temporal resolution necessarily produces datasets that can be unwieldy in size and severely degraded by noise, rendering traditional image processing approaches impractical and ineffective at extracting useful scientific information. For example, recording a 64 megapixel in situ ETEM movie at 2.5 millisecond time resolution would produce around 100 gigabytes and many hundreds of frames of image data every second. We are interested in exploring innovative approaches to image processing that leverage new advances in data science on large, noisy, atomic-resolution in situ ETEM data sets.

Currently our efforts have focused on simple and scalable real-space processing techniques that involve fitting atomic columns with two-dimensional Gaussian functions [4]. This method yields information on the time-resolved position and intensity of atomic columns throughout the ETEM image series. Additionally, the results of this method serve as a starting point for comparison to results produced from advanced image processing done via artificial intelligence and machine learning-based approaches. We are also working toward the generation of an extremely large dataset of simulated ETEM images (10,000+), which could serve as the training set for a convolutional neural network that identifies the best possible match between an experimentally acquired image and a given structural model that was used in the image simulation. Developing a methodology that assigns a confidence level to the structural model that best matches the experimental image is important to assess the reliability of the results produced through such approaches, which could ultimately provide highly desirable information on the atomic scale structural evolution of catalyst nanomaterials [5].


S.CT01.07.11
Transferable Neural Networks for High-Throughput Discovery of Supramolecular Chemistries Wujie Wang, William H. Harris and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, United States

Neural network potentials based on atomic embeddings have demonstrated accurate force and energy evaluations to simulate
physical systems [1-5]. Moreover, it also shows good force field transferability across the chemical space of interests, which are critical for efficient computational screening. We propose an active learning strategy [6] that accelerates the sampling and training of transferable neural networks, particularly to capture supramolecular interactions that are critical for applications like designing chelating agents and electrolytes. The proposed method combines deep neural network training and active sampling of both chemical and configurational space in an end-to-end fashion to leverage the transferable configurational information across different but chemically similar species. This workflow has also enabled a high throughput virtual screening over the Ether-ion chemical space, which consists of $10^3 \sim 10^4$ molecules, and successfully discovered candidate highly ion-conducting Ether molecules for organic electrolyte applications[7-10].


S.CT01.07.12
Highly Accurate Neural Network-Based Structure-Informed Prediction of Formation Energy Based on the Voronoi Tessellation
Adam M. Krajewski, Jonathan Siegel, Zhengqi Liu, Jinchao Xu and Zi-Kui Liu; The Pennsylvania State University, United States

Recently Machine Learning (ML) is becoming an increasingly important tool for material discovery, thanks to its ability to predict results of time and cost-intensive calculations like first-principles calculations based on the density functional theory (DFT)[1]. In simple terms, each ML model predicts some property and is composed of three equally important elements: a database, a descriptor, and a ML technique.

In this project, we are predicting formation enthalpies ($\Delta H_f$) of arbitrarily defined compounds. To create the model, we have taken an open-source DFT database (OQMD), state of the art Voronoi tesselation-based descriptor developed by the Wolverton group[1], and then designed a new neural network which allowed us to improve the predictability of formation energy significantly.

The neural network architecture design was done in an empirical fashion. We started with a simple neural network and made iterative modifications to structure and hyper-parameters until we reached Mean Average Error (MAE) around uncertainty in the data. Our best performing network achieved MAE of 35 meV/atom when cross-validated on the test set of randomly selected 5% of the entire OQMD (21,800 entries).

When compared to competing models based on the Random Forest technique, this MAE value represents a two-fold improvement compared with the model using the same descriptor ($\approx 70$ meV/atom)[1] and a three-fold improvement compared to the Coulomb Matrix descriptor ($\approx 100$ meV/atom)[1,2].

Furthermore, we have used our model to investigate the OQMD data set and have found a small number of OQMD entries that had non-physical $\Delta H_f$. After the removal of three such entries from our test set (3/21,800), the cross-validation MAE has dropped to 28 meV/atom.
Our model provides excellent predictability, takes milliseconds to run, and is available ready-to-use in open-source MXNet format, that can be easily deployed on any device ranging from a supercomputer to an iPhone 5S.

References:

S.CT01.07.14
Using Machine Learning to Predict the Critical Temperature of New Ternary Superconductors
Sumner B. Harris, Cheng-Chien Chen and Renato P. Camata; The University of Alabama at Birmingham, United States

Superconductivity has been an area of intense research for more than a century, yet the intentional design of new superconductors remains a daunting challenge. The massive databases of experimental and calculated materials properties that have developed over recent years makes the use of a data-driven search for new superconducting materials possible. In this study, machine learning is used to model the Tc for 21,000+ known metallic and oxide superconductors in the SuperCon database [1]. The model uses 60 features that are generated based on a compound’s chemical composition. The accuracy of a random forest model with 10-fold cross validation is found to be 92%. Using this model, the Tc of ~4,500 new theoretically stable ternary compounds, with unknown structure, is predicted. Of these compounds, 571 are predicted to have a Tc within 30-77 K and 8 with Tc expected in the range 85-100 K. Examples of identified materials include chalcogen-containing compounds such as BeSe5Cs8, BiCs2Se2.5, and TeBaO2, as well as hydrogen-rich compounds such as TeO2H6, CuO2H6, and AgO5H5. Evolutionary structural prediction of identified promising compounds will enable ab-initio studies and provide guidance for corresponding material synthesis and characterization.


S.CT01.07.16
Accelerated Exploration of Stability between Layered and Complex Structures in PrBa1-xSrxCoc2-yFeyO5.5
Jun-Yeong Jo, Ingyu Choi and Yeong-Cheol Kim; KoreaTech, Korea (the Republic of)

Layered perovskite structures show high performance as an air electrode in solid oxide fuel cells and proton ceramic fuel cells [1]. Radii difference among metal elements at site A of ABO3 is a prerequisite for conversion of perovskite structure from complex to layered [2]. In this study, we study energetically favorable structures according to change in composition of site A elements (Pr, Ba, Sr) and site B elements (Co, Fe). 25 compositions were determined by changing x and y in PrBa1-xSrxCoc2-yFeyO5.5 (x = 0, 0.25, 0.5, 0.75, 1, and y = 0, 0.5, 1, 1.5, 2). The 2×2×2 supercells with the compositions were studied using DFT. Since the number of possible atomic arrangements for each composition is very large, however, a genetic algorithm was used to search energetically favorable structure efficiently [3]. The highest energy difference between complex and layered structures among the 25 compositions was obtained at x=0 and y=1.


SESSION S.LP02.02: Live Poster Session: Characterization and Theory (S.CT01, S.CT03, S.CT04, S.CT07 and S.CT08)
Session Chairs: Nicholas Kotov and Alexander Van Driessche
Monday Morning, November 30, 2020
11:30 AM - 1:30 PM
S.CT01

S.CT01.07.02
Design and Development of Metamaterial-Inspired Sensor Assisted by Machine Learning—Improvised Hazardous Chemical Sensor
Srjeet Srivastava, Vivek Kale, Saurabh Parmar, Suwarna Datar and Sangeeta N. Kale; Defence Institute of
Any sensor material, even if proved as an excellent performer at the research level, it can be put to less use if it does not meet the product criteria. The salient parameters include sensitivity, selectivity, recovery and re-usability. In order to thoroughly evaluate these parameters, huge amount of data is required; using which definite conclusions can be drawn. Calibration, life of the sensor and its scope of selectivity can be well defined. The most crucial part of any successful sensor system is its selectivity and close to 100% accuracy. In this regard statistical analysis along with the sensor design play a crucial role. It can decide how many sensors are required in an array of sensors to determine the presence of a particular analyte and its concentration with highest accuracy. In this context, through this abstract, we present the work done on a metamaterial-inspired ring resonator circuit, which works as an excellent sensor for chemically hazardous gases and liquids, which are propellant materials. Since the molecules in this category mostly have SOx / NOx groups, their chemical differentiation becomes difficult for sensing. We have already shown that metamaterial-inspired ring resonator works on the principle of sensing the changes in the dielectric media in its vicinity, thereby generating a change in the resonant frequency.

In this work we further discuss the approach towards sensor optimization for sensing fixed library of propellant molecules by first. Machine learning algorithms like, Linear Discriminant analysis, Random Forrest and so on, would be optimized to achieve maximum selectivity and accuracy in the sensor. The data would be collected for the sensor operating at 430 MHz, and Vector Network Analyser is used to measure the sensor response. Sensing time, power shift, frequency shift and the recovery time are the basic parameters which would be measured. Sensor output is calibrated for the ppm concentration varying from 10 ppm to 1000 ppm. The data is submitted to the machine learning algorithm and the algorithm is subsequently trained for the unknown sample of the propellant material with unknown concentration, to establish the correctness of the device developed. The emerging data-driven techniques based on statistics collected from the actual sensor testing, and use of machine learning, and artificial intelligence (AI) to unlock predictions of the performance of resonator-based sensor, will be discussed elaborately in this presentation.

**S.CT01.07.06**

**Rapid Identification of X-Ray Diffraction Spectra Based on Very Limited Data by Convolutional Neural Networks**

Hong Wang, Yunchao Xie, Dawei Li, Heng Deng, Ming Xin and Jian Lin; University of Missouri-Columbia, United States

Large volumes of data generated during high-throughput synthesis and rapid characterizations call for rapid and automatic data analysis to accelerate material discovery. Herein, we report a convolution neural network (CNN) that was trained based on theoretic data and very limited experimental data for fast identification of experimental X-ray diffraction (XRD) spectra of metal-organic frameworks (MOFs). To augment the theoretical spectra as the training datasets, noise extracted from...
experimental spectra was applied to the theoretic spectra. The optimized CNN model can successfully identify all individual spectrum within Top 2 choice. Data dimension reduction analysis on the experimental XRD spectra by the local linear embedding (LLE) shows that the spectra from the same material are clustered in groups in the LLE component map. Some groups are highly distinguishable, while others are very close or overlapped. The reported CNN model together with the data-augmentation technique and procedure for interpreting the black box would not only open the numerous potential applications for identifying XRD spectra for different materials, but also pave avenues to autonomously analyze data by other characterization tools such as FTIR, Raman, and NMR.

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Estimating Sound-Induced Piezoelectric Voltage—PDE and Machine Learning Approach Jason J. Kim; Korea International School, Korea (the Republic of)

We suggest a practical and scientific method to select the optimal piezoelectric material to generate electricity from vibration induced by sound. The proposed method begins by modeling deflections caused by given voltages using partial differential equations (PDE), then implementing machine learning (shallow neural network) to estimate the generated electricity from varying deflections. During the PDE computations, while the geometry such as width and length is fixed, material properties such as the Poisson’s Ratio, Shear Modulus, and Elastic modulus are changed according to the selected piezoelectric material. By running a machine learning simulation trained by these data, we obtain the relationship between voltage changes and deflections which provides the way to select optimal materials. Among the 33 easily accessible, mostly commercialized piezoelectric materials, the trained learning model predicts voltage from given sound/deflection. Upon analysis, it is observed that the Steel Stainless Austenitic 304, Nickel Alloys, and Cork performed highest for our application by showing higher sensitivity between induced voltage to the deflections. This result demonstrates the versatile applicability of our scheme. It shows its transferability and, in other words, how readily the simulation can be applied to other materials with different properties and deflection variations.

S.CT01.07.09
Big Data-Driven and Machine Learning Approaches to Processing Large Atomic-Resolution In Situ TEM Image Datasets of Structural Reconfigurations in Catalytic Nanomaterials Joshua L. Vincent, Barnaby D. Levin and Peter A. Crozier; Arizona State University, United States

Heterogenous catalysts are an important class of materials that receive considerable research attention due to their large impact on energy and the environment. Aberration-corrected in situ environmental transmission electron microscopy (ETEM) is a powerful catalyst characterization tool capable of providing atomic-scale structural information from active catalysts under reaction conditions. Recent advancements in the realization of highly efficient direct electron detectors now enable atomically-resolved ETEM images to be acquired with a temporal resolution in the millisecond or sub-millisecond regime where catalytically relevant structural reconfigurations are thought to occur [1,2,3]. While there is potentially much to be gained from applying these new detectors to catalytic nanomaterials characterization, acquiring ETEM image series with high temporal resolution necessarily produces datasets that can be unwieldy in size and severely degraded by noise, rendering traditional image processing approaches impractical and ineffective at extracting useful scientific information. For example, recording a 64 megapixel in situ ETEM movie at 2.5 millisecond time resolution would produce around 100 gigabytes and many hundreds of frames of image data every second. We are interested in exploring innovative approaches to image processing that leverage new advances in data science on large, noisy, atomic-resolution in situ ETEM data sets.

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2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
Transferable Neural Networks for High-Throughput Discovery of Supramolecular Chemistries

Wujie Wang, William H. Harris and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, United States

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Accurate Neural Network-Based Structure-Informed Prediction of Formation Energy Based on the Voronoi Tessellation

Adam M. Krajewski, Jonathan Siegel, Zhengqi Liu, Jinchao Xu and Zi-Kui Liu; The Pennsylvania State University, United States

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The neural network architecture design was done in an empirical fashion. We started with a simple neural network and made iterative modifications to structure and hyper-parameters until we reached Mean Average Error (MAE) around uncertainty in
the data. Our best performing network achieved MAE of 35 meV/atom when cross-validated on the test set of randomly selected 5% of the entire OQMD (21,800 entries).

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S.CT01.07.16
Accelerated Exploration of Stability between Layered and Complex Structures in PrBa$_{1-x}$Sr$_x$Co$_{2-y}$Fe$_y$O$_{5.5}$ Jun-Yeong Jo, Ingyu Choi and Yeong-Cheol Kim; KoreaTech, Korea (the Republic of)

Layered perovskite structures show high performance as an air electrode in solid oxide fuel cells and proton ceramic fuel cells \cite{1}. Radii difference among metal elements at site A of ABO$_3$ is a prerequisite for conversion of perovskite structure from complex to layered \cite{2}. In this study, we study energetically favorable structures according to change in composition of site A elements (Pr, Ba, Sr) and site B elements (Co, Fe).

25 compositions were determined by changing x and y in PrBa$_{1-x}$Sr$_x$Co$_{2-y}$Fe$_y$O$_{5.5}$ ($x=0, 0.25, 0.5, 0.75, 1$, and $y=0, 0.5, 1, 1.5, 2$). The 2x2x2 supercells with the compositions were studied using DFT. Since the number of possible atomic arrangements for each composition is very large, however, a genetic algorithm was used to search energetically favorable structure efficiently \cite{3}. The highest energy difference between complex and layered structures among the 25 compositions was obtained at $x=0$ and $y=1$.


S.CT04.07.04
IFF-R Model to Accurately Simulate Stress-Strain and Failure Properties of Carbon Allotropes and Polymer
Composites  

Jordan Winetrout¹, Krishan Kanhaiya¹, Ravindra Pandey², Gregory Odegard² and Hendrik Heinz¹; ¹University of Colorado Boulder, United States; ²Michigan Technological University, United States

Stress induced mechanical failure of polymeric materials is a result of the breakage of covalent bonds. The occurrence of bond breakage and formation is only observed during reactions. This study focuses on the novel bond-breaking capabilities of the Interface Forcefield (IFF-R). Traditional IFF models simulated systems using harmonic potentials. The IFF-R model incorporates Morse potentials; thereby, eliminating the restoring force experienced by bonded atoms stretched at large distances. This enables accurate predictions of mechanical responses in a variety of periodic systems. This study shows moduli and strength predictions of a single-walled carbon nanotube, poly(acrylonitrile) crystal, cellulose β crystal, and steel FCC lattice to be comparable to experimental values. Mechanical property predictions using IFF-R models are realized magnitudes faster than reactive forcefield (ReaxFF).

S.CT04.07.05

Porous Materials – Graphene Hybrid Nanostructures with Tailored Interfaces as Membrane and Adsorbent Components in Gas Separation  

Anish Varghese, Swati Singh, Suresh Kuppireddy and Georgios Karanikolos; Khalifa University, United Arab Emirates

Combinations of different materials into hybrid/composite structures are highly sought after as to enable multifunctionality in many of today’s demanding applications. 2-dimensional graphene can combine with porous nanostructures, such as metalorganic frameworks (MOFs), zeolites, and porous carbons, to yield hybrids with improved surface, interface, and activity characteristics. In this work, we will present examples of such material hybridizations via in-situ microstructural tuning of the interface between the involved counterparts. The resulting composites were tested for their gas separation performance, and specifically optimized to exhibit enhanced capture activity for carbon dioxide as adsorbents, as well as nanofillers in mixed matrix polymer-based membranes.

S.CT04.07.06

Site-Specific Surface Modification and Functionalization of Porous Nanostructured Scaffolds for Tunable Adsorption Applications  

Adetola Ogungbenro, Suresh Kuppireddy, Maryam Khaleel and Georgios Karanikolos; Khalifa University, United Arab Emirates

To reveal the full potential of high surface area materials, strategies to tailor their surface characteristics and tune their active sites with high spatial precision and order are needed. In this work, we employ porous materials having surface areas of several hundreds of m² per g and we apply customized chemistry based surface tailoring as to spatially create active sites and subsequently graft functional molecules on them. Such examples of surface features can have a multitude of applications, yet we focus on tuning the affinity of the materials to bound with selective species from mixtures as to enable separation. In particular, innovative CO₂-phylic amines are immobilized on the treated surfaces to yield multifunctional adsorbents for carbon dioxide capture. Examples of silica- and graphene-based materials with controlled covalent positioning of various aminosilanes on the modified surface sites will be presented. Controlled grafting ensured stability and sustainable adsorption, tuned effects of locality, spacing, orientation, and interconnectivity of the functionalities on the surface, and minimized diffusion limitations while maximizing capture and release performance for the adsorbate species.

S.CT04.07.07

Improving Oxidative Stability of MXenes via Tailoring Surface Chemistry  

Bryan T. Seymour¹,², James E. Heckler¹,², Gregory R. Neher¹,², David B. Lioi¹,², Ali Jawaid¹,², Faisal Mehmood¹,², Ruth Pachter², Richard A. Vaia², W. J. Kennedy² and Dhriti Nepal²; ¹Universal Technology Corporation, United States; ²Air Force Research Laboratory, United States; ³UES, Inc., United States

MXenes are an emerging class of two-dimensional layered transition metal carbides, carbonitrides, and nitrides. Their intriguing properties have attracted significant attention as promising materials for next-generation coatings and devices. One of the significant challenges of this material (e.g. Ti₃C₂Tx) is the rapid oxidation into TiO₂ anatase through hydrolysis in water, though water has proved to be the most effective solvent for solubilizing exfoliated Ti₃C₂Tx. Organic solvents routes for processing of MXenes and functionalization of its surface with specific ligands provide avenues to tailor the surface properties, which could eventually influence the colloidal stability as well as oxidative stability. Herein, we discuss the influence of various organic solvents such as ethanol, isopropanol, toluene, and N, N-Dimethylformamide on Ti₃C₂Tx colloidal stability, oxidative stability at room temperature, and thermo-oxidative properties. We also demonstrate the use of silane and catechol ligands for tailoring the physical properties of Ti₃C₂Tx.
Currently Gas sensors have a great impact in direct monitoring of environmental hazardous gas as well widely used in healthcare such as exhaled breath analysis. In this work we report a ZnO/Silicon nanowires (ZnO/p-Si NWs) based p-n heterojunction array based Nitric Oxide (NO) gas sensor operating at room temperature with extremely high response at least down to 0.5 ppm with noise limited response ~ 10 ppb. Utilization of cost effective chemical technique for fabrication of sensor on silicon is compatible with wafer level processing and easily connecting with silicon IC technology. The vertically aligned Si NWs array has been made by electroless etching method and the ZnO nanostructure was made by chemical solution deposition and spin-coating. We observe that the heterostructure leads to a synergetic effect where the sensing response is more than the sum total of the individual components, namely the ZnO and the Si NWs. The response is much enhanced in the p-n junction when the n-ZnO nanostructure interfaces with p-Si NW compared to that in the n-n junction formed by ZnO on n-Si NW. Extensive cross-sectional electron microscopy and composition analysis by line EDS allowed us to make a physical model. The comparison of the simulation results with the experiment point out the device parameters that enhance the device response. The characteristics values of the parameters of ZnO/Si NWs heterojunction for the best fits obtained from the simulation and it can be seen that all the parameters undergo change in the electrical model and this leads to enhancement of current in the device on gas exposure. The top layer of ZnO takes part in electrical current conduction. The Si NWs also has an all-round layer of ZnO that also acts as chemical sensing gate to modulate the depletion layer on the surface of the NW. The main inference from the simulation is that the observed high performances of the sensor device depends on change in resistances of the constituents as well change in the reverse saturation current at the ZnO/p-Si NW p-n junction.

A novel route to fabricate a hybrid ceramic matrix composite by utilizing preceramic polymers, chopped carbon nanofiber (CNF) precursors and subsequent additive manufacturing was introduced in this study. An allyl hydrido polycarbosilane (SMP-10) and 1,6-dexanediol diacylate (HDDA) were mixed with a photo initiator to form a photo sensitive resin. The resulting resin was loaded with distinct weight percentages of polyacrylonitrile (PAN) nanofiber. These mixtures were 3D printed followed by pyrolysis. The end objective of the pyrolysis cycle is that the pycarbosilane resin is converted into a silicon carbide matrix, with the PAN converted into reinforcing carbon nanofibers. The impact of the CNF percentages on structural and mechanical properties was investigated using scanning electron microscopy, transmission electron microscopy, and nano-indentation characterization techniques, respectively. The prepared precursor resin proved to have outstanding photo-curing properties and the ability to transform to the silicon carbide phase at temperatures as low as 850 °C. The result of this work showed that ceramic matrix composite components can be successfully fabricated using 3D printing and a specific pyrolysis cycle. The obtained ceramic hybrid composite was fully dense with nearly linear shrinkage and a shiny, smooth surface after pyrolysis. Furthermore, around 60% retained weight after pyrolysis to 1350 °C was confirmed by thermogravimetric analysis. In terms of crystallography, the ceramic matrix composite appeared to have three coexisting phases including silicon carbide, silicon oxycarbon, and turbostratic carbon. The results are very promising to fabricate hybrid composites working at high temperatures with improved mechanical properties and complex geometries.

We successfully synthesized Ge$_x$Se$_{1-x}$ (x = 0.225) glass samples and doped the samples with commercially produced (Protein Mods) carbon nanotubes (CNTs). We investigated the glass transition temperature ($T_g$) using Modulated Differential Scanning Calorimetry (MDSC). The glass samples without the CNTs have a $T_g$ of ~220°C and the $T_g$ was found to be independent of starting materials from different suppliers as well as water-bath temperature. CNTs, being a very hygroscopic material as well as oxygen absorbing material, needed to be cleaned under vacuum with the hot water-bath. We found that the $T_g$ decreases when 5% and 10 % CNTs by mass is added to the glass samples as compared to the base Ge$_x$Se$_{1-x}$ glass. The decrease in $T_g$ indicates the occurrence of an intermediate phase (reduced-stress glass phase) at lower temperature, which could be potentially useful in material science applications.
Optimization of Geometry and Edge Passivation for High-Performance Si Heterojunction (SHJ) Microcells

Niva K. Jayswal, Dipendra Adhikari and Nikolas J. Podraza; The University of Toledo, United States

Abstract:
Glancing angle deposition (GLAD) radio frequency (RF) magnetron sputtering enables production of polycrystalline CdTe with different microstructural properties including grain size, grain orientation, and crystal phase. In GLAD sputtering, the normals extending from the centers of the sample and sputtering target are at controllable angles with respect to each other. At lower source flux angles, films grow as the expected more energetically stable cubic zinc blende CdTe phase whereas at higher source flux angles the metastable wurtzite phase forms. During the GLAD process different microstructure and crystal phases are produced in the film due to increased atomic scale self-shadowing effects at higher source flux angles which result in limited diffusion of ad-atom precursors on the substrate. This wurtzite phase CdTe produced at high source flux angles is used to tailor the interface between the n-type hexagonal wurtzite CdS window layer and p-type cubic zinc blende CdTe absorber in the standard CdS/CdTe solar cell. Application of this wurtzite phase CdTe interlayer results in better lattice matching to both hexagonal CdS and cubic CdTe leading to higher photovoltaic device performance. Using spectroscopic ellipsometry (SE) and x-ray diffraction (XRD), the optical and microstructural properties of the GLAD CdTe interlayers before and after CdCl2 treatment are obtained. CdS/CdTe heterojunction solar cells are fabricated with GLAD interlayers prepared using source flux angles from 0° (normal incidence) to 80°, at substrate temperatures from room temperature to 250 °C, and with CdCl2 post-deposition treatment times up to 30 minutes. Photovoltaic device performances are compared between devices with and without the introduction of these GLAD CdTe interlayers. Improvements in photovoltaic device performance parameters including open circuit voltage, short circuit current, fill factor, and power conversion efficiency are related to GLAD CdTe interlayer characteristics.

Optimization of Geometry and Edge Passivation for High-Performance Si Heterojunction (SHJ) Microcells

Marjorie Potter1, Megan E. Phelan2, Pradeep Balaji3, Phillip Jahelka2, Rebecca Glaudell2, Michael Enright1, André Augusto1, Harry A. Atwater2 and Ralph G. Nuzzo1; 1University of Illinois at Urbana Champaign, United States; 2California Institute of Technology, United States; 3Arizona State University, United States

Perimeter recombination in micron-sized III-V photovoltaic (PV) materials has been studied extensively for performance at high concentrations, but minimal work toward understanding and optimizing edge recombination for Si-based photovoltaics has been pursued. Here, through both modelling and microcell fabrication, we explore the performance of Si heterojunction (SHJ) solar cells with varying edge to total surface area ratios by examining performance characteristics at different micron-scale lateral dimensions (between 200 µm × 200 µm and 1000 µm x 1000 µm microns) and device thicknesses (80 - 200 microns). We explore edge passivation strategies by determining the impact of a-Si:H and oxide- and nitride-based passivation coating materials on recombination at the edges and consequently device open-circuit voltage, VOC. Finally, we compare the impact of deep reactive ion etching (DRIE) and micro-laser cutting for solar cell dicing on edge surface quality and process scalability. Modelling results indicate that microcell device short-circuit current, JSC, increases with device thickness (up to 35 mA/cm2) and is generally independent of lateral dimensions, while device VOC decreases with thickness and increases with lateral dimensions, exceeding 700 mV at most geometries with high quality edge passivation. Consequently, device power conversion efficiency (PCE) is largely independent of thickness and increases with lateral dimensions, with a maximum PCE of > 20% at the largest lateral sizes. Notably, we found that edge passivation quality, rather than device geometry, dictates performance via the magnitude of edge recombination and is therefore the most important variable in this study to optimizing performance; high-quality a-Si:H was determined to be the best passivation material by virtue of minimizing edge recombination velocity (as indicated by dark current measurements) and thus maximizing VOC. Corroboration of modelling results with that of fabricated and tested SHJ microcell devices will be discussed, along with DRIE and micro-laser cutting routes to fabrication of micron-sized SHJ PV devices and the associated high-level cost-benefit analyses. This work will contribute to understanding of micro-scale Si-based PV and provide a framework for optimizing device parameters for integration with large-scale energy-harvesting systems.

Surface Morphology-Directed Nanoparticle Assembly for Versatile Sensors

Sayli Jambhulkar, Weiheng Xu, Dharneedar Ravichandran and Kenan Song; Arizona State University, United States

Well-controlled ‘pick-and-place’ of nanoparticles has vast potential in technological applications such as sensing, energy harvesting and transport, data storage, light composites, interfacial and functional modifiers, as well as other applications. These nanoparticles are anisotropic, including two-dimensional (2D) (e.g., nanosheets, nanolayers, nanoplatelets,
nanoribbons) and one-dimensional (1D) (e.g., nanorods, nanotubes, nanowhiskers, nanofibers) nanomaterials that are chemically composed of carbon, semiconductor, and metal elements. While the organization and alignment of anisotropic nanomaterials have been explored in many pathways, each method has its strengths and weaknesses. For example, non-directed methods (e.g., casting and drying) are simple and quite elegant but are somewhat limited in the morphologies they can access. As well, non-directed methods can be susceptible to factors such as solution concentrations and drying thermodynamics. Surface modification significantly expands the versatility of anisotropic nanomaterial assembly, but often requires challenging surface chemistry to modulate nanomaterial properties. Traditional use of prefabricated templates can control both the positional and orientational orders but requires the potentially difficult fabrication of a template. Therefore, our research aims to develop improved assembly strategies at microscales, coherently implemented into additive manufacturing (AM) infrastructure, to readily and simultaneously achieve orientational and positional control of anisotropic nanomaterials over arbitrarily large areas and volumes. The AM proposed here is an in-house designed process supported by layer-by-layer deposition of polymers with alternative and selective addition of nanoparticles. The printing and deposition mechanisms from the two-step manufacturing are compatible on the same processing platform that can greatly improve the precision and throughput.

Our proposed 3D printing mechanism will control the processing and material parameters along the working path such that each voxel of printed material itself can be a spatially varying architecture of particles giving rise to a response that differs locally from highly anisotropic to isotropic. Hence, this manufacturing enables the design and fabrication of composites with site-specific optimization of particle orientations, programmable surface morphology, and designable interfacial transitions. One-dimensional (1D) carbons, namely carbon nanofibers (CNF), will be demonstrated as an example here due to their superior anisotropic properties especially the higher conductivity or sensitivity along the fiber axis as compared to that along with the cross-section directions. We used 3D printing for surface morphologies controls and the CNFs were deposited via layer-by-layer self-assembly (LBL) techniques. The samples with different roughness and pattern features were compared for the efficiency of directed self-assembly. The solid-liquid-air interfaces were proven to be critical in determining the selective deposition of CNF for surface conductive paths and sensitivity degrees. The electricity characterizations showed a strong anisotropy along with the fiber alignment directions, showing resistivity of 0.27 kW/sqr along with the CNF band as compared to 1.21 kW/sqr along with the normal directions. This phenomenon was taken advantage of their sensing capabilities. We observed significantly improved sensitivity to strain, temperature, and chemical liquid/gas as compared to randomly distributed CNF microstructures. The high sensitivity with exposure to different volatile chemicals was obtained from our research and suggests the potential in health monitoring, human-robotics interactions, microelectronics design, and environmental sustainability.

S.CT07.11.04
Self-Aligned Copper Oxide Passivation Layer? A Study on the Reliability Effect Yue Kuo and Jia Quan Su; Texas A&M Univ, United States

Due to its high conductivity, copper is an important interconnect material for high density as well as large area electronic and optoelectronic products, such as ICs, TFT LCDs, and OLEDs. The reliability of the copper line is critical to these applications. In general, the copper interconnect line needs a bottom adhesion layer as well as a passivation layer. The adhesion layer effect on the line reliability has been well studied. The passivation layer is commonly formed by adding a CVD or sputter deposited dielectric or metallic layer. There are some studies on the influence of these passivation layers on the reliability of the copper line (1,2). However, there are few studies on the copper oxide passivation effect on the copper line's reliability.

Since oxide can be easily formed on the copper pattern under a well-controlled condition, it can be an effective self-aligned passivation layer. In this paper, authors report the reliability study of the copper oxide passivated copper line that is etched with the plasma-based etch process (3,4,5). The copper oxide layer was formed from the oxygen plasma method. Copper lines of various thicknesses and widths with and without the oxide passivation layer were prepared. The line breakdown phenomena under the constant current density stress condition are discussed. The composition and structure of the passivation layer before and after the high current stress condition have been examined and discussed. In summary, copper oxide is a potentially important passivation layer for the copper interconnect line in many products.


2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
S.CT07.11.05
Design, Microfabrication and Characterization of Bismuth and Glassy Carbon Based Sensor for Heavy-Metal in Drinking Water Ryan Butler and Sammuel Kassegne; San Diego State University, United States

In the past several decades, the US has experienced a rising concern over toxic pollution from heavy metal sources. For example, the pollution based natural disaster of Flint, Michigan garnered an abundance of media attention for its devastating impact on the lives of those in the local community. Although this negative press was rightly deserved, there are many places in America with much higher recorded heavy metal poisoning rates – three thousand to be exact. A big concern of much of this pollution comes in the form of water toxicity. Often, heavy metals find their way into water supplies for local communities which results in the indirect poisoning of citizens. Therefore, there is great need for a commercially available and portable device which would provide an easy method to test the level of poisonous elements in community water supplies.

Herein, the creation of a novel microfluidic device for the measurement of trace heavy metal ions is described. The work presented within focuses on these ions due to their health hazards and low concentration limits lending to an interesting challenge in detection.

The first effort in this project revolved around determining the form factor of a MEMS device which would act as an environmental sensor for minute concentrations of lead. Much background research into similar devices was performed before starting to conceptualize the preliminary design. Taking the equipment of the San Diego State University Clean Room facility into consideration, a rough model was presented and refined over several weeks. A final design then followed with a basic 3D model and fabrication process presented.

After much time testing and redesigning, results were generated for the measurements of trace heavy metal ions in solutions of water. Additional results were then obtained by altering various parameters within the experiment such as the analyte concentration. They were then compared to other experimental and commercial devices to determine the efficacy and practicality of the device. Finally, a study was performed to determine future work and technological extensions of the tool presented within.

S.CT07.11.07
Mass Analysis of Neuropeptides in Salty Environment Using Hydrophilic Ring-Shaped Anchors Sook Yoon and Chang Young Lee; Ulsan National Institute of Science and Technology, United States

For more than a decade, researchers have studied cell-to-cell signaling peptides using various analytical methods. Signaling peptides have been known to have important role in the physiological mechanisms. Currently available approaches for analyzing peptides have drawbacks such as loss of peptides and complicated steps for sample preparation. We developed an efficient platform for mass analysis of neuropeptides that simultaneously concentrates and desalts the analytes via coffee ring effect. Our approach is to use C18-Au coated patterned substrate. When peptide solution with high salt content is dropped onto the patterned C18-Au surrounded by donut-shaped hydrophilic anchors, salts are removed by outward flow generated during evaporation, while peptides are collected onto the central C18-Au region. Our approach greatly simplifies the sample preparation for matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). We also found that our patterns can be regenerated and used 5 times or more without any performance degradation. We have developed a simple kinetic model that describes the correlation between the evaporation rate and the surface coverage of peptides. Moreover, the performance could be dramatically increased by concentrating absorbed peptides into a crystal using PDMS contact printing. Applying these drop-dry methods to MALDI-MS sample preparation potentially enables high-throughput analyses, including time-lapse mass analysis. Our approach is easily accessible to researchers who do not have special expertise in mass spectrometry, so it is possible to contribute to bringing new ideas to neuropeptide analysis.

S.CT07.11.11
Preparation of Nano Raspberry Particles Using Chemically Adsorbed Monolayers Teruyoshi Sasaki, Kazufumi Ogawa and Yoshifumi Suzaki; Kagawa University, Japan

Since the nano world can be observed with SEM and SPM, nanomaterials have been actively developed. Among them, nanoparticles are often used for both metals and non-metals, such as cosmetics, home appliances / electrical electronic products, paints / inks, etc. In general, nanoparticles are produced by a vaper phase method or a liquid phase method. However, it is still difficult to produce nanoparticles with a desired shape such as raspberry particles. For example, the prototype raspberry particles are on the order of the micro level at the minimum. In this study, the surface of two kinds of large and small nano level silica nanoparticles were coated with different reactive chemically adsorbed monomolecular film. Thereafter, the particles were bonded to each other by the interaction of the
functional groups at the ends of the chemically adsorbed monomolecular film on the surface of each particle to produce nano sized raspberry particles. As an application example of nano raspberry particles, the nano raspberry particles were coated on the surface of a glass substrate to form a nano fractal surface structure. Furthermore, a light transmitting super water repellent glass substrates could be produced by forming a fluorocarbon based chemical adsorbed monomolecular film on the surface without damaging the surface of the fractal structure.

S.CT07.11.12
Nano-Engineering in Confined Spaces—Size- and Shape-Controlled Growth of Functional Nanostructures in Self-Assembled Block Copolymer Nanoreactors
Naman Arora¹, Anna Perdikaki², Paschalis Alexandridis³, T. J. (Lakis) Mountziaris⁴ and Georgios Karanikolos¹,¹; ¹Khalifa University, United Arab Emirates; ²Demokritos National Research Center, Greece; ³University at Buffalo, The State University of New York, United States; ⁴University of Massachusetts Amherst, United States

Self-Assembly of amphiphilic block copolymers in selective solvents can yield a variety of organized structures at the nanoscale of different sizes, shapes, and interfacial characteristics. Such rich structural polymorphism has been tuned and subsequently utilized in this work to controllably prepare a variety of colloidal systems of nanoparticles by templated growth in the self-assembled nanodomains. Nanomaterials spanning compound semiconductors with 0-, 1-, and 2-D morphologies to metallic nanostructures grown in poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) assemblies will be presented. The metallic systems in particular were applied as antibacterial agents exhibiting enhanced and sustainable performance due to the block copolymer colloidal configuration.

S.CT07.11.13
Characterization of Device Edge Illumination of Si Heterojunction (SHJ) Microcells for Luminescent Solar Concentrator (LSC) Applications
Megan E. Phelan¹, Maggie Potter², Pradeep Balaji³, André Augusto³, David Needell¹, Ralph G. Nuzzo⁴ and Harry A. Atwater¹; ¹California Institute of Technology, United States; ²University of Illinois at Urbana-Champaign, United States; ³Arizona State University, United States

In dense urban environments, with limited rooftop space, communities must look towards new photovoltaic (PV) technologies that can be integrable into the existing building envelope. Luminescent solar concentrators (LSCs), which sustain performance in both direct and diffuse lighting conditions and boast tunable transparencies, present an attractive option for building integrated (BI) PV. In this talk, we report performance optimization and characterization for varied illumination conditions of Si heterojunction (SHJ) microcells embedded within an LSC for BIPV applications. For this design, we propose a grid-like array of SHJ microcells, beneath a poly-lauryl methacrylate (PLMA) waveguide that has embedded InAs/InP/ZnSe quantum dots as the luminophore. Given the proposed architecture, the microcell can be illuminated from the top surface of the cell as well as each of its device edges; this illumination results from each direct sunlight and from quantum dot photoluminescence (PL) within the LSC waveguide, respectively.

In this talk, we compare SHJ microcell performance when illuminated on each i) the top surface, ii) one device edge, and iii) all four device edges simultaneously. We present both simulated and experimental measurements to corroborate our results around photonic interactions at each surface, and perform the following characterizations and measurements: light current-voltage (LIV), dark current-voltage, photocurrent mapping, external quantum efficiency (EQE), and internal quantum efficiency (IQE). By varying the dimensions (width and length) of the SHJ micro cell (from 400um to 800um), we further report how cell performance for each surface illumination (top vs. edge) varies for different sized devices. Results of these measurements show that Jsc increases when illuminating the microcell on the edge (in comparison to top surface illumination) due to an increased absorption depth. However, Voc drops for edge illumination vs. top illumination, due to an additional darkness factor and increased recombination. The mechanisms and photonics behind the contrasting microcell performance at each of these surfaces will be discussed during this talk. By understanding microcell performance at each interface, we are able to better design a SHJ/LSC integrated device, with optimized luminophore PL to match the edge illumination performance, for BIPV applications.

S.CT08.04.01
Superlattice Nucleation and Underlying Mechanism of Magnetite Nanocube Assembly
Xin Huang and Zhongwu Wang; Cornell University, United States

The self-assembly of colloidal nanoparticles into ordered superlattices provides significant expansions for the capability of functional materials design. As the new type of building blocks, the geometric shapes of nanocrystals, such as sphere, cube and octahedron, play critical roles in determining the structure of assembled supercrystal. In the nanocube system, the
observed superlattices were dominated by the three phases of simple cubic (SC), rhombohedral (Rh), and face-centered cubic (FCC), but how they nucleate and grow and transform from one to another remain largely unknown. In this work, we applied highly monodispersive magnetite nanocubes with an average side length of 12.5 nm, and controlled various assembly environments, and revealed the formation and growth of three major phases (SC, acute Rh and FCC). Taking advantage of synchrotron-based SAXS techniques, we also explored the structural correlations between three superlattices phases. With additional simulations and computations, we further discussed the driving forces and constructed a reasonable superlattice phase diagram of nanocube-based assembly. Our results not only dramatically expand our understanding on the shape-dependent phase behaviors of nanocrystal, but also provide insights for design and fabrication of novel functional materials.

S.CT08.04.02
DFT Study of Graphene Formation in Carbon Droplets Condensed in Stellar Atmospheres Chathuri Silva, Philip Fraundorf, Eric H. Majzoub and Philip Chrostoski; University of Missouri-St. Louis, United States

Because macroscopic clusters of elemental carbon at low (ambient) pressure sublimate to vapor near 4000K, liquid carbon is seldom considered to play a role in nature even though quenched carbon droplets have been reported in laboratory laser ablation studies [1,2]. However, a subset of meteoritic carbon particles from red giant atmospheres show a “graphene-core”/graphite-rim structure [3,4], likely following condensation of super-cooled carbon droplets from the vapor phase, which nucleated graphene sheets on randomly-oriented 5-member rings before solidification and subsequent coating with a graphite rim. Similar core-rim particles can be formed by slow cooling of carbon vapor in the lab [5]. It remains a challenge to study the properties of liquid carbon in a lab due to the difficulty of experimentation under extreme conditions. Therefore, we investigated nucleation and growth of carbon rings and graphene sheets using density functional theory (DFT). We assume low pressure, with an experimental 1.8 g/cc density estimate, and relax randomized positions of liquid-like 13/20-carbon atom clusters in a cubic supercell. Inter-atom distances characteristic of covalent vs. metallic interactions (with a gap in 1.7-2.0 Å range) allow us to identify covalent “bonds” with small separation. Local energy minima at T = 0K show a mix of sp2 and sp, plus few sp3 coordination numbers as in the literature which reports that liquid carbon favors sp coordination at lower densities, sp2 coordination at higher densities, and a mix of sp and sp2 coordination at intermediate densities [6-10]. Ring sizes vary from triangle to heptagon, but pentagons are more abundant than hexagons, also consistent with previous reports [9,10]. Further work remains to see if such ab initio studies can confirm that abundant pentagonal rings at this density, during slow cooling of the liquid, can nucleate the growth of faceted pentacones as suggested by electron phase-contrast imaging of the presolar cores [11]. In summary DFT relaxation of random configurations of 13/20-atom clusters in a supercell, along with literature reports of the same, suggest that: (a) covalent bonds can be identified by interatom spacings below 1.85Å, (b) sp2 coordination is expected at that density, and (c) pentagonal rings are more abundant than hexagonal rings as possible nucleation seeds. The properties of unlayered graphene sheets in a frozen liquid matrix, e.g. as a diffusion barrier, should be interesting to explore further both experimentally and computationally.

References
(PS) and polyethylene glycol (PEG) were used as an example for demonstrating the feasibility of the core/shell fiber fabrication. A two-phase liquid-state microstructure was first achieved via the co-axial spinneret with the exterior layer composed of PS pellets (PSp)/PEG/organic solvent (e.g., xylene or dimethylformamide) solutions and the interior layer containing dispersed PS spheres (PSs)/PEG/water solutions. Procedures of coagulation, heat-treatment, and phase-separation-based selective dissolution were used to generate the porous-shell/particle-core fibers. The pore sizes and density were controlled by the porogen (i.e., PEG) concentrations and examined using scanning electron microscopy (SEM). The fiber formation dynamics and microstructural features were studied via rheology tests and gelation measurements, tensile tests, thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC).

S.CT08.04.05
Hematite Mesocrystal Formation through Near Interface Nucleation and Oriented Aggregation Guomin Zhu1, Maria Sushko2, John Loring2, Miao Song2, Benjamin Legg1, Xiaopeng Huang2, Kevin Rosso2 and James J. De Yoreo2;1; 1University of Washington, United States; 2Pacific Northwest National Laboratory, United States

A diverse class of materials exhibit characteristics of mesocrystals: single crystals constituting distinct nano-sized domains that are atomically aligned. The formation of such structures is often attributed to crystallization through oriented attachment. However, many questions about the fundamental drivers and dynamic progression of this phenomenon remain. And the process become more complexed when coupled with phase transformation. Here we focus on the crystallization of hematite (hm, Fe2O3) mesocrystals from ferrihydrite (fh) nanoparticles. In the oxalate-free solution, the resulting hm crystals are well faceted rhombohedron, while in the presence of oxalate, hm forms nanoporous spindle-shaped mesocrystals. We applied in situ liquid phase TEM with heating temperatures of 80 °C to investigate the formation. We directly observed both the dissolution of fh and the nucleation of new hm particles, which formed within close proximity (~ 1 nm) of the hm/solution interface. Immediately after nucleation, the hm particles attached to the nearby seed to form a hm mesocrystal. Post analyses using EDX mapping and electron diffraction after disassembling the liquid cell confirmed the growth of spindle-shaped hematite during the liquid phase TEM experiments. In addition, we utilized a quasi in situ approach of using indexed TEM grids to cycle samples between the growth reactor and the TEM in order to track the pathway of crystallization. The results were consistent with those of the in situ experiments and confirmed that the fh serves as a buffer and the Hm grow by creation of new particles in the solution near the hm interface. Based on ATR FTIR measurements, ion chromatography and classic DFT calculation we propose that oxalate plays the role of inhibiting classical monomer-by-monomer growth of the hematite particles while promoting the nucleation of new hm particles at the hm/solution interface by modifying the interfacial energy of hm close to the hm/solution interface. In this way, the oxalate ligands bias the growth process away from classical mechanisms and towards oriented attachment.
SESSION S.CT03.10: Live Keynote: Expanding the Frontiers of Actinide Materials Science Through Experiment and Theory
Session Chairs: Ladislav Havela and Jindrich Kolorenc
Saturday Afternoon, November 28, 2020
S.CT03

12:30 PM INTRODUCTORY COMMENTS

12:35 PM *S.CT03.01.01
Bypassing the Computational Bottleneck of Quantum-Embedding Theories for Strong Electron Correlations with Machine Learning
John Rogers¹, Tsung-Han Lee², Sahar Pakdel³, Vladimir Dobrosavljevic⁴, Ove Christiansen⁵ and Nicola Lanata⁶; ¹Texas A&M University, United States; ²Rutgers, The State University of New Jersey, United States; ³Aarhus University, Denmark; ⁴Florida State University, United States

A cardinal obstacle to performing quantum-mechanical simulations of strongly-correlated matter is that, with the theoretical tools presently available, sufficiently-accurate computations are often too expensive to be ever feasible. Here we design a computational framework combining quantum-embedding (QE) methods with machine learning. This allows us to bypass altogether the most computationally-expensive components of QE algorithms, making their overall cost comparable to bare Density Functional Theory (DFT). We perform benchmark calculations of a series of actinide systems, where our method describes accurately the correlation effects, reducing by orders of magnitude the computational cost. We argue that, by producing a larger-scale set of training data, it will be possible to apply our method to systems with arbitrary stoichiometries and crystal structures, paving the way to virtually infinite applications in condensed matter physics, chemistry and materials science.


12:55 PM *S.CT03.06.04
The JRC Surface Science Labstation—A Unique Set-Up to Investigate Actinides in Support of Nuclear Safety and Non-Power Application of Nuclear Materials
Rachel Eloirdi¹, Thomas Gouder¹, Ghada El Jamal², Concettina Andrello¹, Frank Huber¹ and Roberto Caciuffo¹; ¹JRC Karlsruhe, Germany; ²KTH Royal Institute of Technology, Sweden

Knowledge about the interaction of UO₂ with the environment is of high importance to assess its stability in oxidizing and in reducing condition. For this reason, understanding the UO₂ oxidation process is central to the performance assessment of nuclear fuels. Oxidizing condition can convert UO₂ into U₃O₈ leading, in some cases, to powdering of the fuel matrix or to failure of the cladding [1]. The redox behaviour of UO₂ is also relevant for the management of nuclear waste forms, as oxidation results in the production of soluble uranyl cations, UO₂²⁺, that can easily migrate in the biosphere. This talk summarizes surface science research activities carried out at JRC Karlsruhe in support of nuclear safety and non-power application of nuclear materials. I will also describe a unique set-up developed in-house, the Labstation [2], including sample preparation modules, by DC Sputtering or evaporation, and several surface characterisation techniques. Among the latter, High-resolution X-ray Photoelectron Spectroscopy (XPS) and Bremsstrahlung Isochromat Spectroscopy (BIS) are particularly useful to characterize the uranium oxidation state in single and mixed oxides. In a first example, I will show the process of oxidation and reduction of U oxides using O₂, H₂O and H₂ plasma. For the first time, U₂O₅ films [3-4] could be produced and studied, filling a gap in the knowledge about U⁵⁺ oxidation state. While U⁴⁺, U³⁺ and U⁵⁺ have representative satellite peaks positioned, respectively, at 7, 8 and 10 eV out of the main 4f⁵/₂,7/₂ excitation lines, a satellite peak at 9 eV is observed when UO₂+x in contact with sodium is heated at 400 °C under oxygen. In a second example, we report the first in-situ preparation of ThF₄ [5] whose band gap of 10.2(2) eV is significantly larger than the 229mTh excitation energy, making ThF₄ a possible candidate material for a solid-state nuclear clock based on the vacuum ultraviolet γ decay.

References


SESSION S.CT03.11: Live Lightning/Flash: Expanding the Frontiers of Actinide Materials Science Through Experiment and Theory
Session Chairs: Ladislav Havela and Jindrich Kolorenc
Saturday Afternoon, November 28, 2020
S.CT03

1:15 PM INTRODUCTORY COMMENTS

1:20 PM *S.CT03.02.01
Hybridization Effect on the X-Ray Absorption Spectra for Actinide Materials Jian-Xin Zhu¹, Wei-ting Chiu¹,², Roxanne Tutchton¹, Giacomo Resta³, Tsung-Han Lee³, E.D. Bauer¹, Filip Ronning¹ and Richard T. Scalettar²; ¹Los Alamos National Laboratory, United States; ²University of California, Davis, United States; ³Rutgers, The State University of New Jersey, United States

Studying the local moment and 5f-electron occupations sheds insight into the electronic behavior in actinide materials. X-ray absorption spectroscopy (XAS) has been a powerful tool to reveal the valence electronic structure when assisted with theoretical calculations. In this work, we employed the DFT+Gutzwiller rotationally-invariant slave boson method to obtain the local Hamiltonian of the single-impurity Anderson model (SIAM), and used exact diagonalization (ED) method to calculate the XAS spectra from the model. An in-house built computational code was developed for the ED method. By applying this technique to the recently discovered 5f-electron topological Kondo insulator plutonium tetraboride (PuB₄), we were able to determine the signature of 5f-electronic correlation effects in the theoretical X-ray spectra. We found that the Pu 5f-6d hybridization effect provides an extra channel to mix the j=5/2 and 7/2 orbitals in the 5f valence. As a consequence, the resultant electron occupation number and spin-orbit coupling strength deviate from the intermediate coupling regime. We have also applied this approach to the d-phase of Pu.

1:30 PM *S.CT03.01.03
Role of Electronic Interactions on Structural Properties of Actinides and Phases of Plutonium Bernard Amadon, Jean Baptiste Morée and Boris Dorado; CEA DAM DIF, France

We discuss the impact of 5f electron interactions on structural properties of pure actinides and phase of plutonium[1][2]. We first use an ab initio calculation of effective Coulomb interactions and we find that the calculated interactions in plutonium and americium are much smaller than usually expected. With these interactions, we reproduce the experimental transition from low volume early actinides (uranium, neptunium, α-plutonium) to high- volume late actinides (δ-plutonium, americium, and curium) and a good agreement of volume of phases of plutonium with experiment. We also discuss phonon spectra of plutonium. Then we discuss our values of effective 5f electron interactions U. In some lanthanides and actinides [3], higher values are expected to reproduce experimental photoemission spectra and structural properties. We discuss general ways to improve the calculation to be more predictive.


1:40 PM S.CT03.01.02
Electronic Correlation Induced Expansion of Compensated Electron and Hole Fermi Pockets in δ-Plutonium Roxanne Tutchton¹, Wei-ting Chiu², Robert C. Albers¹, Gabriel Kotliar³ and Jian-Xin Zhu¹,⁴; ¹Los Alamos National Lab, United States; ²University of California, Davis, United States; ³Rutgers, The State University of New Jersey, United States; ⁴Center for Integrated Nano Technologies, United States

2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
Due to its position at the boundary between the light and heavy actinides, Plutonium (Pu) has liminal characteristics that make modeling its 5f-orbital electrons especially challenging. Consequently, a complete understanding of the electronic structure of this elemental solid remains in question. In order to explore the role of strong electronic correlations in the δ-phase of Pu, we have performed Fermi surface calculations using the generalized gradient approximation with dynamical mean-field theory and the Gutzwiller wavefunction approximation to compare their differing approaches to electron correlation effects. The de Haas-van Alphen (dHvA) frequencies and effective masses were then calculated to analyze correlation induced renormalization effects on the Fermi surface topologies. We have predicted that the electronic correlation gives rise to a volume expansion of 200% in both the hole and electron pockets of the Fermi surface in addition to an intermediate mass enhancement. This is in agreement with the band renormalization theory for strongly correlated materials.

LANL LDRD Program. NNSA Advanced Simulation and Computing Program. Center for Integrated Nanotechnologies, a DOE BES user facility, in partnership with LANL Institutional Computing Program for computational resources.

Probing the Limits of 5f Ferromagnetism in UC$_2$P$_2$
Ladislav Havela$^1$, Jiri Prchal$^1$, Jaroslav Valenta$^1$, Martin Divis$^1$, Fuminori Honda$^2$, Ilya Turek$^1$, Dariusz Kaczorowski$^3$, Dexin Li$^2$, Arvind Maurya$^2$ and Dai Aoki$^2$; $^1$Charles University, Czechia; $^2$Tohoku University, Japan; $^3$Polish Academy of Sciences, Poland

Magnetic order in 5f materials offers interesting benefits, based in principle on very strong spin-orbit interaction, bringing large orbital moments into systems with itinerant, i.e. bonding, states. This yields very strong magnetocrystalline anisotropy, determined not by CEF effects as in lanthanides, but by bonding anisotropy. Hybridization of the 5f states with other states having low effective mass means that a re-orientation of 5f magnetic moments can have a dramatic effect of electrical conduction, bringing a giant magnetoresistance effect. Other related prominent characteristics include a giant Kerr rotation as one of important magnetooptical phenomena.

Although highly tunable by composition and external variable, the 5f magnetism remained restricted to low temperature range, discarding e.g. inexpensive uranium from the pool of prospective magnetic materials. For example, Curie temperatures of U-based 5f-ferromagnets only exceptionally exceeds the limit of 200 K. The trick of mixing the f magnetism with 3d magnetism of transition metals, so successful in lanthanide-based permanent magnets, does not work in the case of light actinides. Both 3d and 5f states being band-like, they strongly hybridize, which degrades both the 3d and 5f desirable characteristics. Due to the same reason U-compounds very rich in Fe or Co simply lose any distinct 5f contribution. Heavy actinides (from Am onwards), in principle analogous to heavy lanthanides, undergo a fast radioactive decay. We have been trying to understand which type of tuning can support the 5f magnetism besides the traditional game with inter-actinide spacing. The case of uranium hydrides showed that using a ionic-covalent bonding can lead to a suppression of the 5f-6d hybridization, which is an undesirable mechanism, contributing the washout of U moments. The 6d hybridization with ligand states can efficiently liberate the 5f states, although they can still maintain their band character. A general hint is to look at U compounds with a certain charge transfer and to use external pressure for fine tuning of crystal structure. We have focused on U pnictides, and chose UC$_2$P$_2$ as the material with record high $T_C = 216$ K [1]. Applying hydrostatic pressure the $T_C$ value increases, reaching a maximum of 290 K in $p = 7-8$ GPa, i.e. first time obtaining a room temperature ferromagnetism with pure 5f ferromagnet. Details of electronic structure and their pressure variations have been provided by ab initio calculations.


This work was supported by the Czech Science Foundation under the grant No. 18-02344S.

Identifying Structural Features That Result in Activation and Coupling of Vibrational Modes in Actinyl Materials
Tori Forbes; University of Iowa, United States

The actinyl cation (D$_{3h}$ point group) possesses symmetric and asymmetric stretching modes that are typically Raman and Infrared active, respectively. Lowering the symmetry of the actinyl moiety will activate both modes causing two stretching
bands to be present within the spectral window. While activation of these bands suggests perturbation to the actinyl bond, there is currently a limited understanding on how intermolecular forces influence this process or the extent of the effect on the actinyl bond in solid state compounds. In this presentation, I will focus on the analysis of Raman spectra associated with neptunyl (NpO$_2^+$/NpO$_2^{2+}$) compounds and explore activation and vibrational coupling effects of these materials. Specifically, the impacts of counterions and hydrogen bonding will be explored experimentally and compared to theoretical calculations. In addition, the neptunyl system will be compared to the related uranyl complexes to further explore the subtle differences in bonding within actinyl cations.

2:25 PM CLOSING REMARKS

SESSION S.CT03.01: Correlated Electrons in Actinide Materials
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-CT03

5:00 AM *S.CT03.01.01
Bypassing the Computational Bottleneck of Quantum-Embedding Theories for Strong Electron Correlations with Machine Learning
John Rogers¹, Tsung-Han Lee², Sahar Pakdel³, Vladimir Dobrosavljevic⁴, Ove Christiansen⁵ and Nicola Lanata⁶; ¹Texas A&M University, United States; ²Rutgers, The State University of New Jersey, United States; ³Aarhus University, Denmark; ⁴Florida State University, United States

A cardinal obstacle to performing quantum-mechanical simulations of strongly-correlated matter is that, with the theoretical tools presently available, sufficiently-accurate computations are often too expensive to be ever feasible. Here we design a computational framework combining quantum-embedding (QE) methods with machine learning. This allows us to bypass altogether the most computationally-expensive components of QE algorithms, making their overall cost comparable to bare Density Functional Theory (DFT). We perform benchmark calculations of a series of actinide systems, where our method describes accurately the correlation effects, reducing by orders of magnitude the computational cost. We argue that, by producing a larger-scale set of training data, it will be possible to apply our method to systems with arbitrary stoichiometries and crystal structures, paving the way to virtually infinite applications in condensed matter physics, chemistry and materials science.


5:30 AM S.CT03.01.02
Electronic Correlation Induced Expansion of Compensated Electron and Hole Fermi Pockets in δ-Plutonium
Roxanne Tutchton¹, Wei-ting Chiu², Robert C. Albers¹, Gabriel Kotliar² and Jian-Xin Zhu¹; ¹Los Alamos National Lab, United States; ²University of California, Davis, United States; ³Rutgers, The State University of New Jersey, United States; ⁴Center for Integrated Nano Technologies, United States

Due to its position at the boundary between the light and heavy actinides, Plutonium (Pu) has liminal characteristics that make modeling its 5f-orbital electrons especially challenging. Consequently, a complete understanding of the electronic structure of this elemental solid remains in question. In order to explore the role of strong electronic correlations in the δ-phase of Pu, we have performed Fermi surface calculations using the generalized gradient approximation with dynamical mean-field theory and the Gutzwiller wavefunction approximation to compare their differing approaches to electron correlation effects. The de Haas-van Alphen (dHvA) frequencies and effective masses were then calculated to analyze correlation induced renormalization effects on the Fermi surface topologies. We have predicted that the electronic correlation gives rise to a volume expansion of 200% in both the hole and electron pockets of the Fermi surface in addition to an intermediate mass enhancement. This is in agreement with the band renormalization theory for strongly correlated materials.

Role of Electronic Interactions on Structural Properties of Actinides and Phases of Plutonium

Bernard Amadon, Jean Baptiste Morée and Boris Dorado; CEA DAM DIF, France

We discuss the impact of 5f electron interactions on structural properties of pure actinides and phase of plutonium[1][2]. We first use an ab initio calculation of effective Coulomb interactions and we find that the calculated interactions in plutonium and americium are much smaller than usually expected. With these interactions, we reproduce the experimental transition from low volume early actinides (uranium, neptunium, α-plutonium) to high-volume late actinides (δ-plutonium, americium, and curium) and a good agreement of volume of phases of plutonium with experiment. We also discuss phonon spectra of plutonium. Then we discuss our values of effective 5f electron interactions U. In some lanthanides and actinides [3], higher values are expected to reproduce experimental photoemission spectra and structural properties. We discuss general ways to improve the calculation to be more predictive.


Hybridization Effect on the X-Ray Absorption Spectra for Actinide Materials

Jian-Xin Zhu1, Wei-ting Chiu1,2, Roxanne Tutchton1, Giacomo Resta2, Tsung-Han Lee1, E.D. Bauer1, Filip Ronning1 and Richard T. Scalettar2; 1Los Alamos National Laboratory, United States; 2University of California, Davis, United States; 3Rutgers, The State University of New Jersey, United States

Studying the local moment and 5f-electron occupations sheds insight into the electronic behavior in actinide materials. X-ray absorption spectroscopy (XAS) has been a powerful tool to reveal the valence electronic structure when assisted with theoretical calculations. In this work, we employed the DFT+Gutzwiller rotationally-invariant slave boson method to obtain the local Hamiltonian of the single-impurity Anderson model (SIAM), and used exact diagonalization (ED) method to calculate the XAS spectra from the model. An in-house built computational code was developed for the ED method. By applying this technique to the recently discovered 5f-electron topological Kondo insulator plutonium tetraboride (PuB4), we were able to determine the signature of 5f-electronic correlation effects in the theoretical X-ray spectra. We found that the Pu 5f-6d hybridization effect provides an extra channel to mix the j=5/2 and 7/2 orbitals in the 5f valence. As a consequence, the resultant electron occupation number and spin-orbit coupling strength deviate from the intermediate coupling regime. We have also applied this approach to the d-phase of Pu.

Electronic Structures of Uranium Compounds Studied by Photoelectron Spectroscopy

Shin-Ichi Fujimori; Japan Atomic Energy Agency, Japan

The electron correlation effect gives rise to an abundant variety of physical properties particularly in the d- and f-based materials. Among this class of materials, the actinide compounds share a unique position due to the interplay between their magnetic and superconducting properties. Particularly, the coexistence of a large magnetic moment and unconventional superconductivity is the most significant aspect of uranium-based compounds. These distinctive behaviors are due to the strongly correlated U 5f states which are located at the boundary between simple localized and itinerant pictures of electrons. To understand the origin of these remarkable physical properties, it is essential to unveil the U 5f electronic structures.

In this talk, I will review the electronic structure studies of strongly correlated uranium compounds by photoelectron
spectroscopies with soft X-ray synchrotron radiation \cite{1,2}. The following subjects will be discussed.

**Resonant photoelectron spectroscopy study of heavy fermion superconductors**

We have elucidated the nature of the electron correlation effect in heavy fermion superconductors UPd$_2$Al$_3$ \cite{3} and UTe$_2$ \cite{4} by imaging their partial U 5f density of states (pDOS) using U 4d-5f resonant photoelectron spectroscopy. It was found that incoherent peaks emerge on the higher binding energy side in their U 5f pDOS, suggesting that the electron correlation effect takes an essential role in their electronic structures.

**Three-dimensional angle-resolved photoelectron spectroscopy study of URu$_2$Si$_2**

The complete volume electronic structure of the heavy fermion superconductor URu$_2$Si$_2$ in the paramagnetic phase was revealed by the three-dimensional (3D) angle resolved photoelectron spectroscopy (ARPES). It was found that the electronic structure of URu$_2$Si$_2$ has a strong dependence along the perpendicular $k_z$ direction, suggesting that it has a considerable 3D nature. Furthermore, the U 5f states in URu$_2$Si$_2$ form dispersive bands with their energy dispersions of sub-electron volts, and contribute to the Fermi energy. This suggests that U 5f electrons in URu$_2$Si$_2$ have an itinerant aspect.


**References**


**6:00 AM S.CT03.02.04**

Electronic Structure and Magnetism of UGa$_2$: LDA+DMFT Study Banhi Chatterjee and Jindrich Kolorenc; Institute of Physics, Czech Academy of Sciences, Czechia

The debate whether uranium 5f electrons are closer to being localized or itinerant in the intermetallic compound UGa$_2$ is not yet fully settled, partly due to inconclusive spectroscopic observations of the uranium 5f electrons \cite{1,2}. The present state of the theoretical understanding of the UGa$_2$ electronic structure is not satisfactory either. The magnetic moments carried by the uranium atoms in the low-temperature ferromagnetic phase are severely underestimated by the band theory (LDA), and although the correlated band theory (LDA+U) makes the moments larger, the increase is still not large enough to match the experiment \cite{3,4}.

We attempt to gain more insight into the electronic structure of UGa$_2$ by means of LDA+DMFT calculations using exact diagonalization as the impurity solver \cite{5}. The LDA+DMFT definitely improves the description of magnetism with respect to LDA, but obtaining magnetic moments as large as in experiments turns out to be difficult even for this advanced electronic structure method – even though the uranium 5f electrons come out as rather localized. Apart from the magnetism, we calculate and analyze also the spectral properties to be compared with experimental valence-band photoemission and M-edge x-ray absorption.

Identifying Structural Features That Result in Activation and Coupling of Vibrational Modes in Actinyl Materials
Tori Forbes; University of Iowa, United States

The actinyl cation (D_{6h} point group) possesses symmetric and asymmetric stretching modes that are typically Raman and Infrared active, respectively. Lowering the symmetry of the actinyl moiety will activate both modes causing two stretching bands to be present within the spectral window. While activation of these bands suggests perturbation to the actinyl bond, there is currently a limited understanding on how intermolecular forces influence this process or the extent of the effect on the actinyl bond in solid state compounds. In this presentation, I will focus on the analysis of Raman spectra associated with neptunyl (NpO_{2}\textsuperscript{2+}/NpO_{2}\textsuperscript{2-}) compounds and explore activation and vibrational coupling effects of these materials. Specifically, the impacts of counterions and hydrogen bonding will be explored experimentally and compared to theoretical calculations. In addition, the neptunyl system will be compared to the related uranyl complexes to further explore the subtle differences in bonding within actinyl cations.

5:30 AM S.CT03.03.02
Crystal Structures of CdUO\textsubscript{4}: Space Group Symmetry and Phase Transformations
Zhaoming Zhang\textsuperscript{1}, Gabriel L. Murphy\textsuperscript{1,2,3}, Maxim Avdeev\textsuperscript{1,2} and Brendan J. Kennedy\textsuperscript{2}; \textsuperscript{1}Australian Nuclear Science and Technology Organisation, Australia; \textsuperscript{2}The University of Sydney, Australia; \textsuperscript{3}Forschungszentrum, Germany

Inspired by our recent discoveries of the remarkable and unexpected structural behaviors in SrUO\textsubscript{4} [1] and CaUO\textsubscript{4} [2], which both show reversible oxygen-vacancy ordering and symmetry lowering with increasing temperature, we have revisited the closely related CdUO\textsubscript{4} using synchrotron X-ray and neutron powder diffraction supported by X-ray absorption spectroscopic measurements and thermogravimetric analysis. Depending on synthesis conditions, CdUO\textsubscript{4} was previously reported to form two structural types based on laboratory X-ray powder diffraction [3]. One polymorph (α-CdUO\textsubscript{4}) was described as isostructural to α-SrUO\textsubscript{4} and CaUO\textsubscript{4}, having a rhombohedral structure in space group R\textsuperscript{3}m. The other polymorph (β-CdUO\textsubscript{4}) was described as orthorhombic in space group Cmmm. A high temperature third polymorph, denoted as γ-CdUO\textsubscript{4}, was also suggested based on a thermogravimetric study [4]. The structure of γ-CdUO\textsubscript{4} was not solved but described as a form of the rhombohedral α-CdUO\textsubscript{4} that is substoichiometric.

We have synthesized both α- and β-CdUO\textsubscript{4} and determined their crystal structures using high resolution synchrotron X-ray and neutron powder diffraction for the first time. While the structure of α-CdUO\textsubscript{4} was confirmed as previously reported rhombohedral structure in R-3m, we propose that the correct space group for the orthorhombic β-CdUO\textsubscript{4} is Ibmm, isostructural to β-NiUO\textsubscript{4} [5].

In situ synchrotron X-ray diffraction measurements were also carried out with both α- and β-CdUO\textsubscript{4} from room temperature to 1000°C in sealed quartz capillaries. β-CdUO\textsubscript{4} was found to undergo an irreversible reconstructive structural phase transformation around 900°C. Although the X-ray diffraction pattern of the high temperature phase has a passing resemblance to that of α-CdUO\textsubscript{4}, there are clear peak splittings that cannot be accounted for by the rhombohedral structural model. Note that these splittings are too small to be resolved by laboratory X-ray diffractometers, therefore they were not observed in previous studies. Using a similar approach to that in our earlier study of SrUO\textsubscript{4} [1], the high temperature structure of CdUO\textsubscript{4}, denoted as δ-CdUO\textsubscript{4-x}, was solved for the first time as triclinic in space group P\textsuperscript{-1}. When α-CdUO\textsubscript{4} was heated to around 750°C it also underwent a first order phase transformation to a mixture of the β and δ phases. Similar to SrUO\textsubscript{4}, oxygen vacancies are believed to play a key role in the phase transformation behavior of CdUO\textsubscript{4}. The results of this study will be discussed with the other related monouranates.

References
SESSION S.CT03.04: Analytical Techniques for Actinide Materials
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-CT03

5:00 AM *S.CT03.04.01
Development of Rapid Measurement Techniques to Aid in Pu Development at LANL John D. Auxier; Los Alamos National Laboratory, United States

The focus of this talk highlights on-going research efforts on laser spectroscopy. At present, there are a number of challenges that are involved with meeting the 30 ppy (pits/year) and some of them are scientific and engineering. In this presentation, an overview of hand-held laser induced breakdown spectroscopy (HH-LIBS) and initial measurements on alpha and delta Pu metal standards. There will also be collaborative research that involves the use of chemometric techniques that have been applied to Ce samples for the purpose of method development. Highlights from on-going USMA/LANL collaboration will be discussed.

5:30 AM S.CT03.04.03
Multiplatform Microanalysis of Plutonium Oxide Scales for Nuclear Forensics Brandon W. Chung, David J. Roberts, William A. Talbot, Denise D. Ashley, Scott Donald and Art J. Nelson; Lawrence Livermore National Laboratory, United States

Nuclear forensics requires accurate identification of distinguishing material characteristics to determine the history of interdicted nuclear materials. Key material signatures, such as morphological and chemical variations, that pinpoint recent provenance can reside within the bulk oxide scale formed over nuclear materials. This paper identifies improvements in extracting and analyzing key material signatures that exists within the oxide scale formed at the surface of Pu metals. We will describe our multiplatform approach using high-resolution microscopic techniques to identify spatially resolved morphological and chemical features of Pu oxide scales. The approach involves electron microanalysis with scanning electron microscopy (SEM), focused ion-beam (FIB) tomography with SEM, three-dimensional (3D) spatial modeling, chemical analysis with Auger and X-ray photoemission spectroscopies. Our work shows the distinguishing morphological and chemical characteristics between the original oxide scale formed from the controlled storage environment and the scale that is formed during subsequent exposure to external environments. Internal chemical composition, structure, and pore geometry of oxide scales are different, attributable to oxidative corrosion from exposure to outside the storage environment. These altered oxide scales provide distinguishing characteristics for recent environmental exposures. Furthermore, we will discuss our continuing effort to improve understanding internal morphologies and methods to generate database of morphological and chemical features including quantification applicable to nuclear forensics. Prepared by LLNL under Contract DE-AC52-07NA27344. This work was supported by the Office of Defense Nuclear Nonproliferation Research and Development within the U.S. Department of Energy’s National Nuclear Security Administration. This support does not constitute an express or implied endorsement on the part of the Government. LLNL-ABS-795544

SESSION S.CT03.05: Actinide Forensics
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-CT03

5:00 AM *S.CT03.05.02
Searching for Clues—Nuclear Forensic Signatures Naomi Marks; Lawrence Livermore National Laboratory, United States

2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
Nuclear forensic science is the science of identifying the purpose and provenance of radiological and/or nuclear material found outside of regulatory control. Because the ability to perform a nuclear forensics examination can help to identify gaps or weaknesses in physical security or safeguards of nuclear material, (which can then be strengthened in response) it is increasingly recognized as an integral part of a robust nuclear security program.

Nuclear forensic science matured as a discipline in the mid-1990s, coincident with an increasing number of nuclear smuggling incidents (Kristo et al., 2016). Labs were tasked with responding to incidents involving interdictions of low enriched uranium (LEU), highly enriched uranium (HEU), and even Pu in Russia, Lithuania, Germany, Bulgaria and elsewhere (IAEA, 2011; Kristo, 2012). As the casework increased throughout the mid-1990’s, so too did the sophistication of the analytical approaches to nuclear forensics examinations. Nuclear forensics practitioners seek to identify not only what materials are on the most basic level, but what might have been their intended use as well as how, when and where the materials were produced, used or stored. As the casework and policy implications of the field have evolved, so too has the science of nuclear forensics.

A combination of geochemical, materials science, and radiochemical analysis methods have traditionally formed the basis for nuclear forensics examination approaches. These methods exploit the characteristics of front end materials produced through mining, milling, and conversion in which the geologic and materials processing signatures are significant. Methods with a geochemical basis are also important for materials from the back end of the fuel cycle, including radiochronometric techniques that allow age-dating of the purification of materials (e.g. Mayer et al., 2013; Eppich et al., 2013; Kristo et al., 2016).

The search for identifying characteristics, or signatures, has been the focus of nuclear forensics research since the beginning. In the context of a nuclear forensics examination, signatures are defined as characteristics or sets of characteristics of a given sample that enables the assessment and evaluation of that sample’s provenance. The most valuable signatures are both readily measurable and also persistent through the fuel cycle. Some examples of signatures that persist up to the point of enrichment might include REE patterns, U isotopic compositions, or isotope compositions of certain trace elements including $^{87}\text{Sr}/^{86}\text{Sr}$ or $^{98}\text{Mo}/^{95}\text{Mo}$ (Varga et al., 2009; Brennecka et al., 2010; Rolison et al., 2019).

Other signatures, while not persistent, are characteristic of specific places or processes. These could include enrichment, minor U isotopic composition, parameters associated with grinding and metallurgy, trace elements, or even trace organic compounds (e.g. Pajo et al, 2001; Svedkauskaite-LeGore et al., 2008; Badaut et al., 2009; Kennedy, 2013).

The future of nuclear forensics research is focused on developing a greater understanding of signatures, both those that are persistent, as well as those that are characteristics of places, production methods, and design parameters.

Recently, we have acquired and analyzed samples of uranium ore material and uranium ore concentrate for a variety of analytes in order to assess the behavior of isotopic and elemental signatures during processing. This work is focused on identifying persistent signatures that may serve as a predictive indicator of material provenance. Results of this work will be presented, as well as an overview of the current state of nuclear forensic signatures for materials from the front end of the nuclear fuel cycle. The talk will conclude with a discussion of some promising future directions for the field.

SESSION S.CT03.06: Uranium Oxides and Uranium Magnetism

On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

S-CT03

5:00 AM S.CT03.06.03

Local Structure and Magnetism of $\text{La}_{3-x}\text{M}_{x}\text{PO}_4$ (M=RE, An, 0≤x≤1) Laura Martel¹, Ashraful Islam², Karin Popa¹, Aydar Rakhmatullin³, José J. Baldoví⁴, Mauro Perfetti⁵, Michael Deschamps⁶, Eric Colineau⁶, Attila Kovács⁷, Hélène Bolvin² and Jean-Christophe Griveau⁴; ¹JRC-Karlsruhe, Germany; ²LCPQ-IRSAMC, France; ³CEMHTI, France; ⁴University of Valencia, Spain; ⁵Department of Chemistry, University of Copenhagen, Denmark

Lanthanide orthophosphates with the monazite crystalline structure are considered as potential matrices for encapsulation of
nuclear materials due to their high resistance to radiation damage. Here, we will present a review done on a series of monazites having the crystalline structure La$_x$M$_{1-x}$PO$_4$ (M=RE, An, 0≤x≤1). We have studied their local structure using high resolution $^{31}$P solid-state NMR. The experiments were done using the dedicated NMR facility for transuranic materials which is available at JRC-Karlsruhe. In a second part, in order to understand the magnetic nature of these samples, we also performed magnetic susceptibility measurements. Analyses of the magnetic susceptibility data were carried out using the free ion model, crystal field theory and/or ab initio calculations allowing to extract the electronic structure. All of these data will be discussed and a comparison between the actinide monazites and their lanthanide surrogates will be presented.

5:15 AM S.CT03.06.04
The JRC Surface Science Labstation—A Unique Set-Up to Investigate Actinides in Support of Nuclear Safety and Non-Power Application of Nuclear Materials Rachel Eloirdi1, Thomas Gouder1, Ghada El Jamal2, Concettina Andrello1, Frank Huber1 and Roberto Caciuffo1; 1JRC Karlsruhe, Germany; 2KTH Royal Institute of Technology, Sweden

Knowledge about the interaction of UO$_2$ with the environment is of high importance to assess its stability in oxidizing and in reducing condition. For this reason, understanding the UO$_2$ oxidation process is central to the performance assessment of nuclear fuels. Oxidizing condition can convert UO$_2$ into U$_2$O$_5$ leading, in some cases, to powdering of the fuel matrix or to failure of the cladding [1]. The redox behaviour of UO$_2$ is also relevant for the management of nuclear waste forms, as oxidation results in the production of soluble uranyl cations, UO$_2^{2+}$, that can easily migrate in the biosphere.

This talk summarizes surface science research activities carried out at JRC Karlsruhe in support of nuclear safety and non-power application of nuclear materials. I will also describe a unique set-up developed in-house, the Labstation [2], including sample preparation modules, by DC Sputtering or evaporation, and several surface characterisation techniques. Among the latter, High-resolution X-ray Photoelectron Spectroscopy (XPS) and Bremsstrahlung Isochromat Spectroscopy (BIS) are particularly useful to characterize the uranium oxidation state in single and mixed oxides. In a first example, I will show the process of oxidation and reduction of U oxides using O$_2$, H$_2$O and H$_2$, plasma. For the first time, UO$_2$ films [3-4] could be produced and studied, filling a gap in the knowledge about U$^{5+}$ oxidation state. While U$^{4+}$, U$^{5+}$ and U$^{6+}$ have representative satellite peaks positioned, respectively, at 7, 8 and 4 & 10 eV out of the main 4f$^{5/2,7/2}$ excitation lines, a satellite peak at 9 eV is observed when UO$_{2-x}$ in contact with sodium is heated at 400 °C under oxygen. In a second example, we report the first in-situ preparation of ThF$_4$ [5] whose band gap of 10.2(2) eV is significantly larger than the 229mTh excitation energy, making ThF$_4$ a possible candidate material for a solid-state nuclear clock based on the vacuum ultraviolet $\gamma$ decay.

References

5:45 AM S.CT03.06.05
Probing the Limits of 5f Ferromagnetism in UCu$_2$P$_2$: Ladislav Havela$^1$, Jiri Prchal$^1$, Jaroslav Valenta$^1$, Martin Divis$^1$, Fuminori Honda$^2$, Ilja Turek$^1$, Dariusz Kaczorowski$^3$, Dexin Li$^2$, Arvind Maurya$^2$ and Dai Aoki$^2$; $^1$Charles University, Czechia; $^2$Tohoku University, Japan; $^3$Polish Academy of Sciences, Poland

Magnetic order in 5f materials offers interesting benefits, based in principle on very strong spin-orbit interaction, bringing large orbital moments into systems with itinerant, i.e. bonding, states. This yields very strong magnetocrystalline anisotropy, determined not by CEF effects as in lanthanides, but by bonding anisotropy. Hybridization of the 5f states with other states having low effective mass means that a re-orientation of 5f magnetic moments can have a dramatic effect of electrical conduction, bringing a giant magnetoresistance effect. Other related prominent characteristics include a giant Kerr rotation as on of important magnetooptical phenomena. Although highly tunable by composition and external variable, the 5f magnetism remained restricted to low temperature
range, discarding e.g. inexpensive uranium from the pool of prospective magnetic materials. For example, Curie temperatures of U-based 5f-ferromagnets only exceptionally exceeds the limit of 200 K. The trick of mixing the f magnetism with 3d magnetism of transition metals, so successful in lanthanide-based permanent magnets, does not work in the case of light actinides. Both 3d and 5f states being band-like, they strongly hybridize, which degrades both the 3d and 5f desirable characteristics. Due to the same reason U-compounds very rich in Fe or Co simply lose any distinct 5f contribution. Heavy actinides (from Am onwards), in principle analogous to heavy lanthanides, undergo a fast radioactive decay.

We have been trying to understand which type of tuning can support the 5f magnetism besides the traditional game with inter-actinide spacing. The case of uranium hydrides showed that using a ionic-covalent bonding can lead to a suppression of the 5f-6d hybridization, which is an undesirable mechanism, contributing the washout of U moments. The 6d hybridization with ligand states can efficiently liberate the 5f states, although they can still maintain their band character. A general hint is to look at U compounds with a certain charge transfer and to use external pressure for fine tuning of crystal structure.

We have focused on U pnictides, and chose UCu2P2 as the material with record high $T_C = 216$ K [1]. Applying hydrostatic pressure the $T_C$ value increases, reaching a maximum of 290 K in $p = 7$-8 GPa, i.e. first time obtaining a room temperature ferromagnetism with pure 5f ferromagnet. Details of electronic structure and their pressure variations have been provided by ab initio calculations.

This work was supported by the Czech Science Foundation under the grant No. 18-02344S.

SESSION S.CT03.07: Fuel Cycle Chemistry
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Saturday Morning, November 21, 2020
S-CT03

5:00 AM *S.CT03.07.01
Development of Liquid Fuel for Molten Salt Nuclear Reactors—The Physical Chemistry of Molten Fluoride Salts Raluca Scarlat; University of California, Berkeley, United States

Molten fluoride salts are used as solvents for uranium and thorium fuel for molten salt nuclear reactors. The relatively low volatility and high solubility of actinides and fission products in fluoride salt mixtures at temperatures in the range of 500 to 800°C render fluorides highly attractive solvents for liquid nuclear fuel. While a molten salt reactor experimental reactor operated in the 1960s and was supported by an extensive experimental campaign on the chemistry and physical chemistry of actinide-bearing molten fluoride salts, important data gaps still remain, and important fundamental understanding questions remain to be explored. This talk will provide a review of recent advances in on the physical chemistry of liquid fluoride salt fuel, in the context of development and licensing of molten salt reactors.

5:30 AM S.CT03.07.02
Species-Specific Mapping of Uranium Oxides in Spent Nuclear Fuel Focused Ion Beam Sections by Oxygen K-edge Spectromicroscopy Alexander Ditter1, Danil Smiles1, Jason M. Harp2, Daniel J. Lussier1,3, Michael W. Mara1,3, Lingfeng He2, Claude Delguedre4, Mitchell K. Meyer2 and David K. Shuh1; 1Lawrence Berkeley National Laboratory, United States; 2Idaho National Laboratory, United States; 3University of California, Berkeley, United States; 4University of Lancaster, United Kingdom

The specific nature of uranium oxides in spent nuclear fuel is a primary concern in the storage of nuclear fuels resulting from both the volumetric expansion of uranium oxides and change in solubility with an increase in oxygen content. In particular, the growth of hyperstochiometric uranium dioxide has been linked to fracturing of spent fuel, resulting in further oxidation and the release of short-lived radionuclides trapped within the UO2 matrix. Oxygen K-edge x-ray absorption spectroscopy is an excellent method to distinguish between different uranium oxide stoichiometries, but samples are limited to 1-2 µm thick as a result of the short penetration length of soft x-rays. To address this, low burnup pressurized water reactor (PWR) spent nuclear fuel samples were processed at Idaho National Laboratories utilizing focused ion beam (FIB) sectioning, resulting in samples ideal for soft x-ray spectroscopy. Here we present the first measurements of oxygen K-edge near-edge x-ray absorption spectroscopy, using the Beamline 11.0.2 scanning transmission x-ray microscope (STXM) at the Advanced Light Source, on FIB sections of spent nuclear fuel. The FIB sections present unique challenges in normalization and data analysis which will be discussed in this presentation. The sensitivity of the oxygen K-edge x-ray absorption spectrum between the different uranium oxides has allowed for species-specific mapping of the spent nuclear fuel at the sub-micron scale, showing
UO$_2$ as the bulk of the fuel, with U$_3$O$_7$ localized near a defected area in the spent nuclear fuel. In addition, spectra at the uranium N$_{4,5}$ edges and the cerium M$_{4,5}$ edges are analyzed and discussed, showing preliminarily a Ce$^{3+}$ oxidation state. This is all presented in the context of comparisons with transmission electron microscopy measurements of the same FIB sections.

SESSION S.CT03.08: Radiation Damage in Actinide Materials
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-CT03

5:00 AM *S.CT03.08.01
Radiation Damage in Actinide Compounds William J. Weber; University of Tennessee, United States

The principal sources of radiation damage in actinide compounds are spontaneous fission and alpha-decay, and self-radiation damage from these processes affect microstructural evolution, phase stability, and thermodynamic properties. In general, alpha-decay is the dominant process for most actinides, and because of the long half-lives of the actinides and their daughter products in used nuclear fuel and actinide waste forms, alpha-decay damage is a concern over very long timescales. Alpha decay produces energetic alpha particles (4.5 to 5.5 MeV) and recoil nuclei (70 to 100 keV), which result in both radiation damage and the accumulation of helium. The evolution of radiation damage due to alpha-decay has been studied using short-lived actinides, such as $^{238}$Pu and $^{244}$Cm, in several candidate glasses and ceramics for the immobilization of actinides, and fission tracks from the spontaneous fission of $^{244}$Cm have been observed in crystalline ceramics. Ion beam irradiations have been more frequently employed to study radiation damage in relevant materials due to decreased costs, shorter irradiation timescales and the non-radioactive nature of the irradiated materials. Furthermore, ion irradiations can be performed over a wider range of irradiation conditions to implant helium, study radiation damage kinetics, understand the separate and combined effects of alpha particles and alpha recoils, and benchmark against alpha-decay damage due to short-lived actinides. At ion energies typically used to study alpha-decay damage in actinide compounds, the electronic and nuclear energy losses are both important, and local ionization along the ion path can affect damage production and evolution, and atomic-level simulations have provided insights into these processes. While alpha particles are much less damaging than alpha recoils, the electronic energy loss from the alpha particles can also cause athermal annealing of heavy ion damage (i.e., alpha-recoil damage) that can impact the evolution of radiation damage. Helium implantation studies have shown that the accumulation of helium and heavy ion damage leads to the formation of helium bubbles above a threshold helium concentration. These results have significant implications for interpreting and modeling the radiation response of actinide compounds.

5:30 AM S.CT03.08.02
Kinetic Response of the δ-phase $^{239}$Pu-Ga Alloy Lattice to Self-Irradiation and Thermal Cycling Alice I. Smith, Franz J. Freibert, Sven C. Vogel, Jianzhong Zhang, Joan E. Siewenie, Scott Richmond and Michael Ramos; Los Alamos National Laboratory, United States

Self-irradiation in plutonium metal at room temperature introduces defect accumulation into the lattice, such as He bubbles and other daughter product impurities, interstitials and vacancies. X-ray diffraction and dilatometry studies have shown that the room temperature self-irradiation of δ-phase Pu-Ga alloys results in swelling of the lattice that saturates after 0.1-0.2 dpa of accumulated lattice damage. For a more complete picture of the poorly understood “aging” processes of defect accumulation and damage evolution δ-phase Pu-Ga alloys, dose, dose rate, thermal history and alloy composition must be considered. This work investigates with time-of-flight neutron diffraction the influence on long-range order of room temperature self-irradiation defects in δ-phase $^{239}$Pu-Ga alloys as they influence the lattice throughout a varied history of damage accumulation and thermal cycling.

In-situ time-of-flight neutron diffraction measurements were performed on the High-pressure Preferred Orientation (HIPPO) diffractometer at Lujan Center, Los Alamos Neutron Science Center. Data were collected between room temperature and 35K in an investigation of ambient aging impact on the lattice effects detectable during thermal cycling on the lattice of a δ-phase $^{239}$PuGa alloys. Repeated thermal cycling of PuGa alloys immediately after annealing at 450°C exhibits lattice swelling similar to ambient temperature isothermal lattice swelling, but at much shorter time scales. Reported here, the amount of lattice swelling for each cycle decreased in magnitude relative to the time before indicative of a saturating strain due to stress.
of local defect evolution to damage accumulation and impact on long-range order. Longer idling times, as observed during the FY16 and FY17 measurements, resulted in incomplete lattice recovery, and a contracted lattice. This study is an attempt at unravelling the complex history dependence of induced stress states and corresponding lattice strain on the kinetic processes of self-irradiation damage and thermal cycling.

SESSION S.CT03.09: Poster Session: Expanding the Frontiers of Actinide Materials Science Through Experiment and Theory
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
5:00 AM - 8:00 AM
S-CT03

SYMPOSIUM S.CT04

Tailored Interphases for High Strength and Functional Composites—Advances in Experiments, Simulations and AI-Based Design
November 21 - November 29, 2020

Symposium Organizers
Hendrik Heinz, University of Colorado-Boulder
Luke Henderson,
Dhriti Nepal, Air Force Research Laboratory
Cheol Park, NASA Langley Research Center

Symposium Support
Gold
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* Invited Paper

SESSION S.CT04.08: Live Lightning/Flash I: Tailored Interphases for High Strength and Functional Composites—Advances in Experiments, Simulations and AI-Based Design
Session Chairs: Hendrik Heinz and Dhriti Nepal
Saturday Afternoon, November 28, 2020
S.CT04

2:45 PM OPENING COMMENTS

2:49 PM *S.CT04.001.09
Maximizing Property Enhancements in Polymer Nanocomposites via Interfacial Effects—Examples Involving Polymer-Grafted Nanofiller and Optimal Matrix Molecular Weight
John M. Torkelson; Northwestern University, United States

Nanocomposite property enhancements originate substantially from interfacial effects. We focus on two examples of nanocomposite interfacial effects. In Example 1, modification of filler surfaces can improve dispersion and compatibilize the polymer-filler interface, leading to property enhancements relative to nanocomposites containing unmodified filler prepared by conventional melt mixing or solvent blending. For the first time, we isolate the effect of interactions between matrix
polymer and polymer-grafted nanoparticles from dispersion quality, revealing how the interactions affect the properties of polypropylene/halloysite nanotube (PP-HNT) hybrids. PP-HNT nanocomposites with pristine filler or PP-grafted filler were prepared by solid-state shear pulverization, leading to excellent dispersion in both cases. Optimal interactions with PP-grafted nanofiller leads to faster PP crystallization and higher yield strength; in contrast, Young’s modulus is determined by the filler dispersion and not filler modification. In Example 2, for the first time, we have decoupled chain dynamics in nanocomposite interfacial layers from chain dynamics of the matrix in poly(2-vinylpyridine) (P2VP)-silica nanocomposites. The interfacial $T_g$ (glass transition temperature) and the matrix $T_g$ (both associated with $\alpha$-relaxation dynamics) were determined by fluorescence. The interfacial layer $T_g$ is higher than the matrix $T_g$ due to H-bonding between P2VP and hydroxyl groups on the silica surface. At the same filler dispersion, 2.1 kg/mol P2VP matrix polymer leads to much greater $T_g$ enhancements in both the interfacial regions and the matrix relative to the use of 110 kg/mol P2VP. We hypothesize that low molecular weight P2VP preferentially aligns at the filler interface, leading to higher H-bonding density and increased $T_g$.

2:56 PM *S.CT04.03.03
Molecular Dynamics Simulations Integrated Machine-Learning Study of Bottlebrush Polymers of Different Shapes Soumil Joshi, Samrendra Singh and Sanket A. Deshmukh; Virginia Tech, United States

Thermosensitive bottlebrush polymers (BBPs) are a type of graft copolymers in which thermosensitive polymer side-chains are grafted on a linear polymer backbone. These side-chains can undergo a coil-to-globule conformational change in response to a change in the surrounding temperature. This also results in a change in the overall shape of the BBPs because of which they can be used for biomedical applications. Here, we will present the results of our recent coarse-grained (CG) molecular dynamics (MD) simulations study of poly(N-isopropylacrylamide) (PNIPAM; transition temperature= 305 K) BBPs of Worm-like, Cone-like, Dumbbell-like shapes. The CG MD simulations were performed at 300 K (below transition temperature) and 320 K (above transition temperature). The analysis of simulation trajectories showed that the shape of BBPs has significant impact on the conformations of individual side-chains.

3:03 PM *S.CT04.01.11
Design of Interphases for High Dielectric Performance in Polymer-Matrix Nanocomposites Evangelos Manias; The Pennsylvania State University, United States

Polyolefin (polyethylene, and ethylene-propylene-diene (EPDM) elastomers) composites were studied in order to elucidate and quantify the effects of the interfaces with ceramic and carbon nanofillers, and particularly of the interphase contributions on the dielectric properties of the composites. For ceramic nanoparticles, it was shown that the interphase contributions dominate the composites’ dielectric properties, often being antagonistic to the contributions of the ceramic fillers: Ceramic fillers with systematically varied dielectric nature –spanning orders of magnitude in dielectric constants– were studied, and the interphasial contributions effectively overwhelmed the ceramic filler permittivities and dominated the dielectric performance of the composites. For composites containing both ceramic and carbon-black nanofillers, proper design of the interphases is crucial, so as to capitalize on the high effective permittivity provided by the carbon while, at the same time, preventing mobile charges to undertake large lengthscale transport (conductivity) or high dissipation of energy in localized vibrations (dielectric loss); in these systems, a third nanofiller is introduced as a means to control conductivity and minimize losses and E-field breakdown.

3:10 PM *S.CT04.01.12
Hybrid Nanocomposites at the Extreme Limits of Molecular-Scale Confinement with Tailored Internal Interfaces Reinhold H. Dauskardt; Stanford University, United States

We review the state-of-the-art in the molecular design and processing of low density organic-inorganic nanocomposite hybrids at the extreme limits of molecular-scale confinement with tailored internal interface chemistry. We probe the mechanical and thermal properties of nanocomposite hybrids where a stiff inorganic matrix phase confines polymer chains to dimensions far smaller than their bulk radius of gyration. We describe a synthesis strategy which involves tailoring the internal interface chemistry between the matrix and the polymer phase. Tuning the interface allows access to extreme levers of molecular “hyper-confinement” where the confined polymer dynamics and resulting thermal behavior are markedly altered. We demonstrate the strategy with polystyrene and polyimide phases. The infiltration of individual polyimide precursors into a nanoscale porous network where imidization reactions under such confinement increase the molecular backbone stiffness. We find that polyimide oligomers can then undergo crosslinking reactions even in such molecular-scale
confinement, increasing the molecular weight of the organic phase and toughening the nanocomposite through a confinement-induced energy dissipation mechanism. This work demonstrates that a confinement-induced molecular bridging mechanism can be extended to thermoset polymers with multifunctional properties, such as excellent thermo-oxidative stability and high service temperatures (> 350 °C).

3:24 PM *S.CT04.02.01
Interfacial Behavior and Self-Organization of Nano-Inclusions in Vesicles Meenaksi Dutt; Rutgers, The State University of New Jersey, United States

The distribution of nano-inclusions at the interface or within soft films is determined by multiple key factors. These factors include the molecular composition, interfacial profile, morphology of the films and the characteristics of the inclusions along with predominant interactions in the systems. We will discuss the role of these factors on the interfacial behavior of nano-inclusions on the surface of spherical soft films, or vesicles. Furthermore, we will discuss the organization of the inclusions in vesicles as a function of nano-inclusion effective chemistry, dimension and concentration. These investigations have been contingent upon the ability to resolve large spatiotemporal scales. Hence, the studies have required the adoption of coarse-grained models used in conjunction with mesoscale simulation methods such as Dissipative Particle Dynamics and Molecular Dynamics. Our observations have the potential to guide the design of composite materials which require precise control on their characteristics including their shape or the dispersion of the inclusions.

3:31 PM *S.CT04.02.03
Chemical and Topological Design of Bioinspired Polymer Adhesives—Interfacial Molecular Mechanics and Applications Yiran Li1,2, Peyman Delparastan1, Cody Higgison1, Katerina Malollari1, Jing Cheng1, Haoqi Wang2, Brylee Tiu1, Kyueui Lee1, Yi Cao2 and Philip B. Messersmith1,3; 1University of California, Berkeley, United States; 2Nanjing University, China; 3Lawrence Berkeley National Laboratory, United States

In mussels, the adhesive proteins that are instrumental for attachment to wet surfaces are known to contain high levels of 3,4-dihydroxy-L-alanine (DOPA), often located adjacent to amino residues such as lysine (Lys). The special synergistic relationship between catechols and amines is a subject of high interest, not only for understanding native proteins but also for informing the design of bioinspired polymer systems. Other research groups have shown that catechol and amine functional groups act synergistically to enhance adhesion at wet surfaces, however reports of catechol-amine interfacial phenomena on a single molecule level have been limited. In this talk we will describe single molecule force spectroscopy (SMFS) measurements that are providing new insights into interactions between Lys-DOPA peptides and various surfaces. Molecular mechanics investigations of catechol and catecholamine polymers are providing new insights into design of novel polymer adhesives, for example pressure sensitive adhesives and high-strength thermoset adhesives.

3:38 PM *S.CT04.03.01

Exfoliated Transition Metal Dichalcogenides (TMDs, MX2) have attracted considerable attention for infrared optical elements due to their high refractive index and extreme nonlinearities (e.g. MoS2, TiS2). Recent high-yield, sonication-free, surfactant-free, exfoliation methods (i.e. Redox Exfoliation) now provide access to oxidatively-resistant and colloidal-stable dispersions at high TMD content (10% w/v), and in an expanded range of polar solvents (e.g. acetonitrile, acetone, alcohols). In addition to transforming approaches to nanocomposite fabrication, ink formulation, and film processing, these characteristics enable direct organic hybridization of Group IV-VI TMDs. For example, Grignards (R-MgBr) are not accessible via traditional Liquid Phase or Li-Intercalation methods due to their extreme reactivity with labile hydrogens (water), amides (NMP), and oxygen. However, the availability of Group VI TMDs dispersions in anhydrous THF enables synthesis of alkyl grafted MoX2, which has zero surface charge, is dispersible in chloroform, and affords subsequent surface-initiated polymerization, all while retaining optoelectronic monolayer properties. In addition, classic redox intercalation chemistries can be applied to Group V monolayer dispersions. For example, a primary alkyl amine reacts at 70°C in anhydrous acetonitrile with semi-metallic, single layer NbS2 via charge transfer from the amine to the half-filled Nb d-orbitals. The resultant organic-grafted NbS2 is a semiconductor, with enhanced oxidative stability (> 7 days ambient) and dispersibility in non-polar dichloromethane that allows for ambient handling and processing. Such access to numerous hybridization approaches will greatly expand the electrical, optical, and chemical property suite of TMDs and enhance the
ability to fabricate device quality films and hetero-structures for optical filters, GRIN optics, and non-linear absorbers.

3:52 PM *S.CT04.03.04
Organic-Inorganic Interfaces—Insight from First Principles Calculations Ruth Pachter; Air Force Research Laboratory, United States

Elucidating the role of organic ligands that are attached to or incorporated within inorganic nanostructures, for example, at the interface of colloidal nanocrystals or as included in the inorganic framework of two-dimensional hybrid organic-inorganic perovskites, is essential in realizing desired functional properties for applications. However, although general guidelines are provided by experimental explorations, an understanding of the underlying mechanisms for efficient materials development is often lacking. Herein, by employing first principles calculations for the design of materials that exhibit optical tunability characteristics, we first discuss atomically precise quantum dots. We highlight challenges in modeling the structure of semiconductor nanoclusters with organic ligands. In this context, we report on the derivation of a potential energy surface using machine learning that overcomes, in part, some of these limitations, and on the importance of the level of theory applied for accurate prediction of the optical response. In addition, we discuss effects of incorporating large chromophores as the ammonium cation in 2D hybrid organic-inorganic perovskites, which have proven promising for optoelectronic applications. Dependent on the organic moiety type, band alignments indicate variability in quantum-well types for a range of materials we examined, as well as structural distortion. Absorption spectra demonstrate tunability in the optical properties, including enhanced absorption and red-shifts, providing recommendation for the choice of the organic cation and motivation for further synthesis and experimental characterization.

3:59 PM *S.CT04.04.06
Exploring Structure, Defects and Behavior of Nanotube Assemblies by Multiscale Modeling Boris I. Yakobson; Rice University, United States

Hetero- or homo-interfaces formed by carbon nanostructures of different C hybridizations are ubiquitous in electronic, structural, and energy-functional materials. Understanding how weak interactions and/or chemical bonding at the interface lead to a meso- and macroscopic behavior warrants a multiscale modeling framework. This will be illustrated with the example of carbon nanotube (CNT) fibers. Starting from the energetics and kinetics of various crosslinks (~nm, ~fs) accessible from accurate DFT calculations, we derive scaling relations of their tensile mechanical response from a μm-long coarse-grained model of a CNT bundle. These inter-tube crosslinks can be expected to behave as “hook-and-loop” fasteners, operational in Velcro, which can have the ability to break and reform and thus resist relative motion in a continuous manner. Such a model can incorporate the effect of interface friction due to inter-tube crosslinks or tube-polymer matrix connects, quantitatively evaluate toughness and fatigue processes and look for ways of performance improvement. Same coarse-grained model allows us to also explore the fundamental problem of basic packing defects in the aligned CNT bundles: the ‘twists’ and ‘inclusions’. We show how a finite characteristic size/length $L$ of such defects emerge as a result of interplay between their intrinsic bending stiffness and the elastic response of the surrounding CNT matrix-crystal, and quantify their energetics scaling. In conjunction with synthesis efforts and novel experimentation, such models are crucial in developing novel carbon nanomaterials.

4:06 PM *S.CT04.04.07
Molecular Dynamics Modeling of Flattened CNT/Polymer Interfaces Matthew Radue1, William Pisani1, Sagar Patil1, Prathamesh Deshpande1, Prashik Gaikwad1, Swapnil Bamane1, Susanta Ghosh1, Traian Dumitrica2 and Gregory Odegard3; 1Michigan Technological Univ, United States; 2University of Minnesota Twin Cities, United States

Current state-of-the-art carbon fiber reinforced composite materials have become a standard structural material used in the aircraft industry. Their relatively high strength-to-density and stiffness-to-density ratios make them useful for reducing vehicle mass and thus improving fuel efficiency. However, for manned space exploration beyond the moon (deep space), further decreases in mass are needed for fuel efficiency. Thus, increases in the strength-to-density and stiffness-to-density ratios are necessary.

Carbon nanotube (CNT)-reinforced composites can potentially provide the needed reductions in composite laminate mass. Relative to carbon fiber, CNTs can have higher strength and modulus, and can potentially provide a larger surface area for polymer interaction and load transfer. Further, flattened CNTs (fCNTs) can form self-assembled arrays with a higher
packing than round CNTs [1]. Although countless studies have examined CNT/polymer interaction on the molecular level [2], little effort has been devoted to understanding flCNT/polymer interaction.

The objective of this research is to use molecular dynamics (MD) simulation to explore the interaction and load transfer characteristics for a range of different polymer resins with flCNTs. Specifically, the interfacial interaction energy, pull-out frictional force, pull-apart force, and resin wetting contact angles have been predicted. These predictions have been performed for two polyimide systems, two cyanate ester systems, polyurea, and PEEK. The results of these studies will be presented, and the best polymer candidates for these flCNT/polymer composites will be discussed.

References


4:13 PM *S.CT04.05.01
Molecular Engineering of Hairy Nanoparticles with Reversible Self-Assembly and Tailored Plasmonic and Luminescence Properties

Zhiqun Lin; Georgia Institute of Technology, United States

Polymer-ligated nanoparticles (NPs) exhibit an exciting variety of physical properties that depend sensitively on the dimension and composition of NPs as well as the surface chemistry of tethered polymer hairs. Herein, we report on a robust nanoreactor strategy for in-situ crafting of monodisperse stable polymer-ligated NPs with well-controlled size and shape as well as tunable plasmonic (e.g., Au) and luminescence (e.g., perovskite MAPbBr3 and CsPbBr3) properties. Central to this strategy is to judiciously design unimolecular amphiphilic star-like block copolymer as nanoreactor for yielding NPs intimately and permanently ligated by polymer hairs. The diameter of polymer-ligated NPs can be precisely tuned by modulating the length of inner hydrophilic block of star-like block copolymers. In the case of Au NPs, the perpetual anchoring of photoresponsive or thermoresponsive polymers on the surface renders the attractive feature of self-assembly and disassembly of NPs on demand by capitalizing on light of different wavelengths or heating/cooling, respectively. Such self-assembly/disassembly process is revealed by tunable surface-plasmon resonance absorption of Au NPs and the reversible transformation of Au NPs between their dispersed and aggregated states. For perovskite NPs, the resulting polymer-ligated MAPbBr3/SiO2 core/shell NPs and CsPbBr3 plain NPs display concurrently a stellar set of significantly improved stabilities (i.e., colloidal stability, chemical composition stability, photostability, water stability), while possessing appealing solution processability, which are unattainable by conventional methods. We envision that the amphiphilic star-like block copolymer nanoreactor strategy may provide a versatile platform for crafting diverse organic-inorganic nanohybrids stably-ligated with polymer of different functionalities (e.g., semiconducting, ferroelectric, photoresponsive, thermal-responsive, or pH-sensitive) for a spectrum of applications in bioimaging, biosensors, photonic materials and devices, perovskite-based LEDs, lasers, high-energy ionization radiation detections, multiphoton emission, and scintillators.

4:20 PM *S.CT04.05.03
Molecular Simulation and Theory Studies Linking Design of Polymer Grafted Nanoparticles to the Polymer Nanocomposite Morphology

Arthi Jayaraman; University of Delaware, United States

In this talk I will present our recent work studying polymer nanocomposites (PNCs) using molecular dynamics (MD) simulations and Polymer Reference Interaction Site Model (PRISM) theory calculations with coarse-grained (CG) models. Specifically, we are interested in linking molecular design of PNCs comprised of grafted nanoparticles in a polymer matrix to their morphology. In this talk I will focus our work on the impact of strength of graft-matrix attraction on interpenetration of matrix and graft chains (known as grafted layer wetting) and dispersion/aggregation of grafted particles in matrix. Previously
for PNCs with attractive graft-matrix interactions, we had shown that wetting/dewetting and dispersion/aggregation are two distinct phase transitions, the former being a continuous transition and the latter being a first-order transition as a function of graft-matrix interaction or temperature. Recently, we found that as the strength of graft-matrix attraction increases, we can also tune the effective size and the hardness of the polymer grafted particle in the PNC. As the attraction between the graft and matrix chains increases, the graft polymer chains extend to make favorable graft-matrix contacts and increase the grafted layer wetting by matrix chains. This leads to larger and ‘harder’ grafted particles compared to analogous fillers with purely entropic (athermal) graft-matrix interactions. Due to the increasing size and hardness of grafted particles with increasing graft-matrix attraction, the PNC structure changes from an aggregated/dispersed morphology governed by entropic driving forces at athermal graft-matrix interaction to a dispersed morphology due to favorable weak graft-matrix attraction, and ultimately, to a correlated fluid of hard grafted particles at stronger graft-matrix attraction. We see these trends in PNCs with high (densely grafted) and low grafting density, and with equal graft and matrix chain lengths as well as cases where the matrix chain lengths are greater than the graft chain lengths.

4:34 PM *S.CT04.05.05
Advances in Using Surface-Initiated Atom Transfer Radical Polymerization and Its Application to Tailoring Particle Interactions and the Design of Functional Materials Michael R. Bockstaller; Carnegie Mellon Univ, United States

Surface Initiated Atom Transfer Radical Polymerization (SI-ATRP) in its various modifications has emerged as a versatile toolbox to control and tailor the properties and interactions of interfaces and to enable the synthesis of hybrid materials with unprecedented property combinations. The resulting materials have attracted interest not only because the high-level structural control of the architecture of polymer-tethered surfaces enables tailoring of the interactions, microstructure and properties of particulate-based materials but also because the confinement of chains on surfaces alters the mechanism of termination reactions that limit conventional polymerization processes.

This presentation will review recent examples of the application of SI-ATRP for the synthesis of functional polymer materials. Examples to be covered include the synthesis of ultra-high molecular weight polymers, materials for optical applications as well as thermal interface materials. Recent examples of the interplay between phononic and photonic properties in brush particle-based materials will be shown to illustrate how the subtle control of polymer chains at interfaces can instigate novel physical properties in hybrid materials that cannot be realized in ‘classical’ composite materials that are fabricated by mixing of particle and polymer constituents. This will provide the basis for a discussion of ‘guidelines’ for the fabrication of novel functional materials that harness ‘chemical confinement’ of polymer chains.

SESSION S.CT04.09: Live Lightning/Flash II and Panel Discussion: Tailored Interphases for High Strength and Functional Composites—Advances in Experiments, Simulations and AI-Based Design
Session Chairs: Hendrik Heinz and Dhriti Nepal
Sunday Morning, November 29, 2020
S.CT04

8:00 AM OPENING COMMENTS

8:03 AM S.CT04.01.15
Nano Materials Hybridization and Its Interfaces for Simultaneous Multifunctionality Ajit K. Roy; Air Force Research Laboratory, United States

For optimal materials usage in numerous defense applications, as well as in aerospace systems, materials are to operate in episodes requiring simultaneous multifunctionality. For example, electronics in munitions and high temperature sensor modules are expected to retain its expected electrical, thermal, and mechanical properties or attributes even in extremely high strain gradient operation. Similarly, in hypersonics coatings, high temperature material oxidation stability plus tailored thermal conductivity are needed in extreme high temperature operation. In this presentation, materials design approaches for simultaneous exhibit of selected multifunctionality will be discussed. Further, such desired multifunctionality is expected to be more optimally feasible by taking the materials design to small scale (say, at atomic level) and then linking that to bulk materials performance. Also, materials hybridization at small (atomic or molecular) scale and optimizing the associated heterostructure phases significantly opens up materials performance domain and its multifunctionality. Examples of several
computational tools (atomistic, Mesa, continuum scale - ab initiation, NEGF, MD, MD Wave Packets, Tight Binding MD, Molecular Mechanics) will be illustrated for tailoring materials functionalities (thermal, electrical, structural) in the material compositional design, along with a few design cases (thermal interface, nano porous carbon, strain-resilient electronics).

8:10 AM *S.CT04.02.04
Biomimetic Nanocomposites for Energy Technologies and Meta Optics Nicholas A. Kotov; University of Michigan, United States

Materials with difficult-to-attain combination of multiple properties - mechanical, electrical, chemical, optical, thermal, and transport, – represent the quintessential bottleneck for nearly all modern technologies. Nanocomposites with molecular, nano-, meso-, and microscale levels of structural engineering can provide such property combinations, while intrinsic ability of nanoscale components to self-assemble make them suitable for simplicity of synthesis.

Biomimetic nanocomposites exemplified by a variety of nanostructured nacre-like materials provide a generalized approach to engineer materials with multiple difficult-to-attain properties. As the continuation of this research, we learn that the unique mechanics of tooth enamel can be replicated combining out-of-plane nanoscale columns with molecular precision of layer-by-layer (LBL) assembly between them. As a result of that, these composites reveal remarkably high vibrational damping unusual for stiff materials that imparts them resilience to aging.

The novel type of biomimetic nanocomposites are those based on aramid nanofibers (ANFs). They spontaneously assemble into three-dimensional percolating networks reminiscent of cartilage. The nanoscale structure of ANF composites reveal nanoscale porosity that can be controlled by nanofiber branching. The latest results from multiple groups demonstrate that ANF composites resolve some of the essential property bottlenecks for ion-selective membranes, dendrite-resistant electrolytes, and structural batteries.

One of the emerging fields for biomimetic nanocomposites are optical devices. The high strain and strong polarization rotation make possible metaoptical devices with wide-angle diffraction gratings for LIDARs and highly efficient quarter wave plates for THz scanners. Both devices can be used for machine vision and biomaterials imaging.

8:17 AM *S.CT04.02.05
Colour with a Twist—Cellulose Photonic Materials with Tailored Visual Appearance Silvia Vignolini; University of Cambridge, United Kingdom

Plant-based polysaccharides such as cellulose and its derivatives are receiving increasing interest in a large variety of applications because they represent an environmentally friendly alternative to plastic. Many of them are commonly used in diverse industrial applications, such as food additives and for biomedical devices due to their non-toxic and water-soluble nature. Moreover, the self-assembly nature and responsiveness of cellulosic bio-polymers makes them also extremely attractive for smart photonic applications including sensing. Among various types of cellulose and its derivatives, hydroxypropyl cellulose (HPC) encompasses all these desirable properties.

Hydroxypropyl cellulose is a liquid crystal polymer, which can form a cholesteric liquid-crystalline phase allowing Bragg-like reflection. The reflected colours can be simply controlled by changing the nature of the solvent, concentration, temperature. Recently, we demonstrated for the first time that a simple aqueous solution of HPC can be used as a photonic strain sensor that displays the applied strain by shifting its colour.

In this seminar, I will introduce how such properties can be enhanced to create a solid-state film with desired optical appearance.

8:24 AM *S.CT04.03.05
Enhanced Multifunctional Nanocomposites with Two-Dimensional Transition Metal Carbides/Nitrides (MXenes) Christine B. Hatter and Yury Gogotsi; Drexel University, United States

Composites offer a wide variety of uses in aerospace, automotive industry, additive manufacturing, and energy storage applications. Discovered in 2011, MXenes have emerged as a new class of two dimensional (2D) materials consisting of transition metal carbides and nitrides. Synthesized MXenes have rich chemistry and 2D morphology offering a combination of high metallic conductivity and hydrophilicity for easy solution processing. Additionally, MXenes have been shown to have excellent mechanical properties with Young’s modulus of 330 GPa, surpassing both GO and rGO making it one of the strongest solution-processable 2D materials. Thus, they can improve mechanical and thermal stability as well as electrical
conductivity of polymers. They can also reinforce ceramics and metals.

The most commonly studied MXene, titanium carbide (Ti3C2), has been combined with various polymer systems producing new multifunctional nanocomposites. When introduced into thermoplastics like PVA, improved mechanical properties were observed at 10 wt% polymer loading with a 34% increase in tensile strength compared to pure Ti3C2 films. Additional studies have shown electrical properties can be successfully transferred to the polymer composite extending its use to electrodes in energy storage systems as well as electromagnetic interference shielding for future electronics. In addition to simple direct mixing with polymers, Ti3C2 MXene has also been incorporated into more complex polymer fibers for integration into textile applications. A recent study on electrospinning of MXene-PAN nanofibers showed MXene content could be increased up to 35 wt% and retain high areal capacitance three times that of pure PAN nanofibers. This presentation will provide an overview of the current MXene-reinforced composites field, including ceramic- and metal-matrix, and the various applications.

8:31 AM *S.CT04.02.02
Interfacial Dynamics of Nanoconfined Molecules and Macromolecules Younjin Min; University of California, Riverside, United States

The properties of fluids, when confined at nanometer scales, differ greatly from their bulk properties and are generally dominated by interfacial effects. In this interfacial region, the nature of the wall–fluid intermolecular interactions can have a significant effect on the fluids, introducing symmetry breaking, structural frustration and confinement-induced entropy loss into nanoscale interactions under confinement. In this presentation, several examples regarding how different degrees of nanoconfinement alter the structural organization and interfacial properties of soft matter ranging from non-biological (e.g. ionic liquids and silica colloidal suspensions) to biological ones (e.g. biopolymer solutions) will be introduced. This talk will particularly focus on describing the mechanisms of how biomacromolecules such as silk fibroin (SF) proteins self-assemble into hierarchical structures at the multiple-length levels in greater details. The presentation will conclude with some perspectives on new fundamental insights for rational design of SF-based materials with desired interfacial features in use of their fabricating superior functional materials and devices.

8:38 AM *S.CT04.05.02
Understanding Self-Assembly of Functional Nanostructures with Actuation Capabilities George C. Schatz; Northwestern University, United States

Molecular self-assembly involves the use of hydrogen bonds and other noncovalent interactions between molecules to create supramolecular structures. A goal of theory is to be able to predict and understand what structures will arise for any given set of conditions, and how the self-assembly can be directed so as to produce useful functional structures. In this talk I will describe recent studies in my group in collaboration with the Stupp and Mirkin groups at Northwestern, and with others, with the goal of making nanostructured materials with broad applications including actuation with various stimuli.

One area of interest concerns studies of peptide amphiphile self-assembly to produce cylindrical micelles and ultimately fiber materials that can be used for applications in biomedicine and for making materials that can be photoactivated for robotic functions. Here we have developed all-atom and coarse-grained models, and specialized molecular dynamics methods, that are capable of describing assembly into fibers, leading to an understanding of biological functions and photoactuation.

In a second direction we are interested in the coupling of self-assembly chemistry involving DNA attached silver and gold nanoparticles to create a new generation of bottom-up nanomaterials of interest for sensing and optical devices. Here we show both coarse-grained and all-atom approaches to the assembly, and how these can be used to understand the formation of plasmonic array structures, including recent studies aimed at understanding programmability of dynamic optical properties.

8:45 AM *S.CT04.01.01
Robust Organized Composites from Synthetic Nanostructures and Polysaccharide Materials for Nanophotonic Applications Vladimir Tsukruk; Georgia Institute of Technology, United States
We summarize recent results from our research group on assembling of robust functional synthetic and biocomposite materials from orthogonal nanoscale components for advanced nanophotonic applications. For flexible biophotonic materials, uniformly aligned chiral structures is critically important to be stabilized to improve mechanical performance without compromising controlled helical morphologies and propagating phase separation. In this aspect, we discuss mixed amorphous polysaccharide polymers and nanocrystals in terms of their hierarchical organization, intercalated structures, ability to form periodic patterned surfaces, and resulting chiral optical properties. Furthermore, we consider how highly emissive semiconducting and carbon quantum dots can be integrated into synthetic polymer matrices, chiral biomolecular structures, and survive microfabrication/printing processing for arresting quenching trends, stimulating bright patterned emission, and prompting directed lasing phenomena.

8:51 AM BREAK

8:56 AM PANEL DISCUSSION

9:56 AM CLOSING COMMENTS
Exchange Processes Zhongyang Wang and Robert Wang; Arizona State University, United States

Assemblies of colloidal nanocrystals and magic-sized-clusters (MSCs) are widely used in a variety of applications due to their unique electronic, optical and magnetic properties. However, these materials show a surprisingly limited range of elastic moduli (~0.5-5 GPa) and hardnesses (50-500 MPa), which presents a challenge for applications in which mechanical robustness is critical. These poor mechanical properties originate from the organic ligands during nanocrystal synthesis that result in weak interparticle interactions in particle assemblies. In this work, we conduct ligand strategies to significantly improve the mechanical properties of colloidal nanocrystal solids. We also report on our ongoing efforts to extrapolate these strategies to assemblies of MSCs.

Our preliminary result shows that inorganically linked nanocrystal solids possess significantly increased elastic moduli and hardness. More specifically, in the case of 3.5 nm CdSe nanocrystal material system, we demonstrate an elastic moduli and hardness increase by a factor of 50 once the native long oleic acid ligand is substituted with a few atomic layers of SnS$_2$ phase. Ligand exchange is carried out through a solution phase ligand exchange and is confirmed through a combination of FTIR, TEM&EDS, and nanoindentation experiments. The nanoindentation experiments demonstrates that the elastic moduli/hardness of 3.5 nm CdSe nanocrystal solid increase from 0.43GPa/34MPa to 30GPa/1.6GPa once native long oleic acid ligand is replaced with a few atomic layers of SnS$_2$ phase.

This observed mechanical reinforcement is due to greatly enhanced mechanical coupling between the neighboring nanocrystals. First of all, the covalent Sn-S bond is much stronger than the van der waals interaction between organic molecules. Second, inorganic ligands occupy much smaller spacing as compared long oleic acid molecules, which suggests enhanced van der waals interaction and electrostatic interaction between the neighboring nanocrystals. In order to quantitatively understand the underlying mechanism, we performed molecular dynamics (MD) simulations. These simulations also allow us to predict other mechanical properties (bending moduli, fracture toughness etc) that are hard to measure directly on inorganically linked nanocrystal solids.

The similarities between colloidal nanocrystals and MSCs suggest it may be possible to extrapolate these ligand exchange strategies to MSCs. MSCs have the advantage of being perfectly monodisperse as well as small enough for full-fidelity density functional theory simulations. This opens possibilities for an in-depth understanding of the mechanical properties enhancements afforded by ligand exchange strategies.

Reference:

6:00 AM S.CT04.01.06
In Situ Characterization of Dynamic Mechanical Response and Adiabatic Shear Band Evolution in AZ31B Magnesium Alloys During High Strain Rate Impact Using 3D-Digital Image Correlation Technique Francis Tetteh and Solomon Boakye-Yiadom; York University, Canada

The deployment of Magnesium (Mg) alloys have increased significantly in the automotive, aerospace and defense industries due to their lightweight structural integrity. In structural applications, these materials components are exposed to a wide range of strain rates such as explosive forming, high speed impact and shock loadings. These alloy components are placed in extreme loading environments where high strain rates are commonly achieved. Therefore, the evolution of failure mechanisms from strain localization and formation of adiabatic shear bands (ASBs) and the mechanical behavior at high strain rates is of desirable interest by the aerospace and automotive industries. However, studies on how failure emanate from ASBs formation to crack initiation and propagation in these materials with regard to their mechanical responses under high strain rates such as shock loadings and impact are limited. Deformation and damage accumulation in Mg alloys at high strain rate loading conditions such as impact are not fully understood. Thus, the correlation between the accuracy of the reported mechanical data and microstructural features that leads to the credence of failure mechanisms within Mg is not well understood. It is therefore critical to extend the understanding of the mechanism of failure of Mg at high strain rates of loadings by exploiting other techniques. In this work, the dynamic mechanical impact response and ASBs nucleation of heat
treated AZ31B Mg alloys at different strain rates and impact momentums are characterized in-situ during impact at room temperature using the Direct Impact Hopkinson Pressure Bar (DIHPB) coupled with an in-situ 3D Digital Image correlation (DIC) and high speed and high resolution thermal imaging techniques. DIC provides an independent measurement of surface strains directly on test specimen during deformation to monitor stain evolution and strain localizations. Both the microstructure of the initial un-deformed and post deformed specimen were characterized. It is found that the flow stress increased gradually to (~50 %) with increasing strain rates and impact momentums and the AZ31B Mg exhibits strain rate sensitivity at dynamic loadings. This is due to an increasing selective and intensive grain refinement evolving at grain boundaries (GBs) which increases strain hardening under dynamic compression. Strain to failure decreases at higher impact momentum. Evaluation of DIC results indicated that strain occurrence is linear at the onset of deformation but becomes heterogeneous at later stage of deformation with multiple nucleation sites of strain localization leading to ASB at ~80% of the specimen length after ~340 us of deformation. Region of peak nonlinearity of maximum strain concentration leads to ASB formation with characteristic fine grains, voids and crack initiation at grain boundaries observed at the extreme end of specimen using DIC with ~22 °C temperature rise observed with insitu high speed and high resolution thermal imaging camera. The temperature rise is however, lower with respect to the homologous temperature of Mg and hence higher degree of strain hardening behaviour is induced after deformation. Sub grains ~0.3μm sizes is found with disintegrated precipitate in voids at ASBs regions and mostly at GBs. In addition, deformation twinning frequency increases(~30 %) with broader thickness at higher impact momentum with disintegrated precipitates on micro-twins boundaries and GBs during plastic deformation at ASB surroundings. Meanwhile at lower impact momentum, freckled pattern selective grain refinement is observed. These results suggest that ASB forms in AZ31B Mg alloy despite its brittle nature that leads to crack initiation and ultimate failure under high strain rates and large strains of deformation and can be used to extend the understanding of the mechanism of failure in Mg alloys.

6:15 AM S.CT04.01.07
Quantitative Analysis of Twinning Occurring During Plastic Deformation of Cobalt Mayerling Martinez1,2, Eric Hug1, Peter Minárik2, František Chmelík2, Michal Knapek2 and Patrik Dobron2; 1CRISMAT/ENSICAEN/CNRS, France; 2Charles University, Czechia

Plasticity in most metallic materials depends essentially on dislocation glide. Metals, which display a wealth of gliding systems, are those having a face centered cubic lattice. On the other hand, metals with hexagonal close packed (hcp) structure, like Mg, or Ti, have a complex deformation behavior [1-2]. In these materials, both dislocation glide and twinning are fundamental mechanisms of plastic deformation. Another hcp metal, cobalt, with distinctly lower stacking fault energy, has been so far studied much less.

The straining mechanisms of cobalt, as shown by acoustic emission experiments and electron microscopy observations, is characterized by two principal stages: the first stage of work hardening is driven by planar glide of dislocations, while twinning is the most active deformation mechanism in the second stage [3].

Important insight into twinning has been recently provided by advanced electron microscopy techniques, such as scanning electron microscopy coupled with the electron backscatter diffraction technique, which is a powerful tool to capture the twinning process appearing in different stages of plastic straining [4].

In the present work, polycrystalline cobalt was monotonously strained in tensile test up to a plastic strain corresponding to the second stage of work hardening. The electron backscattered diffraction technique was used to acquire a large quantity of data, which allows for statistical analyses. The relationships between grain orientation, grain size, twin volume fraction, twinning modes, and twin variants have been established.

The results show that the principal twin mode is the \{10-12\} tension type and that multiple twin variants of this mode can be present inside the same grain. The occurrence of a specific twin variant in a grain is related to the local strain accommodation within this grain; consequently, the higher frequency of the occurrence corresponds to the variants with larger misorientations between them. The statistical analysis shows that the grain orientation has a more pronounced impact on twinning characteristics than the grain size. The Schmid Factor analysis adapted to twinning is used to give a general view of the cobalt behavior, taking into account the significance of grains oriented favorably for twin formation. This approach may also explain cases, in which grains are not favorably oriented, twinning is not expected, but it occurs in reality. The results will be compared with the behavior of other hcp metals.

polypropylene/halloysite nanotube (PP-HNT) hybrids. PP-HNT nanocomposites with pristine filler or PP-grafted filler were prepared by solid-state shear pulverization, leading to excellent dispersion in both cases. Optimal interactions with PP-grafted nanocomposite interfacial effects. In Example 1, modification of filler surfaces can improve dispersion and compatibilize the polymer-filler interface, leading to property enhancements relative to nanocomposites containing unmodified filler prepared from dispersion quality, revealing how the interactions affect the properties of one another in a correlated manner along the strain path. This process leads to shear localization in the form of shear bands. An analytical model is then proposed to relate the probability of the successive operation of discrete STZs, to their nucleation density. The model predicts that, as prior shear events triggers the emergence of new STZs, successive occurrence of discrete shear events speeds up rapidly to an asymptotic state which is exactly the condition of shear localization. Finally, the MD simulations also indicate that the first observable yield point cannot be due to the emergence and operation of one single STZ. Instead, yield or fracture is controlled by the average or extreme behavior of many STZs or shear bands operated in different locations in the wire, which explains length independence of the MG wire strength – a fact also observed in other glass wires.

6:45 AM *S.CT04.01.09
Maximizing Property Enhancements in Polymer Nanocomposites via Interfacial Effects—Examples Involving Polymer-Grafted Nanofiller and Optimal Matrix Molecular Weight John M. Torkelson; Northwestern University, United States

Nanocomposite property enhancements originate substantially from interfacial effects. We focus on two examples of nanocomposite interfacial effects. In Example 1, modification of filler surfaces can improve dispersion and compatibilize the polymer-filler interface, leading to property enhancements relative to nanocomposites containing unmodified filler prepared by conventional melt mixing or solvent blending. For the first time, we isolate the effect of interactions between matrix polymer and polymer-grafted nanoparticles from dispersion quality, revealing how the interactions affect the properties of polypropylene/halloysite nanotube (PP-HNT) hybrids. PP-HNT nanocomposites with pristine filler or PP-grafted filler were prepared by solid-state shear pulverization, leading to excellent dispersion in both cases. Optimal interactions with PP-grafted nanofiller leads to faster PP crystallization and higher yield strength; in contrast, Young’s modulus is determined by the filler dispersion and not filler modification. In Example 2, for the first time, we have decoupled chain dynamics in nanocomposite interfacial layers from chain dynamics of the matrix in poly(2-vinylpyridine) (P2VP)-silica nanocomposites. The interfacial $T_g$ (glass transition temperature) and the matrix $T_g$ (both associated with $\alpha$-relaxation dynamics) were determined by fluorescence. The interfacial layer $T_g$ is higher than the matrix $T_g$ due to H-bonding between P2VP and hydroxyl groups on the silica surface. At the same filler dispersion, 2.1 kg/mol P2VP matrix polymer leads to much greater $T_g$ enhancements in both the interfacial regions and the matrix relative to the use of 110 kg/mol P2VP. We hypothesize that low molecular weight P2VP preferentially aligns at the filler interface, leading to higher H-bonding density and increased $T_g$.

7:15 AM S.CT04.01.10
Computational Study of MOF-Polymer Interface Abhishek Sose, Samrendra Singh and Sanket A. Deshmukh; Virginia Tech, United States

Gas separations via selective transport in polymer membranes are dominating the membrane technologies due to their ease of processing and inexpensive production. However, these polymer membranes fall short of selectivity and permeability. Due to their exceptional structural features, metal organic frameworks (MOFs) have emerged as promising fillers to enhance the performance of a polymer membrane. In these MOF-polymer mixed matrix membranes (MMMs), the polymer-MOF interface is known to play an important role in determining the gas separation mechanism. However, understanding the structure of this MOF-polymer interface and the factors that govern their compatibility using existing experimental characterization methods is very challenging. In this research, we have performed all-atom molecular dynamics (MD) simulation of a model polymer-MOF MMMs with IRMOF-1 and 5 different polymers. Simulation trajectories were analyzed
to understand the effect of different functional groups and rigidity of polymers on the structure of the MOF-polymer interface. Results of this study can be useful for creating MMMs with IRMOF for separation applications.

7:30 AM *S.CT04.01.11
Design of Interphases for High Dielectric Performance in Polymer-Matrix Nanocomposites Evangelos Manias; The Pennsylvania State University, United States

Polyolefin (polyethylene, and ethylene-propylene-diene (EPDM) elastomers) composites were studied in order to elucidate and quantify the effects of the interfaces with ceramic and carbon nanofillers, and particularly of the interphase contributions on the dielectric properties of the composites. For ceramic nanoparticles, it was shown that the interphase contributions dominate the composites’ dielectric properties, often being antagonistic to the contributions of the ceramic fillers: Ceramic fillers with systematically varied dielectric nature –spanning orders of magnitude in dielectric constants– were studied, and the interphasial contributions effectively overwhelmed the ceramic filler permittivities and dominated the dielectric performance of the composites. For composites containing both ceramic and carbon-black nanofillers, proper design of the interphases is crucial, so as to capitalize on the high effective permittivity provided by the carbon while, at the same time, preventing mobile charges to undertake large lengthscale transport (conductivity) or high dissipation of energy in localized vibrations (dielectric loss); in these systems, a third nanofiller is introduced as a means to control conductivity and minimize losses and E-field breakdown.

8:00 AM *S.CT04.01.12
Hybrid Nanocomposites at the Extreme Limits of Molecular-Scale Confinement with Tailored Internal Interfaces Reinhold H. Dauskardt; Stanford University, United States

We review the state-of-the-art in the molecular design and processing of low density organic-inorganic nanocomposite hybrids at the extreme limits of molecular-scale confinement with tailored internal interface chemistry. We probe the mechanical and thermal properties of nanocomposite hybrids where a stiff inorganic matrix phase confines polymer chains to dimensions far smaller than their bulk radius of gyration. We describe a synthesis strategy which involves tailoring the internal interface chemistry between the matrix and the polymer phase. Tuning the interface allows access to extreme levers of molecular “hyper-confinement” where the confined polymer dynamics and resulting thermal behavior are markedly altered. We demonstrate the strategy with polystyrene and polyimide phases. The infiltration of individual polyimide precursors into a nanoscale porous network where imidization reactions under such confinement increase the molecular backbone stiffness. We find that polyimide oligomers can then undergo crosslinking reactions even in such molecular-scale confinement, increasing the molecular weight of the organic phase and toughening the nanocomposite through a confinement-induced energy dissipation mechanism. This work demonstrates that a confinement-induced molecular bridging mechanism can be extended to thermoset polymers with multifunctional properties, such as excellent thermo-oxidative stability and high service temperatures (> 350 °C).

8:30 AM S.CT04.01.14
Identification of the Vitrimer Transesterification Temperature (Tv): Implications for Nanocomposites Amber M. Hubbard, Yixin Ren, Shusil Bhusal, Gary Kedziora, Vikas Varshney, Ajit K. Roy and Dhriti Nepal; Air Force Research Laboratory, United States

Vitrimer materials have gained increasing attention since their introduction in 2011, due to their recyclable and dynamic nature. In addition to a traditional glass transition temperature (Tg), vitrimers have a second vitrimer transesterification temperature (Tv) above which dynamic covalent bonds allow for rapid stress relaxation, self-healing, and shape reprogramming. However, in order to take advantage of these unique properties, it is crucial to correctly identify the Tv and understand the impact of various experimental parameters (e.g., heating and applied force) upon its identification. Herein, we present a unique method to identify the Tv and discuss the impact of catalyst concentration upon the Tv. In addition, we present vitrimer nanocomposites with a variety of nanofillers (e.g., graphene and gold-coated graphene nanoplatelets) and identify the impact of nanofiller addition upon the composite Tv. By embedding graphene nanofillers into the vitrimer matrix, the resulting composite demonstrates increased mechanical properties as well as a photothermal response when exposed to near-infrared (NIR) light. These photothermally activated composites exhibit shape memory and shape reconfigurability for actuators and self-healing behaviors.

8:45 AM S.CT04.01.15
Nano Materials Hybridization and Its Interfaces for Simulteneous Multifunctionality Ajit K. Roy; Air Force Research Laboratory, United States
For optimal materials usage in numerous defense applications, as well as in aerospace systems, materials are to operate in episodes requiring simultaneous multifunctionality. For example, electronics in munitions and high temperature sensor modules are expected to retain its expected electrical, thermal, and mechanical properties or attributes even in extremely high strain gradient operation. Similarly, in hypersonics coatings, high temperature material oxidation stability plus tailored thermal conductivity are needed in extreme high temperature operation. In this presentation, materials design approaches for simultaneous exhibit of selected multifunctionality will be discussed. Further, such desired multifunctionality is expected to be more optimally feasible by taking the materials design to small scale (say, at atomic level) and then linking that to bulk materials performance. Also, materials hybridization at small (atomic or molecular) scale and optimizing the associated heterostructure phases significantly opens up materials performance domain and its multifunctionality. Examples of several computational tools (atomistic, Mesa, continuum scale - ab initation, NEGF, MD, MD Wave Packets, Tight Binding MD, Molecular Mechanics) will be illustrated for tailoring materials functionalities (thermal, electrical, structural) in the material compositional design, along with a few design cases (thermal interface, nano porous carbon, strain-resilient electronics).

SESSION S.CT04.02: Biomimetic and Bioinspired Interfaces and Interphases
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-CT04

5:00 AM *S.CT04.02.01
Interfacial Behavior and Self-Organization of Nano-Inclusions in Vesicles Meenakshi Dutt; Rutgers, The State University of New Jersey, United States

The distribution of nano-inclusions at the interface or within soft films is determined by multiple key factors. These factors include the molecular composition, interfacial profile, morphology of the films and the characteristics of the inclusions along with predominant interactions in the systems. We will discuss the role of these factors on the interfacial behavior of nano-inclusions on the surface of spherical soft films, or vesicles. Furthermore, we will discuss the organization of the inclusions in vesicles as a function of nano-inclusion effective chemistry, dimension and concentration. These investigations have been contingent upon the ability to resolve large spatiotemporal scales. Hence, the studies have required the adoption of coarse-grained models used in conjunction with mesoscale simulation methods such as Dissipative Particle Dynamics and Molecular Dynamics. Our observations have the potential to guide the design of composite materials which require precise control on their characteristics including their shape or the dispersion of the inclusions.

5:30 AM *S.CT04.02.02
Interfacial Dynamics of Nanoconfined Molecules and Macromolecules Younjin Min; University of California, Riverside, United States

The properties of fluids, when confined at nanometer scales, differ greatly from their bulk properties and are generally dominated by interfacial effects. In this interfacial region, the nature of the wall–fluid intermolecular interactions can have a significant effect on the fluids, introducing symmetry breaking, structural frustration and confinement-induced entropy loss into nanoscale interactions under confinement. In this presentation, several examples regarding how different degrees of nanoconfiment alter the structural organization and interfacial properties of soft matter ranging from non-biological (e.g. ionic liquids and silica colloidal suspensions) to biological ones (e.g. biopolymer solutions) will be introduced. This talk will particularly focus on describing the mechanisms of how biomacromolecules such as silk fibroin (SF) proteins self-assemble into hierarchical structures at the multiple-length levels in greater details. The presentation will conclude with some perspectives on new fundamental insights for rational design of SF-based materials with desired interfacial features in use of their fabricating superior functional materials and devices.

6:00 AM *S.CT04.02.03
Chemical and Topological Design of Bioinspired Polymer Adhesives—Interfacial Molecular Mechanics and Applications Yiran Li1,2, Peyman Delparastan1, Cody Higginson1, Katerina Malollari1, Jing Cheng1, Haoqi Wang2, Brylee Tiu1, Kyueui Lee1, Yi Cao3 and Phillip B. Messersmith1,3; 1University of California, Berkeley, United States; 2Nanjing University, China; 3Lawrence Berkeley National Laboratory, United States
In mussels, the adhesive proteins that are instrumental for attachment to wet surfaces are known to contain high levels of 3,4-dihydroxy-L-alanine (DOPA), often located adjacent to amino residues such as lysine (Lys). The special synergistic relationship between catechols and amines is a subject of high interest, not only for understanding native proteins but also for informing the design of bioinspired polymer systems. Other research groups have shown that catechol and amine functional groups act synergistically to enhance adhesion at wet surfaces, however reports of catechol-amine interfacial phenomena on a single molecule level have been limited. In this talk we will describe single molecule force spectroscopy (SMFS) measurements that are providing new insights into interactions between Lys-DOPA peptides and various surfaces. Molecular mechanics investigations of catechol and catecholamine polymers are providing new insights into design of novel polymer adhesives, for example pressure sensitive adhesives and high-strength thermoset adhesives.

6:30 AM *S.CT04.02.04
Biomimetic Nanocomposites for Energy Technologies and Meta Optics Nicholas A. Kotov; University of Michigan, United States

Materials with difficult-to-attain combination of multiple properties - mechanical, electrical, chemical, optical, thermal, and transport, – represent the quintessential bottleneck for nearly all modern technologies. Nanocomposites with molecular, nano-, meso-, and microscale levels of structural engineering can provide such property combinations, while intrinsic ability of nanoscale components to self-assemble make them suitable for simplicity of synthesis. Biomimetic nanocomposites exemplified by a variety of nanostructured nacre-like materials provide a generalized approach to engineer materials with multiple difficult-to-attain properties. As the continuation of this research, we learn that the unique mechanics of tooth enamel can be replicated combining out-of-plane nanoscale columns with molecular precision of layer-by-layer (LBL) assembly between them. As a result of that, these composites reveal remarkably high vibrational damping unusual for stiff materials that imparts them resilience to aging. The novel type of biomimetic nanocomposites are those based on aramid nanofibers (ANFs). They spontaneously assemble into three-dimensional percolating networks reminiscent of cartilage. The nanoscale structure of ANF composites reveal nanoscale porosity that can be controlled by nanofiber branching. The latest results from multiple groups demonstrate that ANF composites resolve some of the essential property bottlenecks for ion-selective membranes, dendrite-resistant electrolytes, and structural batteries. One of the emerging fields for biomimetic nanocomposites are optical devices. The high strain and strong polarization rotation make possible metaoptical devices with wide-angle diffraction gratings for LIDARs and highly efficient quarter wave plates for THz scanners. Both devices can be used for machine vision and biomaterials imaging.

7:00 AM *S.CT04.02.05
Colour with a Twist—Cellulose Photonic Materials with Tailored Visual Appearance Silvia Vignolini; University of Cambridge, United Kingdom

Plant-based polysaccharides such as cellulose and its derivatives are receiving increasing interest in a large variety of applications because they represent an environmentally friendly alternative to plastic. Many of them are commonly used in diverse industrial applications, such as food additives and for biomedical devices due to their non-toxic and water-soluble nature. Moreover, the self-assembly nature and responsiveness of cellulose bio-polymers makes them also extremely attractive for smart photonic applications including sensing. Among various types of cellulose and its derivatives, hydroxypropyl cellulose (HPC) encompasses all these desirable properties. Hydroxypropyl cellulose is a liquid crystal polymer, which can form a cholesteric liquid-crystalline phase allowing Bragg-like reflection. The reflected colours can be simply controlled by changing the nature of the solvent, concentration, temperature. Recently, we demonstrated for the first time that a simple aqueous solution of HPC can be used as a photonic strain sensor that displays the applied strain by shifting its colour. In this seminar, I will introduce how such properties can be enhanced to create a solid-state film with desired optical appearance.
Optical Devices From Covalent Functionalized, Redox-Exfoliated, Layered Transition Metal Dichalcogenides

Ali Jawaid, Peter Stevenson, Luke Baldwin, Ruth Pachter and Richard A. Vaia; Air Force Research Laboratory, United States

Exfoliated Transition Metal Dichalcogenides (TMDs, MX₂) have attracted considerable attention for infrared optical elements due to their high refractive index and extreme nonlinearities (e.g. MoS₂, TiS₂). Recent high-yield, sonication-free, surfactant-free, exfoliation methods (i.e. Redox Exfoliation) now provide access to oxidatively-resistant and colloidally-stable dispersions at high TMD content (10% v/v), and in an expanded range of polar solvents (e.g. acetonitrile, acetone, alcohols). In addition to transforming approaches to nanocomposite fabrication, ink formulation, and film processing, these characteristics enable direct organic hybridization of Group IV-VI TMDs. For example, Grignards (R-MgBr) are not accessible via traditional Liquid Phase or Li-Intercalation methods due to their extreme reactivity with labile hydrogens (water), amides (NMP), and oxygen. However, the availability of Group VI TMDs dispersions in anhydrous THF enables synthesis of alkyl grafted MoX₂, which has zero surface charge, is dispersible in chloroform, and affords subsequent surface-initiated polymerization, all while retaining optoelectronic monolayer properties. In addition, classic redox intercalation chemistries can be applied to Group V monolayer dispersions. For example, a primary alkyl amine reacts at 70°C in anhydrous acetonitrile with semi-metallic, single layer NbS₂ via charge transfer from the amine to the half-filled Nb d-orbitals. The resultant organic-grafted NbS₂ is a semiconductor, with enhanced oxidative stability (> 7 days ambient) and dispersibility in non-polar dichloromethane that allows for ambient handling and processing. Such access to numerous hybridization approaches will greatly expand the electrical, optical, and chemical property suite of TMDs and enhance the ability to fabricate device quality films and hetero-structures for optical filters, GRIN optics, and non-linear absorbers.

Molecular Dynamics Simulations Integrated Machine-Learning Study of Bottlebrush Polymers of Different Shapes

Soumil Joshi, Samrendra Singh and Sanket A. Deshmukh; Virginia Tech, United States

Thermosensitive bottlebrush polymers (BBPs) are a type of graft copolymers in which thermosensitive polymer side-chains are grafted on a linear polymer backbone. These side-chains can undergo a coil-to-globule conformational change in response to a change in the surrounding temperature. This also results in a change in the overall shape of the BBPs because of which they can be used for biomedical applications. Here, we will present the results of our recent coarse-grained (CG) molecular dynamics (MD) simulations study of poly(N-isopropylacrylamide) (PNIPAM; transition temperature= 305 K) BBPs of Worm-like, Cone-like, Dumbbell-like shapes. The CG MD simulations were performed at 300 K (below transition temperature) and 320 K (above transition temperature). The analysis of simulation trajectories showed that the shape of BBPs has significant impact on the conformations of individual side-chains.

Organic-Inorganic Interfaces—Insight from First Principles Calculations

Ruth Pachter; Air Force Research Laboratory, United States

Elucidating the role of organic ligands that are attached to or incorporated within inorganic nanostructures, for example, at the interface of colloidal nanocrystals or as included in the inorganic framework of two-dimensional hybrid organic-inorganic perovskites, is essential in realizing desired functional properties for applications. However, although general guidelines are provided by experimental explorations, an understanding of the underlying mechanisms for efficient materials development is often lacking. Herein, by employing first principles calculations for the design of materials that exhibit optical tunability characteristics, we first discuss atomically precise quantum dots. We highlight challenges in modeling the structure of semiconductor nanoclusters with organic ligands. In this context, we report on the derivation of a potential energy surface using machine learning that overcomes, in part, some of these limitations, and on the importance of the level of theory applied for accurate prediction of the optical response. In addition, we discuss effects of incorporating large chromophores as the ammonium cation in 2D hybrid organic-inorganic perovskites, which have proven promising for optoelectronic applications. Dependent on the organic moiety type, band alignments indicate variability in quantum-well types for a range of materials we examined, as well as structural distortion. Absorption spectra demonstrate tunability in the optical properties, including enhanced absorption and red-shifts, providing recommendation for the choice of the organic cation and motivation for further synthesis and experimental characterization.

Enhanced Multifunctional Nanocomposites with Two-Dimensional Transition Metal Carbides/Nitrides
MXenes

Christine B. Hatter and Yury Gogotsi; Drexel University, United States

Composites offer a wide variety of uses in aerospace, automotive industry, additive manufacturing, and energy storage applications. Discovered in 2011, MXenes have emerged as a new class of two dimensional (2D) materials consisting of transition metal carbides and nitrides. Synthesized MXenes have rich chemistry and 2D morphology offering a combination of high metallic conductivity and hydrophilicity for easy solution processing. Additionally, MXenes have been shown to have excellent mechanical properties with Young’s modulus of 330 GPa, surpassing both GO and rGO making it one of the strongest solution-processable 2D materials. Thus, they can improve mechanical and thermal stability as well as electrical conductivity of polymers. They can also reinforce ceramics and metals.

The most commonly studied MXene, titanium carbide (Ti3C2), has been combined with various polymer systems producing new multifunctional nanocomposites. When introduced into thermoplastics like PVA, improved mechanical properties were observed at 10 wt% polymer loading with a 34% increase in tensile strength compared to pure Ti3C2 films. Additional studies have shown electrical properties can be successfully transferred to the polymer composite extending its use to electrodes in energy storage systems as well as electromagnetic interference shielding for future electronics. In addition to simple direct mixing with polymers, Ti3C2 MXene has also been incorporated into more complex polymer fibers for integration into textile applications. A recent study on electrospinning of MXene-PAN nanofibers showed MXene content could be increased up to 35 wt% and retain high areal capacitance three times that of pure PAN nanofibers. This presentation will provide an overview of the current MXene-reinforced composites field, including ceramic- and metal-matrix, and the various applications.

SESSION S.CT04.04: Next Generation Structural Composite—Nature Inspiration and Challenges

On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

5:00 AM ANISUR RAHMAN, OFFICE OF NAVAL RESEARCH

5:15 AM EVA CAMPO, NATIONAL SCIENCE FOUNDATION

5:30 AM CHRISTOPHER L. SOLES, NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY

5:45 AM S.CT04.04.04

Outlook of Air Force Composite Materials Research Ming-Jen Pan; Air Force Office of Scientific Research, United States

Composite materials are increasingly replacing metals as the top choice for airframe structures because the advantages they offer, including light weight, high strength, high fatigue resistance, flexibility in manufacturing, and fuel efficiency. For Air Force platforms, composites offer the opportunities in enhanced thermal management, electromagnetic absorption, integrated sensing, and other capabilities not achievable in conventional monolithic components. Among the routes to achieving game-changing improvements in composite materials, the Low Density Materials program currently emphasizes: 1) materials discovery to increase the temperature capabilities of matrix resin, fiber sizing, reinforcing fibers; 2) mechanisms and thermodynamics of polymer-to-ceramic conversion for tailored nanoscale heterostructures; 3) understanding of interfacial phenomenon at the molecular level in heterogeneous systems; 4) concepts and processing methods for integrated multifunctionality; and 5) multiscale modeling and experimental validation of composite behavior. The details will be reviewed at the panel discussion.

6:00 AM INTRODUCTION AND PANEL DISCUSSION

7:30 AM S.CT04.04.06

Exploring Structure, Defects and Behavior of Nanotube Assemblies by Multiscale Modeling Boris I. Yakobson; Rice University, United States

Hetero- or homo-interfaces formed by carbon nanostructures of different C hybridizations are ubiquitous in electronic,
structural, and energy-functional materials. Understanding how weak interactions and/or chemical bonding at the interface lead to a meso- and macroscopic behavior warrants a multiscale modeling framework. This will be illustrated with the example of carbon nanotube (CNT) fibers. Starting from the energetics and kinetics of various crosslinks (~nm, ~fs) accessible from accurate DFT calculations, we derive scaling relations of their tensile mechanical response from a μm-long coarse-grained model of a CNT bundle. These inter-tube crosslinks can be expected to behave as “hook-and-loop” fasteners, operational in Velcro, which can have the ability to break and reform and thus resist relative motion in a continuous manner. Such a model can incorporate the effect of interface friction due to inter-tube crosslinks or tube-polymer matrix connects, quantitatively evaluate toughness and fatigue processes and look for ways of performance improvement. Same coarse-grained model allows us to also explore the fundamental problem of basic packing defects in the aligned CNT bundles: the ‘twists’ and ‘inclusions’. We show how a finite characteristic size/length $L$ of such defects emerge as a result of interplay between their intrinsic bending stiffness and the elastic response of the surrounding CNT matrix-crystal, and quantify their energetics scaling. In conjunction with synthesis efforts and novel experimentation, such models are crucial in developing novel carbon nanomaterials.

8:00 AM *S.CT04.04.07
Molecular Dynamics Modeling of Flattened CNT/Polymer Interfaces Matthew Radue$^1$, William Pisani$^1$, Sagar Patil$^1$, Prathamesh Deshpande$^1$, Prashik Gaikwad$^1$, Swapnil Bamane$^1$, Susanta Ghosh$^1$, Traian Dumitrica$^2$ and Gregory Odegard$^1$; 1Michigan Technological Univ, United States; 2University of Minnesota Twin Cities, United States

Current state-of-the-art carbon fiber reinforced composite materials have become a standard structural material used in the aircraft industry. Their relatively high strength-to-density and stiffness-to-density ratios make them useful for reducing vehicle mass and thus improving fuel efficiency. However, for manned space exploration beyond the moon (deep space), further decreases in mass are needed for fuel efficiency. Thus, increases in the strength-to-density and stiffness-to-density ratios are necessary.

Carbon nanotube (CNT)-reinforced composites can potentially provide the needed reductions in composite laminate mass. Relative to carbon fiber, CNTs can have higher strength and modulus, and can potentially provide a larger surface area for polymer interaction and load transfer. Further, flattened CNTs (flCNTs) can form self-assembled arrays with a higher packing than round CNTs [1]. Although countless studies have examined CNT/polymer interaction on the molecular level [2], little effort has been devoted to understanding flCNT/polymer interaction.

The objective of this research is to use molecular dynamics (MD) simulation to explore the interaction and load transfer characteristics for a range of different polymer resins with flCNTs. Specifically, the interfacial interaction energy, pull-out frictional force, pull-apart force, and resin wetting contact angles have been predicted. These predictions have been performed for two polyimide systems, two cyanate ester systems, polyurea, and PEEK. The results of these studies will be presented, and the best polymer candidates for these flCNT/polymer composites will be discussed.

References
**Luminescence Properties** Zhiqun Lin; Georgia Institute of Technology, United States

Polymer-ligated nanoparticles (NPs) exhibit an exciting variety of physical properties that depend sensitively on the dimension and composition of NPs as well as the surface chemistry of tethered polymer hairs. Herein, we report on a robust nanoreactor strategy for **in-situ** crafting of monodisperse stable polymer-ligated NPs with well-controlled size and shape as well as tunable plasmonic (e.g., Au) and luminescence (e.g., perovskite MAPbBr$_3$ and CsPbBr$_3$) properties. Central to this strategy is to judiciously design unimolecular amphiphilic star-like block copolymer as nanoreactor for yielding NPs **intimately and permanently** ligated by polymer hairs. The diameter of polymer-ligated NPs can be precisely tuned by modulating the length of inner hydrophilic block of star-like block copolymers. In the case of Au NPs, the **perpetual** anchoring of photoresponsive or thermoresponsive polymers on the surface renders the attractive feature of self-assembly and disassembly of NPs on demand by capitalizing on light of different wavelengths or heating/cooling, respectively. Such self-assembly/disassembly process is revealed by tunable surface-plasmon resonance absorption of Au NPs and the reversible transformation of Au NPs between their dispersed and aggregated states. For perovskite NPs, the resulting polymer-ligated MAPbBr$_3$/SiO$_2$ core/shell NPs and CsPbBr$_3$ plain NPs display concurrently a stellar set of significantly improved stabilities (i.e., colloidal stability, chemical composition stability, photostability, water stability), while possessing appealing solution processability, which are unattainable by conventional methods. We envision that the amphiphilic star-like block copolymer nanoreactor strategy may provide a versatile platform for crafting diverse organic-inorganic nanohybrids stably-ligated with polymer of different functionalities (e.g., semiconducting, ferroelectric, photo-responsive, thermal-responsive, or pH-sensitive) for a spectrum of applications in bioimaging, biosensors, photonic materials and devices, perovskite-based LEDs, lasers, high-energy ionization radiation detections, multiphoton emission, and scintillators.

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5:30 AM *S.CT04.05.02
**Understanding Self-Assembly of Functional Nanostructures with Actuation Capabilities** George C. Schatz; Northwestern University, United States

Molecular self-assembly involves the use of hydrogen bonds and other noncovalent interactions between molecules to create supramolecular structures. A goal of theory is to be able to predict and understand what structures will arise for any given set of conditions, and how the self-assembly can be directed so as to produce useful functional structures. In this talk I will describe recent studies in my group in collaboration with the Stupp and Mirkin groups at Northwestern, and with others, with the goal of making nanostructured materials with broad applications including actuation with various stimuli.

One area of interest concerns studies of peptide amphiphile self-assembly to produce cylindrical micelles and ultimately fiber materials that can be used for applications in biomedicine and for making materials that can be photoactivated for robotic functions. Here we have developed all-atom and coarse-grained models, and specialized molecular dynamics methods, that are capable of describing assembly into fibers, leading to an understanding of biological functions and photoactuation.

In a second direction we are interested in the coupling of self-assembly chemistry involving DNA attached silver and gold nanoparticles to create a new generation of bottom-up nanomaterials of interest for sensing and optical devices. Here we show both coarse-grained and all-atom approaches to the assembly, and how these can be used to understand the formation of plasmonic array structures, including recent studies aimed at understanding programmability of dynamic optical properties.

6:00 AM *S.CT04.05.03
**Molecular Simulation and Theory Studies Linking Design of Polymer Grafted Nanoparticles to the Polymer Nanocomposite Morphology** Arthi Jayaraman; University of Delaware, United States

In this talk I will present our recent work studying polymer nanocomposites (PNCs) using molecular dynamics (MD) simulations and Polymer Reference Interaction Site Model (PRISM) theory calculations with coarse-grained (CG) models. Specifically, we are interested in linking molecular design of PNCs comprised of grafted nanoparticles in a polymer matrix to their morphology. In this talk I will focus our work on the impact of strength of graft-matrix attraction on interpenetration of matrix and graft chains (known as grafted layer wetting) and dispersion/aggregation of grafted particles in matrix. Previously for PNCs with attractive graft-matrix interactions, we had shown that wetting/dewetting and dispersion/aggregation are two distinct phase transitions, the former being a continuous transition and the latter being a first-order transition as a function of
graft-matrix interaction or temperature. Recently, we found that as the strength of graft-matrix attraction increases, we can also tune the effective size and the hardness of the polymer grafted particle in the PNC. As the attraction between the graft and matrix chains increases, the graft polymer chains extend to make favorable graft-matrix contacts and increase the grafted layer wetting by matrix chains. This leads to larger and ‘harder’ grafted particles compared to analogous fillers with purely entropic (athermal) graft-matrix interactions. Due to the increasing size and hardness of grafted particles with increasing graft-matrix attraction, the PNC structure changes from an aggregated-dispersed morphology governed by entropic driving forces at athermal graft-matrix interaction to a dispersed morphology due to favorable weak graft-matrix attraction, and ultimately, to a correlated fluid of hard grafted particles at stronger graft-matrix attraction. We see these trends in PNCs with high (densely grafted) and low grafting density, and with equal graft and matrix chain lengths as well as cases where the matrix chain lengths are greater than the graft chain lengths.

6:30 AM *S.CT04.05.05
Advances in Using Surface-Initiated Atom Transfer Radical Polymerization and Its Application to Tailoring Particle Interactions and the Design of Functional Materials Michael R. Bockstaller; Carnegie Mellon Univ, United States

Surface Initiated Atom Transfer Radical Polymerization (SI-ATRP) in its various modifications has emerged as a versatile toolbox to control and tailor the properties and interactions of interfaces and to enable the synthesis of hybrid materials with unprecedented property combinations. The resulting materials have attracted interest not only because the high-level structural control of the architecture of polymer-tethered surfaces enables tailoring of the interactions, microstructure and properties of particulate-based materials but also because the confinement of chains on surfaces alters the mechanism of termination reactions that limit conventional polymerization processes. This presentation will review recent examples of the application of SI-ATRP for the synthesis of functional polymer materials. Examples to be covered include the synthesis of ultra-high molecular weight polymers, materials for optical applications as well as thermal interface materials. Recent examples of the interplay between phononic and photonic properties in brush particle-based materials will be shown to illustrate how the subtle control of polymer chains at interfaces can instigate novel physical properties in hybrid materials that cannot be realized in ‘classical’ composite materials that are fabricated by mixing of particle and polymer constituents. This will provide the basis for a discussion of ‘guidelines’ for the fabrication of novel functional materials that harness ‘chemical confinement’ of polymer chains.

7:00 AM S.CT04.05.06

MXenes represent an emerging class of two-dimensional layered transition metal carbides and nitrides with intriguing properties, which have attracted significant attention as a promising material for next-generation functional composites. Control of size (lateral and thickness), layered spacing, and surface chemistry enables tuning of optoelectronic properties and improvement of processibility. To this end, we present fundamental studies aimed at understanding the role of surface terminations and functional groups on the electronic, chemical, and structural properties of MXene flakes. Ultra-thin nanosheets of MXenes are surface modified with catechol [dopamine, pyrocatechol, and tetrachlorocatechol (TCC)] chemistries. UV-Vis spectroscopy shows oxidation of catechol to quinone, confirming the formation of a charge transfer complex with the MXene layer. The reaction kinetics and subsequent colloidal stability are different each catechols, reflecting the different terminal groups (NH2 vs. Cl). FT-IR, XPS, Raman, and AFM-IR support surface binding; XRD reveals changes in layer spacing, further confirming surface modification. These experimental studies are corroborated by theoretical calculations of the electronic properties of both the native and functionalized MXene surfaces. Finally, these functionalized thin flakes exhibit significantly improved thermo-oxidative stability and dispersibility in non-aqueous solvents. Overall, such approaches to surface termination opens up new avenues for synthesis of hybrid functional architectures based on MXenes.

7:15 AM S.CT04.05.07
Spatiotemporal Deformation and Microstructural Evolution Mechanisms During High-Speed Shear Deformation of Metallic Alloys Arun Devaraj1, Tingkun Liu1, Changyong Park2, Bharat Gwalani1, Mathew Olszta1, Tiffany Kaspar1, Yang He1, Jinhui Tao1, Tamas Varga2, Chongmin N. Wang1, Aashish Rohatgi1, Peter V. Sushko1, Suveen Mathaudhu1 and Cynthia Powell1; 1Pacific Northwest National Laboratory, United States; 2Argonne National Laboratory, United States; 3Environment Molecular Science, United States
In order to develop shear-based solid phase processing methods for achieving bulk nanostructured metallic alloys, we aim to better understand the fundamental atomic scale mechanisms of local and global deformation mechanisms and microstructural evolution in polycrystalline materials under shear deformation. To achieve this aim, we employed synchrotron-based in situ and ex situ high-energy x-ray diffraction capabilities under high pressure and shear deformation, using a newly designed high-speed rotational diamond anvil cell. The obtained synchrotron-based XRD results were also correlated with detailed microstructural characterization before and after shear deformation using transmission electron microscopy and atom probe tomography. Atomic scale computational modeling using density functional theory and molecular dynamics was additionally complemented with experimental results to obtain mechanistic insights. Our results on shear induced structural and chemical modifications of several model metallic alloys such as Al-Si, Cu-Nb and Cu-Ni provide new insights on the unique role of shear deformation in formation of metastable states, as well as in modifying the phase transformation pathways of these alloy systems.

SESSION S.CT04.06: Carbon Nanotube and Related Materials Interphases

On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

S-CT04

5:00 AM S.CT04.06.02
Ordering at the BNNT/Water Interface Using Cryo-EM Techniques Hsin-Yun Chao1,2, Alline Myers2, Dmitri Golberg3, Renu Sharma2 and John Cumings1; 1University of Maryland, United States; 2National Institute of Standards and Technology, United States; 3Queensland University of Technology, Australia

Nanotubes used as nanochannels for fluid transport have been of increasing interest. It has been observed that carbon nanotubes (CNT) have uniformly higher permeability compared to other nanochannels, such as polycarbonate membranes, albeit CNTs can achieve smaller diameters [1]. Previous theories attribute the high permeability to nanotube atomic smoothness [2]. However, recent molecular dynamics simulations show that the structure of water at higher densities can align to that of CNTs of small diameter [3]. Furthermore, there are conflicting analyses as to whether the fluid flux is higher for CNT or boron nitride nanotubes (BNNT) [4]–[6]. Therefore, we want to better understand the structural ordering at the atomic scale of nanotube-water interfaces using empirical methods. Here, we use cryogenic electron microscopy (Cryo-EM) techniques to hyperquench water with BNNT into a vitrified state and observe the BNNT/water interface using a transmission electron microscope (TEM) at 80keV. A cryo-transfer holder capable of maintaining the sample at 90-125K facilitates the sample transfer into the TEM. Raman spectroscopy performed in-situ during TEM imaging will enable direct observation of beam-induced phase transformations. We will present results relevant to the preferential ordering of water at the interface with BNNT.

References

5:15 AM S.CT04.06.04
Covalent Sizing of Carbon Fibres—A Route to Optimising Interfacial Phenomena in Composites Luke Henderson, Daniel J. Eyckens, Filip Stojcevski and James D. Randall; Deakin University, Australia

Continuing on our work in the surface modification of carbon fibres, we investigated the validity of tethering polymers to a
carbon fibre surface. Evaluation of both ‘Graft To’ and ‘Graft From’ approaches were undertaken and how these modifications affected performance/the-innate physical properties of the underlying material was determined. During our ‘Graft From’ study, we found that the use of an in situ polymerisation protocol resulted in the generation of carbon fibres with an electric blue colour. The source of colour is proposed to be thin-film interference, similar to that observed in the Morpho butterfly. Swelling the polymer with a solvent resulted in a cascade of colours through the visible spectrum during evaporation and polymer shrinkage. In addition to this, the tensile strength of the fibre increased (13-30%), the interfacial shear strength increases in epoxy polymers (180-320%), and an unusual ability to reversibly form and reshape the fibre was also found.


5:30 AM S.CT04.06.05
Understanding CNT/Polymer Interphase Assembly and Mechanical Strength Using Simulation and Machine Learning Hendrik Heinz; University of Colorado Boulder, United States

Debundling and dispersion of carbon nanotubes (CNTs) in polymer solutions play a major role in the preparation of carbon nanofibers due to early effects on interfacial ordering and mechanical properties. First, we analyzed the propensity to achieve homogeneous dispersions of CNTs in polyacrylonitrile (PAN) and poly(methyl methacrylate) (PMMA) precursor solutions in the solvents DMSO, DMAc, and DMF. Molecular dynamics simulations at 25 and 75 °C with accurate interatomic potentials for graphitic materials that include virtual π electrons show tendencies for PMMA wrapping while PAN exhibits significant interactions only as the concentration is increased or solvent evaporated. Computed conformations, solubility, and temperature dependences correlate well with experimental data from spectroscopy, light scattering, and viscosity measurements.

Subsequent heating and drawing of the precursor gels results in PAN/CNT composites. MD simulations reveal the structure at the atomic scale and relationships to mechanical and thermal properties for different degrees of polymer crystallinity and CNT diameter. Glass transition temperatures correlate with the amount of CNT/polymer interfacial area per unit volume and were predictable with +/-5 K accuracy relative to experiments. Tg increases for higher CNT volume fraction and inversely with CNT diameter. An important aspect is the knowledge of CNT bundle size from experiment, which affects the effective surface area. Computed interfacial shear strengths increase when PAN has at least some degree of crystallinity (at least 50% crystalline).

Third, testing of mechanical properties up to failure has been performed for a wide range of over 500 CNT and defective CNT morphologies to explore the role of structural defects and new information from machine learning models. Hereby, we utilize a new force field, IFF-R, that enables bond breaking in high accuracy and computational speed. Suitable feature representations and processing of the data through reinforcement learning and Bayesian uncertainty quantification will be discussed, and the resulting correlations between structure, Young’s modulus, and tensile strength.

Ongoing questions include the application of supervised learning approaches to polymer composites that have more degrees of freedom and to experimental data from tomography and X-ray diffraction that will become available in large quantities. Progress and opportunities will be discussed.

6:00 AM BREAK

6:45 AM S.CT04.06.08
Characterization of Electroless Copper Deposits on Electrospun PAN Fibers in Aligned and Random Configurations Temitope O. Aminu1, Molly Brockway2, Jack L. Skinner2 and David F. Bahr1; 1Purdue University, United States; 2Montana Tech, United States

The functionalization of electrospun polymer fibers has created potentially radical materials for sensing, tissue scaffolds, flexible electronics and filtration. Fundamentally, the composite material design is enabled by electroless deposition, wherein
conformal coatings (either as complete films or individual nanoparticles of copper) can be achieved on the default random configurations of electrospun fibers through solution-based precipitation reactions. Advantageously, fiber alignment can also be achieved through design modifications in the electrospinning process. We have electrolessly deposited copper on random and aligned PAN fibers utilizing silver nanoparticles as catalytic seeds. Fiber sizes range from diameters of hundreds of nanometers to a few microns. Prior work has established that coating conformity is strongly modulated by density of catalytic seeds: metallic films are obtained with a high density of silver seeds (48 particles/μm²), and discrete particles are observed for low density seeding (15 particles/μm²). X-ray crystallography has been used for phase identification and crystallite size measurements of both the seeds and subsequent copper coatings. We investigate the changes in the chemistry of the fibers due to the exposure to the electroless plating solutions using Raman spectroscopy, focusing on effects of fiber dimensions on surface chemistry and amenability to nucleation events. In addition, tensile tests are carried out on the metallized aligned fibers at distinct strain levels to investigate possible delamination events. Previous strain-to-failure tests on conformally coated, randomly aligned fibers mats showed good adhesion of the copper particles on the fibers. In parallel, we examine the mechanical behavior of the metallized fibers under an equi-biaxial stress state utilizing a novel “leaky” bulge testing system. We demonstrate the links between the mechanics of coated fiber mats in aligned and random configurations to identify the impact of plating on the stiffness of the resulting structure, a critical parameter for use in filtration applications where fluid pressure can alter the achievable minimum pore size.

7:00 AM S.CT04.06.09

Multifunctional Polyurethane Composite Sheets Incorporating Nanotubes at High Loading—Mechanical and Morphological Characterization Yadienka Martinez-Rubi, Behnam Ashrafi, Michael Jakubinek, Shan Zou, Keun Su Kim, Zygmunt Jakubek, Stephane Denommee and Benoit Simard; National Research Council Canada, Canada

Light-weight one-dimensional nanomaterials such as carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs) possess impressive physical, chemical and mechanical properties and are promising reinforcement agents for the development of enhanced multifunctional composite materials. Although BNNTs and CNTs share similar mechanical properties and thermal conductivity they can impart a different set of functionalities in composite material. CNTs are electrically conductive and are usually employed to improve the electrical conductivity of a matrix. On the other hand, BNNTs show transparency in the visible region and are electrically insulating. Thus, BNNTs are very promising nano-fillers for insulating polymer composites. Additionally, BNNTs have higher resistance to oxidation and the ability to shield neutron radiation. High nanotube (NT) contents are often necessary in order to achieve thermal or electrical conductivities requirements for a particular application. However, the incorporation of well dispersed nanotubes into polymer composites can be challenging, especially at high loadings due to re-agglomeration of the nano-filler and a significant increase in viscosity. Here we show the fabrication of CNT-polyurethane (TPU) and BNNT-TPU composite sheets of variable composition using a scalable one-step filtration process. Using this fabrication method the composition of the nanocomposites, which defines the characteristics and properties of the material, can be precisely controlled. Consequently, materials with tailorable properties (e.g. porosity, stiffness, strength and toughness), shapes and functionalities can be fabricated. The trend in mechanical and electrical properties was understood in terms of the NT-TPU interfacial interactions and morphological changes occurring in the nanocomposite sheets as a function of increasing the TPU content. At specific NT-TPU weight ratios (e.g. 35:65 weight ratio for CNT-TPU composites) a better NT exfoliation and optimal NT surface coverage was achieved, which in turn led to an optimal packing of NT–TPU fibers. This optimal packing produced the highest improvement in tensile properties and electrical conductivity in CNT-TPU sheets. Due to their straightforward production and handling, high nanotube content, and superior properties in comparison to dispersed nanotube composites, the resulting conductive, lightweight sheets are of interest for various applications including improved damage tolerance, fire retardancy and electrical properties of laminate composites, and electromagnetic shielding. On the other hand, thermally conductive (4 W/mK), electrically insulating sheets were produced with BNNT materials of different quality/purity. The quality of the BNNT materials was evaluated using several characterization techniques and a recently reported methodology for assessment of relative quality by absorption spectroscopy of regiorandom poly(3-hexyl-thiophene) aggregated on BNNTs. Nano-microscale roughness, which is essential for superhydrophobicity, can also be integrated on the NT-TPU fabrics surface by a novel approach that incorporates a nanomicro size array of functionalized nanotubes on the sheet surface producing highly non-wetting surfaces. Sheets can also be applied as coatings on other structures (e.g. glass fiber reinforced plastics) to create a multifunctional self-cleaning surfaces.

7:15 AM S.CT04.06.10

Interphase Engineering for 1D and 2D Nanocarbon-Included Functional Composites Weiheg Xu, Sayli Jambhulkar, Dharneedar Ravichandran and Kenan Song; Arizona State University, United States

The interface and interphase between a matrix and the fillers will influence the stress transfer, energy transport, stabilization
of dispersant, degree of confinement or bonding, and other new property generations. Both physical (e.g., molecular wrapping on filler surfaces or self-assembly) and chemical (e.g., surface functionalization) can modify the matrix-filler interfacial interactions. This talk will introduce two kinds of interface/interphase manipulations for precisely controlling nanoparticle morphologies. Our unique manufacturing and the resulted advanced composites have potential applications in wearable, robotics, biomedical, and other areas.

The first example was the use of polymer-graphene interphase design to achieve two dimensional (2D) nanoparticle orientation management. As well known that atomically thin 2D materials are challenging to be aligned as compared with their allotropes, such as carbon nanotubes. Free-standing graphene in ambient conditions will wrinkle, crumple or fold due to their instability of thermodynamic states. Our unique design of the different phases consisted of macromolecules and 2D graphene allowed the material system to take advantage of the interphase structural evolutions for confining, exfoliating and aligning the nanoparticles. Different polymers such as semicrystalline polyvinyl alcohol (PVA) and thermoplastic polyurethane were used to study the interphase engineering and their influence on graphene or similar nanocarbons for mechanical enhancement or functionality incorporations. The unique material system of composite fibers were used as piezo- and chemi-resistive sensors.

The second demonstration utilized layer-by-layer-based deposition techniques. Both additive manufacturing (e.g., 3D printing) and dip-coating methods were used on the same processing platform. One dimensional carbon nanofibers (CNF) were used as an example to be selectively deposited on polymer surfaces with pre-printed patterns. The control of the surface patterns and the nanoparticle assembly conditions (e.g., thermodynamic parameters, nanoparticle interactions, solid-liquid-air contact lines, etc.) led to selective deposition and preferential alignment of CNF. As a result, the conductive paths on the substrate were developed to be anisotropic; following this characterization, the multifunctional sensitivity to strain, temperature, chemical liquids and volatile organic compounds (VOCs) were also displayed.


7:30 AM S.CT04.06.11
Trans-Esterification in Vitrimer Polymers—Catalytic Efficiency and Mechanism Using Density Functional Theory Shusil Bhusal, Gary Kedziora, Vikas Varshney, Ren Yixin, Amber M. Hubbard, Dhriti Nepal and Ajit K. Roy; Air Force Research Laboratory, United States

Thermoset vitrimer polymers have recently shown tremendous promise for structural applications such as reshaping and remolding. The trans–esterification reaction plays a vital role in the vitrimer mechanism, in which the efficiency of the reaction is controlled by organic or organometallic catalysts. Understanding the mechanistic insights of the trans-esterification reaction in the bulk phase is difficult due to the highly cross linked complex structure of thermosetting vitrimers. In this work, we employ density functional theory (DFT) to investigate catalytic efficiency and the mechanism of the trans-esterification reaction using transition state theory with model systems that include alkoxy and carboxylic groups as reacting sites for mimicking the trans-esterification reaction. The catalytic efficiency of a number of catalysts, including triazabicyclodecene (TBD), zinc acetate Zn(OAc)2, Dibutyl tin oxide (DBTO) and Methylimidazole (1-MI) is explored. The mechanism of trans-esterification reaction is explored based on results from fukui indices (i.e measure of electrophilicity and nucleophilicity of atomic sites), partial charges, and transition state theory.

7:45 AM S.CT04.06.12
Hierarchical Structures of Gold Nanoparticles Decorated on Graphene Nanoplatelets Yixin Ren1,2, Rahul Rao2, Amber M. Hubbard1, Chen Li3, Shusil Bhusal1, Gary Kedziora2, Zhiting Tian1, Vikas Varshney2, Ajit K. Roy2 and Dhriti Nepal2; 1Universal Technology Company, United States; 2/ Wright-Patterson Air Force Base, United States; 3Cornell University, United States

Hierarchical assembly of plasmonic nanoparticles such as gold nanoparticles (AuNPs) into two-dimensional materials (graphene) is of significant interest for nearfield imaging, sensing, and inducing a photo-thermal response in a material.
However, uniform decoration of AuNPs onto graphene nano-platelets (GNP) is a significant challenge. This is because GNPs tend to aggregate easily via van der Waals force to form graphite, which perturbs the reaction at the interface. Here we demonstrate a simple solution-phase mixing technique to prepare AuNPs decorated GNPs hybrid materials (AuNPs-GNPs). By carefully optimizing the reaction condition, we were successful in maintaining the structural integrity of GNPs and simultaneously decorating it uniformly with AuNPs. High-resolution transmission electron microscopy (TEM) and high-angle annular dark-field imaging (HAADF-STEM) showed few-layered GNPs (< 10 nm thickness, ~ 200 nm lateral dimension) decorated with AuNPs. Here the diameter of AuNP ranges from 10 to 20 nm, which is controlled by the stoichiometry ratio of gold and carbon. Similarly, the average spacing between AuNP can be controlled by the density of defects on the graphene surface and the reaction conditions. Raman spectroscopy confirms the strain sensitivity of G and 2D modes as a result of the covalent interaction at the interface. Finally, these hybrid structures are embedded in a polymer matrix for studying thermal conductivity and plasmon-phonon interactions. Overall, this kind of hierarchical structure opens up new avenues for the next generation of smart coatings and composites.

8:00 AM S.CT04.06.13
Application of Nanoengineered Resin to Improve the Interlaminar Strength of Non-Crimp Carbon Fibre Composites
Ajit D. Kelkar and Vishwas S. Jadhav; North Carolina A&T State University, United States

Due to superior strength and stiffness properties, the use of textile composites for aerospace, automotive and marine applications has increased dramatically. The next generation of reinforcements, namely non-crimp fabric (NCF) is being explored for various structural applications. NCF can exploit low angle plies and can also be stacked as non-symmetric plies about the mid-plane. NCF provides excellent laminate strength, and the cost of fabrication is usually substantially lower than traditional composite manufacturing. Composite laminates are bonded together by a thin layer of resin between them, and the interface layer transfers the displacement and force from one layer to another layer. When these layers damage or weaken, adjacent layers separate, which forms the crack between adjacent plies. This also reduces the strength and stiffness of the laminate and can have a significant impact on the useful life of composites. Eventually, this separation of layers causes stress concentration in the plies which leads to the growth of delamination and results in failure of the laminate. Carbon nanofillers, such as nanoparticles, CNTs or CNFs, within the matrix material of composites has offered new avenues for improving the multifunctional properties of polymer matrix composites due to their high aspect ratio. In the present work, the laminates were manufactured using non-crimp carbon fabric in conjunction with and without nanoengineered enhanced epoxy resin. Mode I fracture toughness was evaluated for the composite panels with and without nanoengineered enhanced laminates. A detailed fractographic examination of the failed interfaces was performed by using state of the art imaging equipment such as Helium Ion, Axio Image upright microscope and scanning electron microscope. The study indicated that nanoengineered composites have significantly higher interlaminar properties as compared to the conventional composite laminates.

SESSION S.CT04.07: Poster Session: Tailored Interphases for High Strength and Functional Composites—Advances in Experiments, Simulations and AI-Based Design
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
5:00 AM - 8:00 AM
S-CT04

S.CT04.07.04
IFF-R Model to Accurately Simulate Stress-Strain and Failure Properties of Carbon Allotropes and Polymer Composites
Jordan Winetrout1, Krishan Kanhaiya1, Ravindra Pandey2, Gregory Odegard2 and Hendrik Heinz1; 1University of Colorado Boulder, United States; 2Michigan Technological University, United States

Stress induced mechanical failure of polymeric materials is a result of the breakage of covalent bonds. The occurrence of bond breakage and formation is only observed during reactions. This study focuses on the novel bond-breaking capabilities of the Interface Forcefield (IFF-R). Traditional IFF models simulated systems using harmonic potentials. The IFF-R model incorporates Morse potentials; thereby, eliminating the restoring force experienced by bonded atoms stretched at large distances. This enables accurate predictions of mechanical responses in a variety of periodic systems. This study shows moduli and strength predictions of a single-walled carbon nanotube, poly(acrylonitrile) crystal, cellulose β crystal, and steel FCC lattice to be comparable to experimental values. Mechanical property predictions using IFF-R models are realized.
magnitudes faster than reactive forcefield (ReaxFF).

S.CT04.07.05
Porous Materials – Graphene Hybrid Nanostructures with Tailored Interfaces as Membrane and Adsorbent Components in Gas Separation
Anish Varghese, Swati Singh, Suresh Kuppireddy and Georgios Karanikolos; Khalifa University, United Arab Emirates

Combinations of different materials into hybrid/composite structures are highly sought after as to enable multifunctionality in many of today’s demanding applications. 2-dimensional graphene can combine with porous nanostructures, such as metalorganic frameworks (MOFs), zeolites, and porous carbons, to yield hybrids with improved surface, interface, and activity characteristics. In this work, we will present examples of such material hybridizations via in-situ microstructural tuning of the interface between the involved counterparts. The resulting composites were tested for their gas separation performance, and specifically optimized to exhibit enhanced capture activity for carbon dioxide as adsorbents, as well as nanofillers in mixed matrix polymer-based membranes.

S.CT04.07.06
Site-Specific Surface Modification and Functionalization of Porous Nanostructured Scaffolds for Tunable Adsorption Applications
Adetola Ogungbenro, Suresh Kuppireddy, Maryam Khaleel and Georgios Karanikolos; Khalifa University, United Arab Emirates

To reveal the full potential of high surface area materials, strategies to tailor their surface characteristics and tune their active sites with high spatial precision and order are needed. In this work, we employ porous materials having surface areas of several hundreds of m² per g and we apply customized chemistry based surface tailoring as to spatially create active sites and subsequently graft functional molecules on them. Such examples of surface features can have a multitude of applications, yet we focus on tuning the affinity of the materials to bound with selective species from mixtures as to enable separation. In particular, innovative CO₂-phylic amines are immobilized on the treated surfaces to yield multifunctional adsorbents for carbon dioxide capture. Examples of silica- and graphene-based materials with controlled covalent positioning of various aminosilanes on the modified surface sites will be presented. Controlled grafting ensured stability and sustainable adsorption, tuned effects of locality, spacing, orientation, and interconnectivity of the functionalities on the surface, and minimized diffusion limitations while maximizing capture and release performance for the adsorbate species.

S.CT04.07.07
Improving Oxidative Stability of MXenes via Tailoring Surface Chemistry
Bryan T. Seymour¹², James E. Heckler¹², Gregory R. Neher¹², David B. Lioi¹², Ali Jawaid³, Faisal Mehmood¹², Ruth Pachter³, Richard A. Vaia³, W. J. Kennedy³ and Dhriti Nepal³¹; ¹Universal Technology Corporation, United States; ²Air Force Research Laboratory, United States; ³UES, Inc., United States

MXenes are an emerging class of two-dimensional layered transition metal carbides, carbonitrides, and nitrides. Their intriguing properties have attracted significant attention as promising materials for next-generation coatings and devices. One of the significant challenges of this material (e.g. Ti₃C₂Tx) is the rapid oxidation into TiO₂ anatase through hydrolysis in water, though water has proved to be the most effective solvent for solubilizing exfoliated Ti₃C₂Tx. Organic solvents routes for processing of MXenes and functionalization of its surface with specific ligands provide avenues to tailor the surface properties, which could eventually influence the colloidal stability as well as oxidative stability. Herein, we discuss the influence of various organic solvents such as ethanol, isopropanol, toluene, and N, N-Dimethylformamide on Ti₃C₂Tx, colloidal stability, oxidative stability at room temperature, and thermo-oxidative properties. We also demonstrate the use of silane and catechol ligands for tailoring the physical properties of Ti₃C₂Tx.

S.CT04.07.08
High Response Nitric Oxide (NO) Gas Sensor with Noise Limited Detectivity Approaching 10 ppb of ZnO/Si NWs p-n Heterojunction Array
Chandan Samanta, Ankita Ghatak, A. K. Raychaudhuri and Barnali Ghosh; S N Bose National Centre For Basic Sciences, India

Currently Gas sensors have a great impact in direct monitoring of environmental hazardous gas as well widely used in healthcare such as exhaled breath analysis. In this work we report a ZnO/Silicon nanowires (ZnO/p-Si NWs) based p-n heterojunction array based Nitric Oxide (NO) gas sensor operating at room temperature with extremely high response at least down to 0.5 ppm with noise limited response ~ 10 ppb. Utilization of cost effective chemical technique for fabrication of sensor on silicon is compatible with wafer level processing and easily connecting with silicon IC technology. The vertically
aligned Si NWs array has been made by electroless etching method and the ZnO nanostructure was made by chemical solution deposition and spin-coating. We observe that the heterostructure leads to a synergetic effect where the sensing response is more than the sum total of the individual components, namely the ZnO and the Si NWs. The response is much enhanced in the p-n junction when the n-ZnO nanostructure interfaces with p-Si NW compared to that in the n-n junction formed by ZnO on n-Si NW. Extensive cross-sectional electron microscopy and composition analysis by line EDS allowed us to make a physical model. The comparison of the simulation results with the experiment point out the device parameters that enhance the device response. The characteristics values of the parameters of ZnO/Si NWs heterojunction for the best fits obtained from the simulation and it can be seen that all the parameters undergo change in the electrical model and this leads to enhancement of current in the device on gas exposure. The top layer of ZnO takes part in electrical current conduction. The Si NWs also has an all-round layer of ZnO that also acts as chemical sensing gate to modulate the depletion layer on the surface of the NW. The main inference from the simulation is that the observed high performances of the sensor device depends on change in resistances of the constituents as well change in the reverse saturation current at the ZnO/p-Si NW p-n junction.

S.CT04.07.11
Additive Manufacturing of Hybrid Silicon Carbide/Carbon Fiber Nano-Composites Saja M. Al-ajrash; University of Dayton, United States

A novel route to fabricate a hybrid ceramic matrix composite by utilizing preceramic polymers, chopped carbon nanofiber (CNF) precursors and subsequent additive manufacturing was introduced in this study. An allyl hydrido polycarbosilane (SMP-10) and 1,6-dexanediol diacrylate (HDDA) were mixed with a photo initiator to form a photo sensitive resin. The resulting resin was loaded with distinct weight percentages of polyacrylonitrile (PAN) nanofiber. These mixtures were 3D printed followed by pyrolysis. The end objective of the pyrolysis cycle is that the polycarbosilane resin is converted into a silicon carbide matrix, with the PAN converted into reinforcing carbon nanofibers. The impact of the CNF percentages on structural and mechanical properties was investigated using scanning electron microscopy, transmission electron microscopy, and nano-indentation characterization techniques, respectively. The prepared precursor resin proved to have outstanding photo-curing properties and the ability to transform to the silicon carbide phase at temperatures as low as 850 °C. The result of this work showed that ceramic matrix composite components can be successfully fabricated using 3D printing and a specific pyrolysis cycle. The obtained ceramic hybrid composite was fully dense with nearly linear shrinkage and a shiny, smooth surface after pyrolysis. Furthermore, around 60% retained weight after pyrolysis to 1350 °C was confirmed by thermogravimetric analysis. In terms of crystallography, the ceramic matrix composite appeared to have three coexisting phases including silicon carbide, silicon oxy carbide, and turbostratic carbon. The results are very promising to fabricate hybrid composites working at high temperatures with improved mechanical properties and complex geometries.

S.CT04.07.12
Systematic Study of the Effect of Incorporation of Carbon Nanotubes into GeₓSe₁₋ₓ Glass System Chari Ramkumar, John Rademacher, Jake Anderson and Wayne Bresser; Northern Kentucky University, United States

We successfully synthesized GeₓSe₁₋ₓ (x = 0.225) glass samples and doped the samples with commercially produced (Protein Mods) carbon nanotubes (CNTs). We investigated the glass transition temperature (T_g) using Modulated Differential Scanning Calorimetry (MDSC). The glass samples without the CNTs have a a T_g of ~220°C and the T_g was found to be independent of starting materials from different suppliers as well as water-bath temperature. CNTs, being a very hygroscopic material as well as oxygen absorbing material, needed to be cleaned under vacuum with the hot water-bath. We found that the T_g decreases when 5% and 10% CNTs by mass is added to the glass samples as compared to the base GeₓSe₁₋ₓ glass. The decrease in T_g indicates the occurrence of an intermediate phase (reduced-stress glass phase) at lower temperature, which could be potentially useful in material science applications.

S.CT04.07.16
Interfacial Tailoring in CdS/CdTe Heterojunction Solar Cells by Glancing Angle Deposition Niva K. Jayswal, Dipendra Adhikari and Nicolas J. Podraza; The University of Toledo, United States

Abstract:
Glancing angle deposition (GLAD) radio frequency (RF) magnetron sputtering enables production of polycrystalline CdTe with different microstructural properties including grain size, grain orientation, and crystal phase. In GLAD sputtering, the normals extending from the centers of the sample and sputtering target are at controllable angles with respect to each other. At lower source flux angles, films grow as the expected more energetically stable cubic zinc blende CdTe phase whereas at higher source flux angles the metastable wurtzite phase forms. During the GLAD process different microstructure and crystal
phases are produced in the film due to increased atomic scale self-shadowing effects at higher source flux angles which result in limited diffusion of ad-atom precursors on the substrate. This wurtzite phase CdTe produced at high source flux angles is used to tailor the interface between the n-type hexagonal wurtzite CdS window layer and p-type cubic zinc blende CdTe absorber in the standard CdS/CdTe solar cell. Application of this wurtzite phase CdTe interlayer results in better lattice matching to both hexagonal CdS and cubic CdTe leading to higher photovoltaic device performance. Using spectroscopic ellipsometry (SE) and x-ray diffraction (XRD), the optical and microstructural properties of the GLAD CdTe interlayers before and after CdCl2 treatment are obtained. CdS/CdTe heterojunction solar cells are fabricated with GLAD interlayers prepared using source flux angles from 0° (normal incidence) to 80°, at substrate temperatures from room temperature to 250 °C, and with CdCl2 post-deposition treatment times up to 30 minutes. Photovoltaic device performances are compared between devices with and without the introduction of these GLAD CdTe interlayers. Improvements in photovoltaic device performance parameters including open circuit voltage, short circuit current, fill factor, and power conversion efficiency are related to GLAD CdTe interlayer characteristics.

SYMPOSIUM S.CT05

Defects, Order and Disorder in Structural and Functional Fluorite-Related Compounds
November 21 - November 21, 2020

Symposium Organizers
Jeffery Aguiar, Lockheed Martin
Gianguido Baldinozzi, University of Paris Saclay
Maulik Patel, University of Liverpool
Zhaoming Zhang, Australian Nuclear Science and Technology Organisation

* Invited Paper

SESSION S.CT05.01: Fluorite Structures
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-CT05

5:00 AM *S.CT05.01.01
Layered Atomic Arrangements in Fluorite Derivative Tungstates and Uranates Kurt E. Sickafus; University of Tennessee, United States

In this presentation, we will compare and contrast the structures of oxide compounds containing lanthanum (La) and either tungsten (W) or uranium (U). We will interrogate the structures of La-tungstates (LWO) versus La-uranates (LUO) using a geometric model based on layer stacking sequences of pseudo close-packed layers. The individual atomic layers in the stacking model considered here have hexagonal symmetry and are based on triangular atom nets or hexanets. The layers in the LWO and LUO compounds can be described based on geometric subdivisions of a triangular atom net, subdivisions originally described by Shuichi Iida. A One unusual layered atom structure involves the LWO compound, La7W1O13.5. This compound has a stoichiometry very close to La6W1O12, which is the stoichiometry associated with 6-1-12 delta (δ) phase oxides (actually, the 6-1-12 compound is not observed in LWO). However, the structure of the 7-1-13.5 stoichiometry is very different compared to the δ-phase. The layer stacking model we develop for the 7-1-13.5 compound is closer to that of pyrochlore, rather than δ-phase. Interestingly, in LUO, the 6-1-12 phase is observed and we can describe the layer stacking in this compound as consistent with a δ-phase structure. We will perform a detailed comparison between layered atom arrangements in La7W1O13.5 and La6U1O12 in an effort to rationalize why the structures of these two compounds, both containing hexavalent metal cations (WVI and UVI), are so different.

Understanding Electrical Properties of Nanocrystalline, Mesoporous Composite Ce$_{0.9}$Gd$_{0.1}$O$_2$-$d$ Thin Films

Christel Laberty$^1$ and Armelle Ringuede$^2$; $^1$Sorbonne Université, France; $^2$PSL, France

Crystalline, mesoporous NiO/GDC thin films with thicknesses ranging from 50 nm to 250 nm were synthesized through templated sol–gel chemistry coupled with the dip-coating process and heat-treatment in air. The thin films’ microstructure is composed of two interpenetrated networks made of mesopores and inorganic components. Efficient coupling between the temperature and the NiO volume fraction (vol%) allows tuning of both the pore size with dimensions ranging from macro- to meso-size and the NiO or GDC crystallite size with a diameter below 10 nm. X-ray diffraction and impedance spectroscopy performed in 10% H$_2$ in Ar allowed the in situ study of the reduction process of NiO to metallic Ni. Coalescence of Ni particles generated by the reduction step and percolation phenomena controls the resulting conductivity of the final materials. Thin films with an initial content of 50 vol% of NiO exhibit lower electrical properties compared to those with an initial content of 70 vol% NiO. Electrical properties in a reducing atmosphere were also studied as a function of microstructure such as the pore dimension and the thickness of the pore wall. Excellent electrical properties are obtained for Ni70/GDC30-porous thin films synthesized with the block-copolymer PS40-PEO36 that have a final conductivity of 9 x 10$^4$ S m$^{-1}$ at 500 °C. These mesostructured nanocomposite thin films exhibit a connected pore network that ensures good gas diffusion and good particle–particle contact for GDC and Ni, which gives satisfactory electrical properties. These films have all the attributes to be used as anodes in micro-SOFCs. This approaches was also extended to mesostructured composite La$_{0.7}$Sr$_{0.3}$Co$_{0.2}$Fe$_{0.8}$O$_3$/$y$Gd–CeO$_2$ (LSCF/$y$GDC) (with $x$ and $y$ representing the volumetric % of LSCF and GDC in the composite films) thin films. This technique allows us to define the heat-treatment, the LSCF content in the composite film and the thickness of the film to achieve good electrical conductivity. Electrical conductivity of 250 S cm$^{-1}$ was achieved for the pure, mesoporous LSCF film at 700 °C.

References:

Local Structure of Uranium-Neptunium and Uranium-Plutonium Mixed Oxides Using High Resolution Solid-State 17O NMR
Laura Martel, Jean-François Vigier, Sarah Nourry, Antony Guiot, Jacobus Boshoven and Joseph Somers; European Commission, Germany

U$_{1-x}$Np$_x$O$_2$ and U$_{1-x}$Pu$_x$O$_2$ mixed dioxides with the fluorite Fm-3m crystalline structures are considered as fuels and targets for the transmutation of the minor actinides in fast neutron reactors. We present an atomic scale structural analysis on a series of U$_{1-x}$An$_x$O$_2$ synthesized by the sol–gel external gelation method, for which longer range structural analysis indicates that the process yields solid solutions. The atomic scale structure is probed using high resolution $^{17}$O solid-state NMR in a unique manner. Indeed, this technique allows a particular insight into the local structure of these solid-solutions as different oxygen signals attributed to the O(Np)$_y$(U)$_{4-y}$ (with 0 ≤ $y$ ≤ 4) units can be identified by increasing Np content. We thus show how the use of solid-state high resolution NMR opens new routes for the fine characterization of local order in these radioactive materials.

Investigating Cerium Doped Indium Oxide as a High Mobility Transparent Conducting Oxide
Joe Willis$^{1,2,3}$, Thomas J. Featherstone$^4$, Benjamin A. Williamson$^5$, Jack Swallow$^4$, Leanne A. Jones$^4$, Tien-Lin Lee$^1$, Pardeep K. Thakur$^3$, Takeshi Koida$^6$, Tim Veal$^4$ and David O. Scanlon$^{1,2,3}$; $^1$University College London, United Kingdom; $^2$Thomas Young Centre, United Kingdom; $^3$Diamond Light Source, United Kingdom; $^4$University of Liverpool, United Kingdom; $^5$Norwegian University of Science and Technology, Norway; $^6$AIST Japan, Japan

Transparent Conducting Oxides are fundamental components of modern optoelectronic devices, bringing together the unusual combination of optical transparency and electrical conductivity. Presently, the champion material is Sn-doped In$_2$O$_3$ (ITO), capable of reaching resistivity as low as 10$^4$ Ω cm and mobility around 40 cm$^2$ V$^{-1}$ s$^{-1}$. However, it has emerged that the use of alternative dopants returns greater mobility on the order of 100 cm$^2$ V$^{-1}$ s$^{-1}$, and in turn can match or even surpass the levels of conductivity reached by ITO.[1] Higher mobility affords a lower carrier concentration, allowing for improvements in NIR transparency due to a lower resonant plasmon frequency, ultimately leading to increased efficiencies in
Here Ce-doped In$_2$O$_3$ (ICO) films grown by rapid plasma deposition demonstrate electron mobility upward of 130 cm$^2$ V$^{-1}$ s$^{-1}$. Hybrid DFT calculations show that Ce 4f states lie well above the conduction band minimum, thereby not affecting its dispersion. A low electron effective mass is maintained at the band edge and therefore high electron mobility is achieved, a feature shared with other successful resonant donors in In$_2$O$_3$.

Defect formation energies place the transition level of the Ce donor from 1+ (active) to neutral (inactive) around 0.1 eV above the CBM – this suggests that only a small shift in the Fermi level will cause Ce (III) to begin to occupy In sites rather than Ce (IV). This is observed in Hard X-ray Photoelectron Spectroscopy, where Ce (III) states begin to emerge as a function of increasing carrier concentration. This potentially places an upper limit on Ce-doping of In$_2$O$_3$ but does not prevent films achieving equal levels of conductivity and surpassing electron mobility of commercial ITO films, with feasible applications in concentrated multi-layer solar cells and beyond.

References:

SESSION S.CT05.02: Pyrochlore Structures
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-CT05

5:00 AM *S.CT05.02.01

New Insight into the Disordering Mechanism in Fluorite-Related Compounds Maik K. Lang; University of Tennessee, United States

Structural disorder plays a critical role in many technological applications to enhance specific functionalities, such as increasing conductivity via chemical doping in semiconductors or improving flux pinning in high-temperature superconductors. Recent results from neutron total scattering experiments have shown that the atomic arrangements of many disordered crystalline materials are not random nor are they represented by the long-range structure observed from diffraction experiments. This structural heterogeneity at different length-scales appears to be a general characteristic of disordered crystalline materials, but the underlying mechanisms are not well understood. This presentation reviews neutron total scattering experiments on a range of fluorite-related compounds that show complex disordering behavior across different length scales. Structural information from pair distribution functions with sensitivity to both cation and anion sublattices were utilized to investigate in detail the disordering process of A$_2$B$_2$O$_7$ pyrochlore oxides. The order-disorder transformation can be understood as a rearrangement of atomic-scale building blocks. The same concept can be used to describe disordering in weberite-type oxides (A$_3$BO$_7$). This knowledge has implications for tailoring the structural response of complex oxides to extreme environments. For example, by choosing a material with specific structural building blocks the resistance to ion irradiation can be greatly improved.

5:30 AM *S.CT05.02.02

Elucidating the Relationship between Chemical Order and Mass Transport in Pyrochlores Blas P. Uberuaga, Cortney Kreller, Matthew T. Janish, James Valdez, Romain Perriot, Ghanshyam Pilania and Yongqiang Wang; Los Alamos National Laboratory, United States

It is becoming ever more apparent that, in complex compounds such as pyrochlores, the detailed arrangement of the cations drives functionality. For example, both radiation tolerance and ionic conductivity have been linked to how easily cations can mix across sublattices. This is due to the fact that mass transport in these materials is a strong function of the cation distributions. However, the actual relationship between the cation, or chemical, structure of these compounds and the rates of transport are still not well established. While some reports find enhanced ionic conductivity in disordered materials, others find higher conductivity in ordered phases. Many of these studies use chemistry to influence the disorder, essentially changing multiple variables at once. However, the degree to which cations mix can be finely controlled using radiation
damage without changing chemistry. Here, we use radiation damage as a tool to induce changes in the cation structure of thin-film model pyrochlores. We then characterize the extent to which those changes impact mass transport. We combine these experimental efforts with state-of-the-art simulation methodologies to understand how atomic scale mechanisms dictating mass transport change when the cation structure is modified. We have found that even small changes in cation structure can lead to large changes in the transport characteristics of the material. Our results provide new insight into mass transport in materials that exhibit chemical complexity well beyond the model systems studied where chemical disorder dictates the fundamental behavior of the material.

6:00 AM S.CT05.02.04
Understanding the Phase Behaviour of Pyrochlore Bi$_2$Sn$_2$O$_7$ Warda Rahim¹, Jonathan M. Skelton², Aron Walsh³ and David O. Scanlon¹; ¹University College London, United Kingdom; ²University of Manchester, United Kingdom; ³Imperial College London, United Kingdom

Ternary oxides with pyrochlore structure (A$_2$B$_2$O$_7$) exhibit a range of interesting properties, including ionic conduction, ferromagnetism, superconductivity, high dielectric character and colossal magnetoresistance.¹ Unlike the majority of the tin-based pyrochlores, Bi$_2$Sn$_2$O$_7$ exists in a number of polymorphic forms, with an α-Bi$_2$Sn$_2$O$_7$ to β-Bi$_2$Sn$_2$O$_7$ transition occurring at ≈400 K and β-Bi$_2$Sn$_2$O$_7$ to γ-Bi$_2$Sn$_2$O$_7$ transition occurring above 900 K.² The structural model for the highest temperature γ-Bi$_2$Sn$_2$O$_7$ is undisputed (Fd-3m) but there has been a controversy over the structural models for its lower temperature polymorphs. Previous studies by Evans et al. suggested the room temperature polymorph belongs to space group 7 (P1Cl) with 352 atoms per cell.³ Recently, a simpler model for α-Bi$_2$Sn$_2$O$_7$ belonging to space group 9 (Clc1) with 88 atoms per cell, and the first ever detailed structural model for β-Bi$_2$Sn$_2$O$_7$ belonging to space group 41 (Aba2) has been reported.⁴ We perform first principles lattice dynamics calculation using Phonopy⁵ with gradient corrected density functional theory, starting from the highest symmetry γ phase, and map out the potential energy surfaces⁶ spanned out by imaginary mode eigenvectors, with the aim of elucidating the lowest energy structure. This approach successfully takes us from the highest temperature structure to the new structural model suggested for α. It also demonstrates that β is a thermal average of a lower symmetry structure separated by a very small energetic barrier. The success of the method highlights the strength of ab-initio lattice dynamics in predicting the dynamically stable structural model of a compound that undergoes displacive phase transitions and can speed up the exploration of different structures for solid-state applications.


6:15 AM S.CT05.02.05
Investigation of Disorder in Ho$_2$Ti$_2$Zr$_x$O$_7$: Pyrochlore to Defective Fluorite Chemical Series Devon L. Drey¹, Eric O’Quinn², Igor Gussev³, Antonio Fuentes³, Joerg Neuefeind³, Michelle Everett³, Gianguido Baldinozzi⁴ and Maik K. Lang¹; ¹University of Tennessee at Knoxville, United States; ²Cinvestav Unidad Saltillo, Mexico; ³Oak Ridge National Laboratory, United States; ⁴Université Paris-Saclay, France

Pyrochlore oxides (A$_2$B$_2$O$_7$) – and other fluorite-derived complex oxides – are interesting for not only their wide variety of desirable properties, such as ionic conduction and radiation tolerance, but also for their complex defect formation and disordering mechanisms that often give rise to their properties. We have used neutron total scattering to study in detail all structural aspects of the disordering of pyrochlore which involves randomization of both cation and anion sublattices. By means of diffraction and pair distribution function analysis of a Ho$_2$Ti$_2$Zr$_x$O$_7$ (x = 0.0-2.0) solid solution series, the disordering mechanism was studied simultaneously over multiple material length scales with novel insight into the local atomic arrangements. With increasing Zr-content, the series exhibits an order-disorder transformation from pyrochlore (space group: Fd-3m) to defective fluorite (space group: Fm-3m) across a narrow compositional range (x = 1.0-1.5) over the long length-scale, while the local atomic arrangement changes gradually to a weberite-type structure (space group: C222₁) over the whole compositional range. This distinct disordering scheme can be explained by the movement of a 48f oxygen to a vacant 8a site, creating 8-coordinated Zr⁴⁺ sites that produce local weberite-type building blocks. These building blocks accumulate until a critical Zr-content (x ~ 1.2) is reached which triggers the rearrangement of weberite-type units into long-range structural defective fluorite.

2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
Phonon Lifetimes and Thermal Conductivity of La$_2$Zr$_2$O$_7$ Maud Einhorn$^1$, Joe Willis$^{1,2}$, Kieran B. Spooner$^1$, Warda Rahim$^1$ and David O. Scanlon$^{1,2}$; $^1$University College London, United Kingdom; $^2$Harwell Science and Innovation Campus, United Kingdom

High-temperature thermal-barrier coatings are an essential component of modern gas-turbine engines. Despite remaining the standard industrial thermal barrier coating, yttria-stabilised zirconia (YSZ) top-coat suffers profound performance issues at very high-temperatures, principally resulting from high-temperature phase instability limiting the maximum operating temperature.1 As a result, alternative materials with superior insulation properties and stability are essential for higher operating temperatures and improve engine efficiencies. To this end, novel ceramic materials, rare-earth zirconates pyrochlores including La$_2$Zr$_2$O$_7$, have been looked to due to their low lattice thermal conductivity, phase stability across a wide temperature range, high melting point and low thermal expansion coefficient.2

Recent work by Voneshen et al. ascribed the exceptionally low thermal conductivity in La$_2$Zr$_2$O$_7$ to a strongly anharmonic phonon mode associated with the kagome planes in the material, observed from inelastic neutron scattering (INS) data.3 In this work we calculate the thermal conductivity and phonon lifetimes of La$_2$Zr$_2$O$_7$ using ab initio lattice dynamics calculations using both the linearised Boltzmann transport theory (LBTE) within the single mode relaxation time approximation (RTA) and the temperature dependent effective potential (TDEP) methods.4,5 These results are supported by new experimental data measuring the phonon-phonon scattering rates of the individual modes in La$_2$Zr$_2$O$_7$.

Complex oxides with fluorite derived structures play a key role in the context of the nuclear fuel cycle. We enhanced wet-chemical synthesis routes, e.g. co-precipitation or internal gelation, to fabricate tailor-made precursors for advanced nuclear fuel forms as well as potential nuclear waste forms with the defect fluorite or pyrochlore crystal structure. The internal gelation route enabled the fabrication of high-performance UO₂ fuel candidates using 1) dopants, such as Cr and Mn, to improve the fission gas retention, and 2) a second phase, here Mo, to enhance the thermal conductivity of UO₂-based nuclear fuel. Characterization of the thermal properties of enhanced UO₂-Mo fuel candidates fabricated via different approaches revealed significant differences in the thermal conductivity of the final fuel candidates. An in-depth understanding about the correlation between the synthesis approaches and the materials properties is underway. Fabrication of Pu-doped Nd₂Zr₂O₇ pyrochlores as potential nuclear waste forms revealed the enormous flexibility of the pyrochlore crystal structure to accommodate Pu(IV) at the usually trivalent A-site. Charge neutrality is achieved by surplus oxygen at formerly oxygen vacant sites. The immobilization of actinides in a zirconate based pyrochlore is known to result in an order/disorder transition from a pyrochlore to a defect fluorite structure, a consequence to self-irradiation. For this order/disorder transition of Nd₂Zr₂O₇ a combined experimental approach of oxide melt solution calorimetry with ab initio thermodynamic modeling revealed a transition enthalpy of ~30 kJ/mol. This transition enthalpy corresponds to an entropy of disordering of ~16 kJ/mol. This presentation will summarize recent activities about developing suitable fabrication routes of fluorite-structure derived ceramics in the nuclear context, how the fabrication avenues affect their properties as well as the effect of radiation induced structural order/disorder transitions towards the materials properties and performance.

6:00 AM *S.CT05.03.03
Radiation Effects in UO₂ and Other Oddities of the Unstable Valences Steven D. Conradson¹, ², ³, Janne Pakarinen⁴ and Gianguido Baldinozzi⁵; ¹Institut Jozef Stefan, Slovenia; ²Washington State University, United States; ³Polaronix Corporation, United States; ⁴Studsvik Nuclear AB, Sweden; ⁵SPMS, CNRS CentraleSupelec, France

Since the stable valences of U in its oxides are IV, V, and VI, the formation of reduced species in UO₂ is problematic. This is demonstrated in XAFS measurements of UO₂ irradiated with protons and helium nuclei. The addition of O occurs by clustering that results in UO₂-U₄O₉ phase separation, facilitated by the virtually identical U sublattices of these two species. Ion beam irradiation that displaces O ions could give the same behavior, but whereas disorder is observed the signatures of U₄O₉ are not. This is most likely because, whereas the O-enriched regions with mixed valence U(IV,V) would be stable, the U(III) formed in the O-depleted regions is not. An different mechanism is activated. This could also be important in the chemistry of the fuel and the O potential formed in response to the temperature gradient.

6:30 AM S.CT05.03.05
Effects of Grain Size on the Radiation Response of CeO₂, ThO₂, and UO₂ William Cureton¹, Raul Palomares¹, ², Cameron Tracy³, ⁴, Eric O’Quinn¹, Rodney Ewing⁴, Gianguido Baldinozzi⁵, Jie Lian⁶, Christina Trautmann⁷, ⁸ and Maik K. Lang¹; ¹The University of Tennessee, Knoxville, United States; ²The Boeing Company, United States; ³Polaronix Corporation, United States; ⁴Stanford University, United States; ⁵University of Paris Saclay, France; ⁶Rensselaer Polytechnic Institute, United States; ⁷GSI Helmholtzzentrum für Schwerionenforschung, Germany; ⁸Technische Universität Darmstadt, Germany

Radiation stability is often a key limiting factor in performance of fluorite-structured materials and determining their suitability for use in energy-related applications. In an effort to mitigate the effects of radiation, nanostructured materials are of interest as they incorporate high defect sink strengths [Rose et al., Nanostructured Materials (1995), Nita et al., Journal of Nuclear Materials (2004)]. Recently, it has been shown that the response of CeO₂, ThO₂, and UO₂ to highly ionizing radiation is strongly dependent on the material’s redox response [Tracy et al., Nature Communications (2015)]. When exposed to swift heavy ions, cations in the material are subject to changes in valence which drives swelling and microstrain as irradiation-induced defects accumulate. In this work, we present new insights into how crystallite size affects irradiation-induced redox response and defect accumulation in fluorite-structured simple oxides. Using 946 MeV Au ions at the UNILAC accelerator of the GSI Helmholtzzentrum, we irradiated microcrystalline and nanocrystalline materials of different compositions containing cations known to reduce (CeO₂), remain univalent (ThO₂), and oxidize (UO₂) under ionizing conditions. Irradiated samples were characterized by synchrotron X-ray diffraction/absorption, neutron total scattering with pair distribution function (PDF) analysis, transmission electron microscopy, and Raman spectroscopy. Each composition exhibits a distinct response between microcrystalline and nanocrystalline forms, such as magnitude of volumetric swelling and secondary phase formation, driven mainly by redox processes. PDF analysis reveals small peroxide-like defects in CeO₂ and mono- and di-interstitial clusters in UO₂. Our findings imply that nanocrystallinity has negative effects on a material’s response to highly ionizing radiation. These results shed more light onto the interplay of particle size and cation
redox behavior and their effect on defect production in an important class of materials, an insight that is essential in developing advanced materials for energy-related applications.

6:45 AM S.CT05.03.06
Self-Irradiation-Induced Disorder in (U0.9238Pu0.1)O2 Emanuele De Bona1,2, Bert Cremer1, Jean-Yves Colle1, Thierry Wiss1, Gianguido Baldinozzi3 and Rudy Konings1; 1European Commission - JRC, Germany; 2Helmholtz-Zentrum Dresden-Rossendorf, Germany; 3Université Paris-Saclay, France

Spent nuclear fuel (SNF) of light water reactors (LWR) is constituted of a matrix of unfissioned UO2 containing a small fraction of fission products (FP) and minor actinides (MA). These MA are mainly α-emitters with very long half-lives: therefore, SNF will keep α-self-irradiating for millennia after discharge from the reactor, resulting in widespread changes of the thermophysical properties of the material. In order to properly coordinate and license any disposal strategy for SNF, the long-term effect of α-self-irradiation has to be known and anticipated.

Due to the lack of real old SNF, a proxy system to study the effect of α-irradiation on the SNF matrix is provided by the synthesis of UO2 doped with short-lived α-emitters. In this way, a significant amount of radiation damage can be stockpiled over a laboratory timescale in a simpler surrogate system that does not combine radiation damage with chemical or density gradients (built-in in real SNF).

In the present work, UO2 doped with 238Pu was produced to study the effect of α-self-irradiation on the crystalline disorder and lattice swelling. The composition of the samples was carefully chosen, based on the dopant specific activity, in order to reach saturation of the lattice parameter swelling within the 3 years timespan of the project. Samples were periodically characterized by means of XRD and Raman spectroscopy up to 0.4 dpa, equivalent to a spent nuclear fuel with a 40 GWd/t UO2 burnup stored during 300 years, or representative of a 65 GWd/t spent MOX fuel (45 % Pu) after 25 years of storage. Lattice swelling as a function of dpa was assessed with very good accuracy and benchmarked against literature data: saturation was reached at a value of 0.3 % around 0.4 dpa. For the first time, microstrain was also monitored in (U,Pu)O2 as a function of self-irradiation.

Periodic Raman spectroscopy acquisitions on (U,Pu)O2 as a function of the dose represent an innovative probe, and they showed fast and progressive degradation of the structural order up to 0.1 dpa, and a slow but persistent increase up to 0.4. SEM characterizations were additionally performed and highlighted that no loss of structural integrity is associated with this microstructural evolution, at least within the measured dpa range.

SESSION S.CT05.04: Fluorite Derived Structures
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-CT05

5:00 AM *S.CT05.04.02
Order/Disorder in Fluorites—Determination and Impact Karl R. Whittle; University of Liverpool, United Kingdom

The basic fluorite structure allows for both ordering and disorder, with multiple options in each such as those that are regular integer repeats of the unit cell, such as with pyrochlore, or those that repeat with a different repeat length. The degree of order/disorder within the atomic structure can often lead to modification of properties, such as ionic conductivity, or how they respond to induced radiation damage. Enhanced understanding of the degree of short/long range order greatly improves the design and development of new materials. The determination of the degree of order/disorder can be challenging given the cubic nature of the fluorite structure. To get round such challenges a combination of experientrial techniques can be applied, however each technique in itself has different sensitivities and ability to provide structural information. This presentation provide an overview of mutliple options and how they can be applied to the determination of order/disorder in fluorites, and how the derived information can be used to develop new material options.

5:30 AM S.CT05.04.03
Global and Local Structural Modifications in Swift Heavy Ion Irradiated Sc4Hf3O12 Maulik K. Patel1, Kurt E. Sickafus2 and Gianguido Baldinozzi3; 1University of Liverpool, United Kingdom; 2The University of Tennessee, Knoxville, United States; 3University of Paris-Saclay, France

Aliovalent cation-doped fluorite oxide structures are ideal candidates to understand phase stability and their transformation
pathways under radiation. These systems are relevant models for nuclear fuels and waste forms. Sc₄Hf₃O₁₂ is a delta phase crystallising in a trigonal symmetry. This and other AₓB₃O₁₂-type systems were observed to transform into a long-range defect fluorite phase upon low energy ion irradiations. On one instance Sc₄Hf₃O₁₂ was also observed to partially turn into a bixbyite phase, however, the reasons behind this were never clearly understood. Thus, in the present study, swift heavy ion irradiated Sc₄Hf₃O₁₂ was investigated as a function of fluence using x-ray diffraction. Structural parameters obtained from quantitative Rietveld analysis reveal that, while the long-range average structure develops into a defect fluorite, the local structure tends to convert into a bixbyite-like arrangement. Similarities in the polyhedra suggest this bixbyite-related local phase is a metastable system that effectively provides radiation resistance by creating large numbers of bixbyite-related replicas within an aristotype fluorite mesocrystal.

5:45 AM S.CT05.04.04
Multicomponent Equiatomic Rare-Earth Oxide Ceramics Matheus Pianassola¹,², Madeline Loveday¹,², Jake McMurray³, Merry Koschan⁴, Charles Melcher⁵,⁶ and Mariya Zhuravleva¹,²; ¹University of Tennessee, Knoxville, United States; ²The University of Tennessee, Knoxville, United States; ³Oak Ridge National Laboratory, United States

Phase formation in multicomponent rare-earth oxides is defined by a competition between the fluorite structure typical of rare-earth dioxides and the hexagonal, monoclinic, and bixbyite structures typical of sesquioxides. This competition is determined by a combination of composition, sintering atmosphere, and cooling rate. Polycrystalline ceramics comprising various combinations of Ce, Gd, La, Nd, Pr, Sm, and Y oxides in equiatomic proportions were synthesized by solid-state sintering. This synthesis method allows a rapid evaluation of the effects of composition (type and number of cations), sintering atmosphere (oxidizing, inert, and reducing), and cooling rate on phase formation. Single fluorite, bixbyite, or monoclinic phase compositions were obtained with a slow cooling of 3.3 °C/min, indicating that rare-earth oxides follow a different phase stabilization process than that of transition metal high-entropy oxides. In an oxidizing atmosphere, both Ce and Pr induce the formation of fluorite or bixbyite phases, while only Ce plays that role in an inert or reducing atmosphere. Samples without Ce or Pr develop a single monoclinic phase. The phases formed at initial synthesis may be converted to a different one when the ceramics are annealed in an atmosphere different than the original sintering atmosphere. Additionally, phase evolution of a five-cation composition was studied as a function of sintering temperature. The binary oxides used as raw materials completely dissolve into a single bixbyite structure at 1450 °C in air.

6:00 AM S.CT05.04.05
High-Solute Grain Boundary Compositional Effects in Ca- and Ba-Doped Ceria Tara M. Boland, Arunima Singh, Peter Rez and Peter A. Crozier; Arizona State University, United States

Ceramic oxides are used for a wide variety of technologically relevant applications from electrochemical devices, novel resistive switching devices, and oxygen sensors. Applications such as these typically rely upon the ability of oxides to conduct ions efficiently through the lattice. However, the grain boundaries (GBs) can be orders of magnitude more resistive than their bulk counterparts. While methods developed for bulk-doping have been successful, they have provided little insight when optimizing the GB ionic conductivity in polycrystalline ceramic oxides such as CeO₂. In recent years, nanoscale compositional characterization of GB composition has revealed different nominal concentrations of solutes at the GBs which could result in orders of magnitude increase in GB ionic conductivity relative to the undoped samples. This study focuses on the impact which concentration plays in modulating the potential energy landscape for two potentially promising solutes, Ca and Ba, which may increase the ionic conductivity across the GB. Computational modeling is employed using density functional theory to optimize the GB interfacial structure for one GB misorientation in CeO₂. This study further develops our understanding of high solute GB composition enabling the development of methods such as selective doping to improve macroscopic ionic conductivity for both the grain and GB.

To understand the key factors which influence GB properties, spin-polarized density functional theory calculations were performed using VASP[1] within the generalized gradient approximation (GGA)[2,3] with the Perdew-Burke-Ernzerhof exchange correlation functional. The strong correlation effects were treated with the Hubbard U correction (GGA+U) formulated by Dudarev et. al.[4]. The GB structures are doped with a local GB solute concentration of 0%, 20%, and 40%. The local bond strain, coordination, electronic structure, and thermodynamic energies are computed for each distinct substitutional solute location at the GB core. The oxygen vacancy binding energy along a few select [0,0,1] paths are computed to assess how changes in the local GB composition impacts the potential energy landscape for oxygen migration. This study further develops our understanding of the interplay between nanoscale GB composition and structure with high solute concentrations enabling the development of methods such as selective doping to improve macroscopic ionic conductivity.
conductivity for both the grain and GB.

References
5. We gratefully acknowledge ASU’s HPC staff for support and assistance with computing resources along with the Extreme Science and Engineering Discovery Environment (XSEDE). We also acknowledge the National Science Foundation grant DMR-1308085 for funding.

6:15 AM S.CT05.04.08
Atomic-Scale Simulation of Defects and Thermophysical Properties in Actinide Mixed Oxides Paul C. Fossati1, Conor O. Galvin2, Patrick A. Burr2, Michael W. Cooper3 and Robin W. Grimes4; 1CEA, France; 2University of New South Wales, Australia; 3Los Alamos National Laboratory, United States; 4Imperial College London, United Kingdom

Defects are known to play an important role in several thermophysical properties of actinide oxides, from ionic self-diffusion to heat transport. Point defects are also related to high-temperature superionic transitions observed with many single actinide oxides and mixed oxides (MOX).

Recent advances in potential development have enabled accurate molecular dynamics (MD) simulations of a broad range of actinide oxide compositions, and have been shown to reproduce defects properties well. This has been used in this work to investigate the effect of defects populations on thermophysical properties such as elastic constants and vibrational properties of several mixed oxides containing U, Pu, and Th. Both the low-temperature fluorite structure and the high-temperature superionic phase have been considered. These results are important to improve our understanding of the behaviour and high-temperature thermodynamics of actinide oxides beyond the superionic transition.

6:30 AM S.CT05.04.09
Locating Facile Oxygen Vacancy Creation and Annihilation Sites on CeO2 Nanoparticle Surfaces Ethan L. Lawrence, Barnaby D. Levin, Tara M. Boland, Shery Chang and Peter A. Crozier; Arizona State University, United States

Reducible oxides can be employed in solid oxide fuel cell anodes and cathodes largely because their redox properties enable fuel oxidation and oxygen exchange [1]. These processes involve creation and annihilation of oxygen vacancies at the surface and transport through the bulk. Here, we show that electron microscopy can be employed to identify the most active sites for vacancy creation/annihilation on the surface of CeO2 (ceria). Under reducing conditions, ceria releases oxygen through the formation of an oxygen vacancy coupled with a cation transition from Ce4+ to Ce3+. Moreover, a lattice expansion (~0.2-0.3 Å) occurs once oxygen vacancies are created on CeO2 surfaces [2]. The relative ease with which oxygen vacancies are created/annihilated on CeO2 is strongly dependent on particle surface structure, and theoretical calculations have predicted significant variations in activation energies for lattice oxygen removal at different surface sites, which is likely to be associated with orders of magnitude differences in local oxygen exchange rates [3]. We are interested in probing and correlating local exchange activity with atomic surface structure and have used time-resolved aberration-corrected transmission electron microscopy (AC-TEM) to observe and analyze dynamic atomic-level cation displacements associated with oxygen vacancy creation and annihilation.

A FEI Titan AC-TEM equipped with a Gatan K2 IS direct detection camera (with high detective quantum efficiency) was used to image CeO2 nanocubes at 40 frames/second and 5000 e/(Å²·s). Ce atomic column displacements were analyzed with picometer precision over time-resolved image sequences using MATLAB codes. By monitoring the frequency of cation displacements at a surface, a local indicator of activation energy for oxygen vacancy creation was obtained. A considerable degree of diversity and heterogeneity in the type of surface sites that show high activity was observed, with low coordination number sites such as steps and edges, as well as locally strained sites, exhibiting the highest displacement frequency and therefore enhanced oxygen exchange activity. Our approach directly links atomic surface structure to vacancy creation, indicating that the ability to quantitatively characterize nanoparticle surfaces to locate active sites can contribute to understanding and tailoring their exchange properties.

Acknowledgements
We acknowledge support of NSF grant DMR-1308085, the use of ASU’s John M. Cowley Center for High Resolution
Fluorite-based nanostructured oxides are promising materials for wide-ranging applications. In these applications, due to the reduced dimensions, surfaces and interfaces play a critical role in influencing novel functionalities. In nanostructured oxides, defects are ubiquitous at surfaces, grain boundaries, and heterointerfaces. The interaction of defects with such structural anomalies are often found to dictate the atomic-scale structure and correlated properties of oxides. Based on atomistic simulations, we elucidate the influence of defects on structure and properties in three different cases – (i) Misfit dislocations in CeO$_2$/MgO heterostructures: We find that dopant–defect complexes at misfit dislocations have extended stability revealing that they would influence ionic transport at heterointerfaces of fluoride-structured thin film electrolytes. (ii) Grain boundaries in nanocrystalline doped CeO$_2$: We find that segregation energies, availability of favorable sites, and overall stronger binding of dopant–defect complexes would influence ionic transport across grain boundaries in nanocrystalline doped ceria. (iii) Steps and trenches at low-index surfaces of pyrochlores oxides: We find that one fundamental mechanism to eliminate the surface dipole in pyrochlores is the formation of structural defects such as steps and trenches, which explain the enhanced reactivity and extraordinary surface-driven properties of pyrochlores. Overall, our results shed light on the complex interplay between defects and structural anomalies, and assist in disentangling the multifaceted role of defects in fluorite-based nanostructured oxides.

The surface strain of oxide nanoparticles plays a crucial role in tuning a materials’ properties [1]. For example, surface strain can regulate and control surface diffusion processes and can change the ability of the surface atoms to bond with adsorbates and thus modify the reactivity of a material [2]. In reducible oxides such as CeO$_2$, the degree of strain can be tuned by different means such as particle size, shape, non-stoichiometry, structural deformations (e.g. oxygen vacancies) etc. A critical step in understanding the properties of nanoparticle surfaces is to measure the surface strain on different crystal facets and in the vicinity of surface defects. We have developed a method to determine the surface strain in oxide nanoparticles with atomic resolution using high resolution transmission electron microscopy (HRTEM). In a typical TEM image, the signal from the heavier Ce atomic columns is much stronger than the signal from the lighter oxygen columns. Consequently, more precise measurements can be made on the cation sublattice in order to map the strain on or near the nanoparticle surface. CeO$_2$ nanoparticles were synthesized by the hydrothermal method [4] and imaged using negative Cs imaging in a FEI Titan AC-ETEM with a single-electron-detection K2 camera operated in the counting mode. The K2 camera allowed high quality electron imaging to be performed. (111), (110), and (100) CeO$_2$ nanoparticle surfaces were imaged in a [110] projection at 5000 e$^-$/Å$^2$/s$^{-1}$ with Ce and O atomic columns visible at the surface. Custom written MATLAB codes are used to identify and determine the positions of atomic columns. Atomic resolution strain maps were created to visualize cation sublattice deformations at different locations in the nanoparticle. The bulk of the nanoparticle is relatively strain free, but the surfaces show varying degrees of compressive and tensile strain along different crystallographic directions of the nanoparticle. The surface strain field varies in a complicated fashion with the highest tensile and compressive strains along different directions occurring at different points on the surface. The highest degree of strain is associated with defects such as step sites. These local strain fields on CeO$_2$ nanoparticle surfaces are correlated with local activity for oxygen vacancy creation and annihilation.

References:
[5] We gratefully acknowledge support of NSF grant DMR-1308085, the use of ASU’s John M. Cowley Center for High Resolution Electron Microscopy and use of the K2 IS camera courtesy of Gatan.

7:30 AM *S.CT05.04.14
Deviation of Stoichiometry in Yttria Stabilized Zirconia and Amorphous Zirconia Simon C. Middleburgh1, Michael J. Rushton1, Lee J. Evitts1, Iuliia Ipatova1 and William E. Lee1,2; 1Bangor University, United Kingdom; 2Imperial College London, United Kingdom

Yttria partially stabilized zirconia (ZrO2)x(Y2O3)½-x and amorphous zirconia have been investigated to understand accommodation of excess oxygen into its structure. Yttria stabilized zirconia was investigated experimentally and through atomic scale simulation methods. A new Raman peak was observed after treatment at 840 cm⁻¹, consistent with previous reports of solid state peroxide ions (O2²⁻). This was corroborated using atomic scale simulation based on density functional theory; these also highlighted the near-zero solution enthalpy for excess oxygen in the monoclinic structure via the formation of a peroxide ion defect.

Amorphous zirconia (a-ZrO2) was simulated using a combination of state-of-the-art atomic scale methods. This combination has enabled the complex chemistry of the amorphous system to be efficiently investigated. Notably, the a-ZrO2 system was observed to accommodate excess oxygen readily – through the formation of neutral peroxide (O2²⁻) defects - the same defect observed in the yttria stabilized zirconia system. This has implications not only in the a-ZrO2 system, but also in other systems employing network formers, intermediates and modifiers.

8:00 AM S.CT05.04.16
Operando Visualization of Catalytically Driven Oxygen Transfer at Three-Phase Boundaries on CeO2 Nanoparticles during CO Oxidation Joshua L. Vincent and Peter A. Crozier; Arizona State University, United States

Oxygen transfer is a critical functionality in many technologies involved in automotive exhaust control and clean energy conversion. In these applications, catalytically active metal nanoparticles (e.g., Pt) are typically dispersed on reducible oxides (e.g., fluorite CeO2), since reducible oxides can transfer their lattice oxygen to reactive adsorbates at the metal-support interface, the so-called three-phase boundary [1,2]. Attaining an atomic-level understanding of the catalytically-driven oxygen transfer process is of great interest to the scientific community and is required to design more efficient catalysts. This work employs aberration-corrected environmental transmission electron microscopy (ETEM) to investigate the atomic-scale structural dynamics that occur at the Pt/CeO2 three-phase boundary under reaction conditions (i.e., in situ) and during catalysis (i.e., operando).

Nanostructured CeO2 cubes and rods were synthesized, loaded with 17 wt.% Pt nanoparticles (NPs), and used as model systems. An ISRI RIG-150 microreactor coupled to a Varian 450 gas chromatograph was used to characterize the CO oxidation performance of the catalysts. An image-corrected FEI Titan ETEM was used to visualize the atomic structures that form under reaction conditions. Modified specimen preparation techniques and in situ electron energy-loss spectroscopy (EELS) was implemented to track the gas composition during catalysis [3,4]. In this way it became possible to correlate active site dynamics with catalytic turnover frequency (TOF) for CO oxidation. It was observed that as the TOF increases, frequent oxygen transfer disrupts the bonds that anchor the ~2 nm Pt nanoparticles, leading to dynamic reconfigurations of the entire nanoparticles and their translational motion ~2-5 Å across the support. Interestingly, proximal Ce surface structures up to ~1 nm away from the Pt/CeO2 interface undergo concurrent dynamics, which is consistent with a Mars-van Krevelen mediated interfacial oxygen transfer process.

An additional investigation was done by coupling a high frame-rate direct electron detector to the ETEM, which enabled the transient dynamic behavior to be observed at higher time resolution (25 milliseconds). During this experiment a Pt NP on the (111) surface of a CeO2 rod was observed to restructure dynamically in a 10 mTorr atmosphere of CO and O2, although the same particle was stable in 0.5 mTorr of inert N2. Interestingly, an examination of the time- series in CO and O2 shows the Pt NP undergoes a sequence of structural reconfigurations that correlate with dynamics at interfacial Ce sites. This paper will present results from both experiments [5].

Diffusion in UO₂ nuclear fuel is important for fuel performance, because it connects to key phenomena such as release of fission gas to the plenum, swelling and fuel creep. Fission gas retention and release also impact nuclear fuel performance in indirect ways by, for example, influencing the fuel thermal conductivity. Diffusion coefficients in fluorite UO₂, which here refer to U self-diffusion and fission gas diffusion, are among the properties with highest uncertainty, especially in irradiation environments. This directly translates to fission gas release, swelling and creep predictions. In this talk, we will highlight the development of new mechanistic models for U and Xe diffusion within the grains of UO₂, both under out-of-pile (no irradiation) and in-pile (irradiation) conditions. The models are applied to standard UO₂ as well as to UO₂ fuel doped with Cr. The point defect and Xe-vacancy cluster properties determining the defect concentrations and diffusion rates are calculated using a combination of density functional theory and empirical potential methods. With this data as input, the interaction of point defects under irradiation, leading to the formation of highly mobile Xe-vacancy clusters, is modeled using a methodology labeled free energy cluster dynamics (FECD). As suggested by the name, this method is based on traditional cluster dynamics but with an explicit connection to the free energy representing the driving force of defect reactions. In addition, this model accounts for the non-stoichiometry in UO₂, as governed by the O chemical potential, which strongly influences the diffusion rates by changing the relative equilibrium concentration of U and O vacancies. In order to build confidence in the modeling approach, our predictions are first validated against experiments for U self-diffusion. Good agreement is found for intrinsic diffusion, but some discrepancies emerge under irradiation, which we speculate may be related to sample non-stoichiometry. Application of the methodology to simulations of Xe diffusion shows that at high temperature and fission rate are in good agreement with experimental data. Next, this model is adapted to Cr-doped UO₂ to predict the Xe diffusion rate. The Xe diffusivity increases compared to standard UO₂, both at high and intermediate temperatures, while there is no effect at low temperatures where atomic mixing dominates. Finally, the importance of interstitial U and O clusters will be discussed in the context of rapid diffusion mechanisms, recombination rates and dislocation loop formation.
replacement for CIGS, but efficiency improvement has been hindered by adverse defect characteristics (band tailing and deep defects), in part due to the similarity in chemistry among component metals and associated anti-site disordering. This talk will discuss promising emerging alternative multinary chalcogenides based on earth-abundant Cu₂BaSn(S,Se)₄ (CBTS) as an example, which offer similarities to CZTS in terms of electronic structure, but with introduced atomic size and coordination preference differences that reduce likelihood of atomic disordering—i.e., the much larger Ba ion, occupying a site that has 8-fold coordination rather than 4-fold (as for Cu, Zn and Sn in CZTS), reduces the probability of anti-site disordering and associated defects [1,2]. Simple solution- and vacuum-based film deposition processes enable fabrication of absorber layers with initial PV device sunlight-to-electricity power conversion efficiencies exceeding 5% for CBTS [3,4] and analogous photoelectrochemical (PEC) cells yielding a stable (over 10 hr) 12 mA/cm² photocurrent at 0 V/RHE [5]. This talk will discuss aspects of defect engineering within this family, as well thoughts on design strategies for expanding the known members of the I₂–II–IV–VI₄ family beyond CBTS (e.g., [6]). If desirable electronic structure tunability associated with a multi-element stoichiometry can be combined with earth-abundant components and control over defect formation, multinary chalcogenides may provide a bright path forward in the quest for high-performance, low-cost and scalable PV and PEC devices.

References:
Several applications to nano/micro-electronics have been reported. Such as patterned magnetic media for a hard disk drive (HDD), light extraction structures of light-emitting diodes (LEDs), organic light-emitting diodes (OLEDs), anti-reflection (AR) structures for displays, metal wire-grid polarizers (WGP), and transparent conductive film (TCF) using nano-meshed metal thin film were demonstrated by these manners. The guided, aligned, or directed self-assembly (DSA) is a key technique, that the larger guides are made by conventional top-down methods then bottom-up self-assembled structures are formed along the guides. The challenges are continuing to fabricate the semiconductor memories. We would explain these potential applications fabricated by self-assembly.

7:30 PM *S.CT07.02.02
A Scalable Micro-Object Assembly and Printing Platform Brad Rupp, Jeng Ping Lu, Anne Plochowietz, Yunda Wang, Dave Biegelesen, Lara Crawford, Sergey Butylkov, Julie Bert, Sourobh Raychaudhuri, Jamie Kalb, Qian Wang, Yu Wang, Pat Maeda and Eugene M. Chow; PARC, United States

Conventional manufacturing is able to assemble products composed of many parts of the size approximately 1mm and above. At the nanometer scale, techniques such as deposition, lithography, and self-assembly are used to make a myriad of heterogeneous products. However, at the mesoscale (1-1000μm) these techniques don’t overlap to produce structures at scale. There is a need for robust and scalable technologies which are able to join structures which can be developed on the micro-scale into large area, heterogeneous assemblies. To address this, we are developing a printing platform which is able to use micro-objects as ink—microLEDs, sensor chips, integrated circuits, micro- and nanoparticles. These objects are dispersed in a dielectric fluid and can be printed similar to a xerographic process, but maintain single object precision and orientation. To do this, an optically-addressed electrostatic actuator array manipulates the particles to move to target locations. From there, an integrated transfer system removes the particles from the assembly platform to be placed on a final substrate while maintaining their relative positioning. This transfer system can either be batch with adhesive transfer, or continuous with a non-contact electrostatic belt. This talk will describe the process in which we are able to rapidly sort, manipulate, orient, assemble, and transfer particles in parallel over a 1-inch wide area. We have demonstrated 1-μm registration, assembly of hundreds of particles in seconds, and roll-to-roll like transfer. With the use of computer vision to aid the assembly process, the technology has the potential to produce highly ordered, custom-patterned, heterogeneous assemblies accurately over a large area much faster than traditional manufacturing techniques while still maintaining fidelity.

7:45 PM *S.CT07.02.01
Stochastic Assembly of microLED Displays Paul J. Schuele; eLux, Inc., United States

Direct emission displays made with inorganic µLEDs can potentially challenge LCD and OLED displays with better performance, efficiency and lifetime. Markets where microLED displays are likely to first appear are large information displays requiring high brightness, home theater applications benefitting from increased dynamic range and automotive displays in which high contrast and reliability are necessary. These displays are made possible by the integration of two mainstream technologies, namely GaN LED developed for general lighting and the large area active matrix backplanes developed for LCD displays.

The unique manufacturing challenge for µLED displays is development of a technology to position and connect millions of small devices with zero defects and low cost. Conventional pick and place tools are capable of positioning µLEDs but the throughput of serial assembly is inadequate while mass-transfer methods have difficulty changing the pixel pitch. To address these challenges eLux has developed a massively parallel fluidic assembly technology which positions each µLED by capture of the device in a well structure that also contains the connecting electrodes. Fluidic assembly technology uses simple low-cost equipment to achieve assembly rates up to 50 million µLEDs per hour and it is anticipated that production equipment could assemble an 8K display with 100 million LEDs in a few minutes. The technology is suitable for µLEDs from 10 to 200 μm diameter offering flexibility to make a wide variety of displays with resolutions from 400 to 10 ppi. Similarly, the microLED emitter area can be changed independently of the assembly technique to increase brightness and it is possible to produce displays over 5,000 cd/m2. Fluidic assembly applies relatively low force on the device so brittle materials such as red µLEDs fabricated from AlGaInP can be assembled in the same way as blue and green emitting GaN µLEDs.

A fully integrated manufacturing system for µLED fluidic assembly will ensure that the assembled µLEDs have acceptable performance with special emphasis on eliminating shorted or high resistance devices. Testing and binning used in the general lighting industry are not practical at the micron scale, so wafers are mapped by cathodoluminescence to identify defective µLEDs. Based on the defect map, a selective harvest technique diverts bad µLEDs from the suspension so only known good die are used for assembly. Fluidic assembly relies on an excess of µLEDs to ensure sufficient capture attempts for complete assembly, so it is also necessary to capture, filter and recycle unassembled µLEDs.

With a suitable choice of complementary characteristic for the device and the trap site, it is possible to use fluidic assembly
techniques to position nanowires or nanoparticles as well as µLEDs. The presentation will give an overview of the integration issues with some suggestions for other possible applications and approaches.

8:00 PM *S.CT07.01.01
MicroLED Manufacturing-Specific Issues and Its Manufacturing Solution Ayano Honda, Katsumi Terada, Yoshiyuki Arai and Eiji Mori; Toray Engineering Co., Ltd., Japan

Studies on the manufacture of displays, smartphones, wearable devices, etc. using MicroLED have become active in recent years. Manufacturing process of MicroLED requires a fast pick and place assembly as there are so many MicroLED chips to be placed onto its substrate and wafer. Such placing shall be accurate and reliable and ideally repairable of each individual MicroLED chip as it takes much time to complete sizable panel. However, it has been very difficult to transfer a large number of microchips with high accuracy. In order to achieve solution against such transfer requirement, a large amount of chip transfer technology, inspection technology for detecting defects on microchips, and repair technology are necessary. We have been successful in both the semiconductor and FPD industries as a business area based on the concept of E & M (engineering and manufacturing). To date, we have made a series of processes necessary to manufacture MicroLED displays (to provide a total solution). We have developed the following three types of equipment that apply our core technology such as inspection, bonding, laser process for semiconductor and so on.

1. Non-contact inspection
2. Laser trimming only NG chips based on inspection results
3. MicroLED bonder for high productivity

Especially MicroLED bonder of Toray Engineering Co., Ltd. is enable to place such precise MicroLED chips very fast. In this presentation we will introduce our solution technology for MicroLED manufacturing method.

8:15 PM S.CT07.04.03
Heterogeneous Integration of Silicon Nanoneedles onto Diverse Soft Elastomer Substrates for Enhanced Interaction with Biological System Yale Jeon1, Chi Hwan Lee2,2 and Dong Rip Kim1; 1Hanyang University, Korea (the Republic of); 2Purdue University, United States

Enhanced interaction of nanoscale structures with soft and curvilinear biological systems requires to reduce their large mechanical mismatches at the interface. Recently, successful development of vertically-aligned silicon nanoneedle (SiNN) arrays integrated onto flexible substrates provides a mechanically elastic interface between SiNNs and biological systems to enable their effective interactions, resulting high-efficacy delivery of biomolecules. To create more versatile platforms, transfer printing methods to integrate vertically-aligned SiNN arrays onto diverse, soft and flexible substrates necessitates further development. Here, we introduce two different transfer printing techniques to integrate vertically-aligned SiNN arrays onto diverse soft elastomer substrates for enhanced interaction between SiNNs and biological systems. First, we discuss the swelling-driven transfer printing technique which employs the volume expansion phenomena of elastomers soaked in solvents to controllably break the SiNNs for their transferring from rigid Si substrates to soft and flexible substrates. Second, we develop the double transfer printing method to realize the heterogeneous integration of the vertically-aligned SiNN arrays onto soft and flexible substrates vulnerable to dissolution in solvents. Both methods successfully transfer the targeted nanoscale structures to diverse, soft and flexible substrates that can benefit the enhancement of interaction between nanoscale devices and biological systems for wide applications.

Acknowledgement
This research was supported by the MOTIE (Ministry of Trade, Industry, and Energy) in Korea, under the Fostering Global Talents for Innovative Growth Program (P0008748, Global Human Resource Development for Innovative Design in Robot and Engineering) supervised by the Korea Institute for Advancement of Technology (KIAT)

8:25 PM *S.CT07.07.01
Electronically Integrated, Microscopic Robots Marc Miskin; University of Pennsylvania, United States

Fifty years of microelectronics scaling have opened up new opportunities for building complex robotic systems that are microscopic in size. Electronic, magnetic, and optical systems now offer an unprecedented combination of complexity, small size, and low cost, and could readily be appropriated to form the intelligent core robots that are too small to be resolved by unaided human vision. But one major roadblock exists: there is no micron-scale actuator system that seamlessly integrates
with semiconductor processing and responds to standard electronic control signals. In this talk, I show how to overcome this barrier, enabling a new generation of microscale robots that utilize on-board, integrated silicon electronics. First, I will present a new class of voltage-controllable electrochemical actuators that operate at low voltages (200 mV), low power (10 nW), and are completely compatible with silicon processing. Next, I'll present a full process flow that uses lithographic fabrication and release techniques to build sub-hundred micrometer robots that walk. Every step in this process is performed massively in parallel, producing over one million robots per 4-inch wafer. I'll show that in spite of their small size, microscopic robots are remarkably robust: they can survive harsh chemistries, large changes in temperature, and can even be injected through hypodermic needles. Finally, I will close by showing our first steps towards transforming sophisticated CMOS circuitry into programmable, autonomous robots too small to be seen by the naked eye.

8:40 PM *S.CT07.04.01
Transfer-Printed Microscale LEDs and ICs for High Performance Emissive Displays Christopher A. Bower; X-Celeprint Ltd, United States

Displays that use combinations of microscale LEDs and ICs within each pixel to control and direct light emission have the potential to be colorful, bright, fast and power efficient. High-throughput mass transfer technologies that accurately and cost-effectively integrate large arrays of wafer-fabricated microscale LEDs onto non-native display substrates with high yield are key enablers for microLED displays. Transfer-printing with elastomer stamps is a candidate mass transfer technology for making next generation displays. A variety of displays, including displays driven by transfer-printed microICs, have been designed and fabricated using transfer-printed microscale microLEDs.

SESSION S.CT07.13: Live Keynote II: Micro-Assembly Technologies and Heterogeneous Integration—Fundamentals to Applications
Session Chairs: Brian Corbett and Seok Kim
Sunday Afternoon, November 29, 2020
S.CT07

12:30 PM *S.CT07.03.03
Manipulation and Assembly of Particles Using Acoustic Field Gradient and Electromagnetic Needle Quan Zhou; Aalto University, School of Electrical Engineering, Finland

Robotic instruments are miniature robots and mechatronic systems that can manipulate small objects and precisely interact with different surfaces. In this talk, I will discuss our recent work in robotic instruments for manipulation and assembly using two techniques: 1) acoustic manipulation devices that can automatically manipulate/assembly a large amount of particles on a surface using the field gradient generated by a single acoustic transducer, both in ambient air and submerged; 2) robotic electromagnetic needle that can precisely extract and independently manipulate/assemble magnetic microparticles in the presence of neighboring magnetic particles by contact or contactless.

References:

12:45 PM *S.CT07.07.02
Micro/Milli Robotic Assembly Using Diamagnetic Surfaces Allen Hsu, Annjoe Wong-Foy and Ronald Pelrine; SRI International, United States

As Moore’s law for digital computation reaches its inevitable limits, future advances in system level integration will lead to the next generation of electronics. Approaches such as heterogeneous integration will enable small and high-performance micro-systems (optical and electronic integration or System-In-Package) necessary for the growing consumer areas such as
wearables, the Internet of Things, and Augmented Reality. Beyond electronics, tools and techniques for heterogenous micro-assembly can lead towards new smart materials (i.e. defect-free constructed materials, digitally tailored electro-mechanical active materials with micro-scale properties and macro-scale performance, etc.) and the micro-assembly of biological and soft components.

While there are many research approaches towards tackling heterogenous micro-assembly (i.e. self-assembly, transfer printing, etc.), in this work, we will discuss our approach of directed robotic assembly using micro/milli robots. Directed micro/milli-robotic assembly has some unique advantages over other methods, such as being relative task agnostic and generalizable to various assembly problems. Furthermore, unlike many batch processes that are open-loop, directed micro-robotic assembly can be closed-loop by integration of metrology and material validation during the assembly process. Thereby swarms of micro/milli-robots can parallelize not only micro-assembly but also micro-metrology, enabling a method of overcoming statistical and thermodynamic limitations of conventional approaches.

Inspired by massive swarms of ants or termites assembling macro-scale objects from micro-scale parts, we utilize arrays of magnetic actuators in conjunction with diamagnetic graphite to create a magnetic collective of levitated micro/milli sized magnetic robots with nm level motion precision for 3D micro-assembly. By leveraging diamagnetic levitation, we can reduce factors such as hysteresis and stiction to enable high-precision and repeatable motion of micro/milli-robots. These passively levitated, but electromagnetically steerable micro/milli-robotic platforms can serve many roles: (1) compact high-precision motion platform for the manipulation and delivery of micro-components, (2) high precision sensors, and (3) motion platform for other micro-scaled MEMS sensors and actuators. We will discuss multiple independently controlled robots (mm-sized) with dexterous behavior for assembling carbon fiber trusses and performing micro-assembly and micro-manipulation of 3d microspheres and silicon microparts, as well as some of the control issues for coordinating parallel robotic swarms for micro-assembly. In addition, by using robots cooperatively, we also demonstrate how teams of micro/milli robots can achieve new functionality and enable extremely high densities of independent micro-manipulation as compared to conventional standard robotic solutions.

1:00 PM *S.CT07.01.05
Open Electrodeposition of Stimuli-Responsive Metal Hydroxides/Oxides for Direct Fabrication of Origami Micro-Robots Alfonso H. Ngan, Runni Wu, Kenneth K.W. Kwan, Wenrui Ma and Pingyu Wang; University of Hong Kong, Hong Kong

Flexible origami structures can mimic the complicated motions of small creatures that are otherwise difficult to be achieved by rigid robots with limited degree of motion freedom. However, actuating origami structures in a compact and self-contained way has been a critical challenge. Here, we demonstrate a versatile approach of actuating origami micro-robots, by printing self-folding creases on compliant polymer membrane substrates. The self-folding creases are made of a type of stimuli-responsive transition metal hydroxides/oxides that can undergo large actuation under electrochemical or light stimulations. Direct printing of the stimuli-responsive material via a microfluidic electrochemical writing method at the locations of the creases enables the creases to self-fold independently “on demand”, with folding curvatures exceeding 1 mm^{-1} under low-intensity visible-light stimulation in ambient conditions, or low-potential electrochemical stimulation in electrolytic environments, with response time as fast as in seconds. Based on the high performance of such active creases, complex miniaturized origami designs powered by hinges activated in an independently controllable way are demonstrated, including self-folding Miura and a full micro-robotic hand with independently programmable finger joints. These results prove a new, versatile paradigm for micro-robotics, where a transferrable approach is applicable to design and fabricate a wide variety of customizable micro-robots with compact construction and complex motions using different stimuli-responsive ceramic-based materials.

1:15 PM *S.CT07.06.01
Extreme Miniaturization of Passive Electronic Components by Strain-Induced Self-Rolled-Up Membrane Nanotechnology Zhendong Yang, Mark Kraman, Derek Wood, Jialiang Zhang, Julian Arthur Michaels, Apratim Khandelwal and Xiuling Li; University of Illinois at Urbana-Champaign, United States

Complex 3D structures enable advanced functionalities that are otherwise out of reach. However, processing issues such as mechanical stability, conformity, alignment, as well as cost, are challenging to address. The overarching physical principle of the Self-Rolled-up Membrane (S-RuM) nanotechnology is strain-driven spontaneous deformation of 2D membranes into 3D architectures. It opens up a new paradigm to achieve 3D functional hierarchical architectures without the difficulties of processing in 3D, and promises to break the constraints of size, weight, and performance of many types of devices. In this talk, we demonstrate S-RuM inductors, transformers, capacitors, and filters with > 10X smaller footprint and unique
performance characteristics, through global and local strain engineering and material hierarchical integration.

1:30 PM *S.CT07.01.03

In Situ Investigation of Mechanisms Underlying Material Synthesis and Processing Dongsheng Li and Miao Song; Pacific Northwest National Laboratory, United States

Understanding the mechanisms of material structures forming processes enables the design and fabrication of structures with improved or tailored properties. The objective of our work is to investigate the mechanisms underlying materials synthesis and processing, including crystal growth, particle self-assembly, and phase transformation, etc., and thus to tune the structures and functions of materials.

For example, particle aggregation, such as oriented attachment, is accepted as a common pathway and leads to well-organized structures and twin interfaces that possess unique or improved properties. However, many fundamental aspects remain unknown, such as the interplay of structures and factors that control them. Here we use in situ transmission electron microscopy and atomic force microscopy to directly observe process of materials synthesis and processing, such as particle assembly and phase transformation. Integrating theoretical calculations and simulations, we revealed the orientation-dependent attachments of particles, interfacial structures, and the factors that affect them, such as temperature, pH, ionic strength, particle shapes, and solvents, etc. In addition, we also demonstrated that defects (edge dislocation), induced via oriented attachments, improving photoactivity of TiO2. Phase transformation and its role in materials functions are also investigated. The specific systems that we investigate are metal (Ag and Au), oxides (TiO2), and minerals (mica), etc. The work provides a deep understanding of mechanisms of materials synthesis and processing and thus provides a guide to design and fabricate the morphologies and structures, which are closely related to material properties and functions.

1:45 PM S.CT07.03.01

A Sono-Assisted Dry Dip Coating Method for Ultra-Fast Nanomaterials Assembly on PDMS Substrate Dong Zhou and Bo Li; Villanova University, United States

While dip coating is a widely used solution-based assembly method to achieve large scale assembly of nanomaterials, its integration with the flexible substrate is hindered by the difficulty to choose a good wetting system of solvent, nanomaterials and polymer substrate. The good wetting solvent may swell or even dissolve the polymer substrate. Here, to the contrary, we utilize the hydrophobic nature of a Polydimethylsiloxane (PDMS) substrate and nanomaterials (e.g., graphene) and create a “dry” dip coating method by choosing water as the solvent. Unlike the traditional dip coating method, there are two important innovations. First, the dip coating speed can reach 5.4 m/min (in comparison with 0.001-0.2 m/min for commercial dip coater) because solvent evaporation is required. A dry substrate with assembly nanomaterial is removed from the solution because water does not wet PDMS and nanomaterials. Second, a weak sono field is applied to the solution during the dip coating process to significantly speed up the assembly process and maintain the disperse status of nanomaterials. The principle can be generalized to a wide range of nanomaterials such as carbon black, carbon nanotube, and two-dimensional materials (graphene, MoS2, and h-BN). The film thickness can be controlled through dip coating times and solution concentration. This strategy can be further integrated with microfabrication processes such as lithography to manufacture arrays of hybrid multilayer devices with different nanomaterials. As a proof-of-concept, strain sensor, electromagnetic interference (EMI) shielding coating, and multilayer capacitor are demonstrated. This ultra-fast dry dip coating strategy paves the way towards affordable flexible devices.
placed onto its substrate and wafer. Such placing shall be accurate and reliable and ideally repairable of each individual MicroLED chip as it takes much time to complete sizable panel. However, it has been very difficult to transfer a large number of microchips with high accuracy. In order to achieve solution against such transfer requirement, a large amount of chip transfer technology, inspection technology for detecting defects on microchips, and repair technology are necessary. We have been successful in both the semiconductor and FPD industries as a business area based on the concept of E & M (engineering and manufacturing).

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1. Non-contact inspection
2. Laser trimming only NG chips based on inspection results
3. MicroLED bonder for high productivity
Especially MicroLED bonder of Toray Engineering Co., Ltd. is enable to place such precise MicroLED chips very fast. In this presentation we will introduce our solution technology for MicroLED manufacturing method.

5:30 AM S.CT07.01.03
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6:00 AM S.CT07.01.04
Liquid Crystalline Behavior of LaPO4 Nanorods in Apolar Solvent Jeongmo Kim, Khalid Lahlil, Jongwook Kim and Thierry Gacoin; Ecole Polytechnique, Institut Polytechnique de Paris, France

Concentrated suspensions of colloidal nanorods can exhibit liquid crystalline (LC) behavior: spontaneous and reversible assembly of nanorods into orientationally ordered nematic phase. Considering to Onsager’s theory predicting the rod concentration threshold (Φ) where the isotropic-to-nematic phase transition occurs, the increased effective radius of charge-stabilized rods can significantly reduce Φ compared to the same rods that are stabilized sterically[i]. This has allowed to prepare relatively dilute colloidal LCs (Φ < 5 vol%) with strongly charged LaPO4 nanorods in polar media[ii]. However, we recently observed a contradictory phenomenon where the ligand stabilized LaPO4 nanorods in apolar media self-assemble into a nematic phase at even lower Φ near 0.5 vol% while the theoretically estimated Φ is 17%. Moreover, Φ varies with the concentration of additional surfactants in a similar way as in polar media when increasing a salt concentration leads to surface charge screening. This observation suggests that the ligand-functionalized surface of nanorods may still be partially charged and thus contributes to a largely extended Debye length (effective radius of rods) when suspended in apolar media with low dielectric constants. Such colloidal systems, both sterically and electrostatically stabilized, have an intriguing potential for exquisitely controlling the dynamics of charged colloids avoiding the common problem of aggregation. We present the LC behavior of the dilute nanorod suspension, their control under external electric field, and the impact of the amphiphilic surfactants on phenomena associated to electrostatic surface charging in apolar media.

**6:15 AM *S.CT07.01.05**

Open Electrodeposition of Stimuli-Responsive Metal Hydroxides/Oxides for Direct Fabrication of Origami Micro-Robots

Alfonso H. Ngan, Runni Wu, Kenneth K.W. Kwan, Wenrui Ma and Pingyu Wang; University of Hong Kong, Hong Kong

Flexible origami structures can mimic the complicated motions of small creatures that are otherwise difficult to be achieved by rigid robots with limited degree of motion freedom. However, actuating origami structures in a compact and self-contained way has been a critical challenge. Here, we demonstrate a versatile approach of actuating origami micro-robots, by printing self-folding creases on compliant polymer membrane substrates. The self-folding creases are made of a type of stimuli-responsive transition metal hydroxides/oxides that can undergo large actuation under electrochemical or light stimulations. Direct printing of the stimuli-responsive material via a microfluidic electrochemical writing method at the locations of the creases enables the creases to self-fold independently “on demand”, with folding curvatures exceeding 1 mm under low-intensity visible-light stimulation in ambient conditions, or low-potential electrochemical stimulation in electrolytic environments, with response time as fast as in seconds. Based on the high performance of such active creases, complex miniaturized origami designs powered by hinges activated in an independently controllable way are demonstrated, including self-folding Miura and a full micro-robotic hand with independently programmable finger joints. These results prove a new, versatile paradigm for micro-robotics, where a transferrable approach is applicable to design and fabricate a wide variety of customizable micro-robots with compact construction and complex motions using different stimuli-responsive ceramic-based materials.

**6:45 AM S.CT07.01.08**

High Symmetry Ordered Multigrain Nanocrystals to Reveal and Maximize the Effect of Grain Boundary Defects

Myounghwan Oh; Lawrence Berkeley National Laboratory, United States

Grain boundary defects-topological defects around grain boundaries (GB)-play an essential role in the optoelectronic, magnetic, mechanical, and chemical properties of the polycrystalline materials. When the grain size of the materials decreases to the nanometer scale, the grain boundary defects predominantly determine those properties, opening up a variety of new applications. Although researchers have sought ways to study the contribution of specific grain boundary defects to the properties, non-uniformity in grain size and shape and random misorientation between the grains make these tasks challenging. This presentation will first discuss controlling 3D heteroepitaxy of colloidal faceted nanocrystals to grow uniform multiple grains organized into a well-defined geometry, which gives a new opportunity for overcoming such limitations from the non-uniformity and randomness. Within the resulting nanocrystals, we will see that the 3D patterned strain field exists in the form of disclinations and dislocations. We will then discuss how we can apply the 3D heteroepitaxy to investigate the effect of microscopic grain geometry on the macroscopic properties. For example, we can obtain a correlation between the GB defects and the catalytic property, because the patterned strain creates exact GB structure in a periodic fashion that serves as the active sites for catalysis. Lastly, we will highlight that the epitaxy-based design principles can significantly extend the library of grain structures in the nanocrystalline materials.

**5:00 AM S.CT07.02: Micro Self-Assembly**

Stochastic Assembly of microLED Displays

Paul J. Schuele; eLux, Inc., United States

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The unique manufacturing challenge for µLED displays is development of a technology to position and connect millions of
small devices with zero defects and low cost. Conventional pick and place tools are capable of positioning µLEDs but the throughput of serial assembly is inadequate while mass-transfer methods have difficulty changing the pixel pitch. To address these challenges eLux has developed a massively parallel fluidic assembly technology which positions each µLED by capture of the device in a well structure that also contains the connecting electrodes. Fluidic assembly technology uses simple low-cost equipment to achieve assembly rates up to 50 million µLEDs per hour and it is anticipated that production equipment could assemble an 8K display with 100 million LEDs in a few minutes. The technology is suitable for µLEDs from 10 to 200 µm diameter offering flexibility to make a wide variety of displays with resolutions from 400 to 10 ppi. Similarly, the microLED emitter area can be changed independently of the assembly technique to increase brightness and it is possible to produce displays over 5,000 cd/m². Fluidic assembly applies relatively low force on the device so brittle materials such as red µLEDs fabricated from AlGaInP can be assembled in the same way as blue and green emitting GaN µLEDs.

A fully integrated manufacturing system for µLED fluidic assembly will ensure that the assembled µLEDs have acceptable performance with special emphasis on eliminating shorted or high resistance devices. Testing and binning used in the general lighting industry are not practical at the micron scale, so wafers are mapped by cathodoluminescence to identify defective µLEDs. Based on the defect map, a selective harvest technique diverts bad µLEDs from the suspension so only known good die are used for assembly. Fluidic assembly relies on an excess of µLEDs to ensure sufficient capture attempts for complete assembly, so it is also necessary to capture, filter and recycle unassembled µLEDs. With a suitable choice of complementary characteristic for the device and the trap site, it is possible to use fluidic assembly techniques to position nanowires or nanoparticles as well as µLEDs. The presentation will give an overview of the integration issues with some suggestions for other possible applications and approaches.

5:30 AM S.CT07.02.02
A Scalable Micro-Object Assembly and Printing Platform Brad Rupp, Jeng Ping Lu, Anne Plochowitz, Yunda Wang, Dave Biegelsen, Lara Crawford, Sergey Butylkov, Julie Bert, Sourobh Raychaudhuri, Jamie Kalb, Qian Wang, Yu Wang, Pat Maeda and Eugene M. Chow; PARC, United States

Conventional manufacturing is able to assemble products composed of many parts of the size approximately 1mm and above. At the nanometer scale, techniques such as deposition, lithography, and self-assembly are used to make a myriad of heterogeneous products. However, at the mesoscale (1-1000µm) these techniques don’t overlap to produce structures at scale. There is a need for robust and scalable technologies which are able to join structures which can be developed on the micro-scale into large area, heterogeneous assemblies. To address this, we are developing a printing platform which is able to use micro-objects as ink—microLEDs, sensor chips, integrated circuits, micro- and nanoparticles. These objects are dispersed in a dielectric fluid and can be printed similar to a xerographic process, but maintain single object precision and orientation. To do this, an optically-addressed electrostatic actuator array manipulates the particles to move to target locations. From there, an integrated transfer system removes the particles from the assembly platform to be placed on a final substrate while maintaining their relative positioning. This transfer system can either be batch with adhesive transfer, or continuous with a non-contact electrostatic belt. This talk will describe the process in which we are able to rapidly sort, manipulate, orient, assemble, and transfer particles in parallel over a 1-inch wide area. We have demonstrated 1-µm registration, assembly of hundreds of particles in seconds, and roll-to-roll like transfer. With the use of computer vision to aid the assembly process, the technology has the potential to produce highly ordered, custom-patterned, heterogeneous assemblies accurately over a large area much faster than traditional manufacturing techniques while still maintaining fidelity.

6:00 AM S.CT07.02.04
Heterostructures of Layered Carbon Nanocomposites and Engineered Resonator Array Structures for Wide-Band Electromagnetic Shielding Vivek Kale, Shravani Kale, Shankar Gaware and Sangeeta N. Kale; Defence Institute of Advanced Technology, India

Radar technology is a field in which the measures (and hence the counter-measures) are continuously emerging. Constant vigilance on the air borders require stringent performance of the Radar stations and hence the counter measures are required to be developed using either the improved engineered structures of aircrafts or improved materials (which could be coated on the body of the aircrafts). A combination of both these approaches would yield much smarter and effective approach. Micro-assembled, engineered thin film structures of silver arrays have been used along with different carbon nanocomposite thin films on flexible substrates for shielding the X-Band (8.2 GHz to 12.4 GHz) Radar range of the electromagnetic spectrum. In this presentation, we discuss on synthesis of flexible thin films of silver arrays of split ring resonators, with varied unit cell dimensions, which are deposited using standard micro-printing technology. These layers are stacked with carbon nanocomposite films (either of multiwalled carbon nanotubes (MWCNTs), graphene sheets and carbon conducting ink; in Polyvinyl dimethyl fluoride / polyacrylonitrile matrix) to obtain wide band electromagnetic shielding.
Nanocomposites were synthesised using standard chemical methods and thin films were synthesised using dip-coating method. The sandwiched (2 layers of nanocomposites and one layer of resonator array) was packed using hydraulic press and standard lamination technique to yield a compact flexible film, which can be inserted in the X-Band wave guide for further testing. Vector Network Analyser was used for further studies of absorption. Shielding in entire X-band with the power loss of $27 \text{ dB}$ ($99.98 \%$ loss) and a minimum of $21 \text{ dB}$ ($99.92 \%$ loss) is demonstrated here, for MWCNT. Similar results for other carbon composites are discussed in this presentation. A strong interplay of carbon nanocomposites with the array of L-C-R equivalent resonators of varied resonant frequencies shows concomitant suppression in the incident electromagnetic power; the results supported by simulation (CST Microwave Studio) studies as well. This work opens up a strategy to obtain wide band shielding using a combination of optimised nanomaterial composites, heterostructured with engineered metallic resonators.

SESSION S.CT07.03: Interactions in Assembling

On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

5:00 AM S.CT07.03.01
A Sono-Assisted Dry Dip Coating Method for Ultra-Fast Nanomaterials Assembly on PDMS Substrate Dong Zhou and Bo Li; Villanova University, United States

While dip coating is a widely used solution-based assembly method to achieve large scale assembly of nanomaterials, its integration with the flexible substrate is hindered by the difficulty to choose a good wetting system of solvent, nanomaterials and polymer substrate. The good wetting solvent may swell or even dissolve the polymer substrate. Here, to the contrary, we utilize the hydrophobic nature of a Polydimethylsiloxane (PDMS) substrate and nanomaterials (e.g., graphene) and create a “dry” dip coating method by choosing water as the solvent. Unlike the traditional dip coating method, there are two important innovations. First, the dip coating speed can reach $5.4 \text{ m/min}$ (in comparison with $0.001-0.2 \text{ m/min}$ for commercial dip coater) because solvent evaporation is required. A dry substrate with assembly nanomaterial is removed from the solution because water does not wet PDMS and nanomaterials. Second, a weak sono field is applied to the solution during the dip coating process to significantly speed up the assembly process and maintain the disperse status of nanomaterials. The principle can be generalized to a wide range of nanomaterials such as carbon black, carbon nanotube, and two-dimensional materials (graphene, MoS$_2$, and h-BN). The film thickness can be controlled through dip coating times and solution concentration. This strategy can be further integrated with microfabrication processes such as lithography to manufacture arrays of hybrid multilayer devices with different nanomaterials. As a proof-of-concept, strain sensor, electromagnetic interference (EMI) shielding coating, and multilayer capacitor are demonstrated. This ultra-fast dry dip coating strategy paves the way towards affordable flexible devices.

5:15 AM S.CT07.03.02
Light Induced Self-Writing and Phase Separation in Monomer-Nanoparticle Mixtures Shreyas Pathreeker, Fu-Hao Chen, Saeid Biria and Ian D. Hosein; Syracuse University, United States

We report direct fabrication of nanoparticle-polymer composite microstructures via a novel light-induced self-writing approach. Light-induced self-writing is an optical phenomenon wherein a light beam permanently inscribes ‘channels’ or ‘fibers’ across the depth of a photo-reactive medium. Self-writing is a scalable, safe and rapid technique that offers a direct single-step route for precise fabrication of polymer composite structures. Herein, we investigated the organization of nanoparticles during light-induced self-writing to assess feasibility of control over composite morphology, as core-shell and nanoparticle embedded structures have found use in various applications such as anodes for secondary batteries, as chemical sensors, and MEMS. By varying the light intensity and beam size employed in self-writing, the photopolymerization kinetics and path length of nanoparticle diffusion can be controlled, which enables directed assembly of nanoparticles and tunable morphology. In this work, a mixture of Silicon nanoparticles in an acrylate type monomer was used to self-write vertically aligned composite pillar-like structures that were then pyrolysed to obtain Carbon/Silicon structures. Use of these structures as an anode for Li-storage is examined. Scanning electron microscopy, X-ray diffraction and Raman spectroscopy were used to characterize morphology and composition of the structures, and other monomer-nanoparticle mixtures are under investigation. This work provides a novel technique to fabricate microscale architectures for energy storage applications and explores ways to control structure morphology by varying photopolymerization process parameters.
5:30 AM S.CT07.03.03
Manipulation and Assembly of Particles Using Acoustic Field Gradient and Electromagnetic Needle Quan Zhou; Aalto University, School of Electrical Engineering, Finland

Robotic instruments are miniature robots and mechatronic systems that can manipulate small objects and precisely interact with different surfaces. In this talk, I will discuss our recent work in robotic instruments for manipulation and assembly using two techniques: 1) acoustic manipulation devices that can automatically manipulate/assembly a large amount of particles on a surface using the field gradient generated by a single acoustic transducer, both in ambient air and submerged; 2) robotic electromagnetic needle that can precisely extract and independently manipulate/assemble magnetic microparticles in the presence of neighboring magnetic particles by contact or contactless.

References:

6:00 AM S.CT07.03.04
Assembly of Thick Nanoparticle Films via Electrophoretic Deposition Prabal Tiwari, Noah D. Ferson and Jennifer Andrew; University of Florida, United States

Materials scientists have been fabricating nanomaterials with unique functionalities for decades. However, there remains a need to develop tools to assemble these materials into devices. To date, there are a variety of assembly techniques that utilize electric fields, magnetic fields, inertial forces, capillary forces, as well as robotic pick and place methods to obtain the desired structure. Among these techniques, electrophoretic deposition (EPD) has the advantage of being cost-effective, fast, and easy to perform for most material systems and substrate geometries. EPD uses electrophoresis to assemble charged nanomaterials from a suspension onto a substrate. However, EPD is currently limited by the fact that the deposition rate decreases with time, limiting the overall yield and thickness of the resulting material. Previously, this limitation has been attributed to the decrease in both the particle concentration as well as the electric field in the suspension during deposition. But, more recent studies have shown that the electrophoretic mobility of the electrostatically stabilized particles is also decreasing with time. Here, we show that decreasing particle mobility is the most critical factor in determining the EPD yield. To demonstrate this, we used alumina nanoparticles suspended in ethanol as a model system. By monitoring the changes in the pHe (pH in non-aqueous solvents) of the suspension during EPD, we observed the particle mobility of the alumina nanoparticles decreased with time. We also showed that this decrease in particle mobility significantly decreased the deposition rate. To overcome this, we developed a new suspension replenish EPD approach that allows us to maintain near constant particle mobility and particle concentration with time. This suspension replenish method results in a linear increase in the mass of the deposited film with time, overcoming the limitation of decreasing deposition rate in conventional EPD. We also saw a 6x improvement in the thickness of the film compared to the conventional EPD. This approach is applicable to a wide range of materials that can be electrostatically stabilized/charged by the adjustment of the pH of the suspension. Thereby, enabling a path to significantly improve the ability to assemble thick films of nano- and micro- materials.

6:15 AM S.CT07.03.05
Carbon Nanotube Alignment Dynamics Under Electric Fields in Different Solutions Atiqur Rahman and Ahmed Zubair; Bangladesh University of Engineering and Technology, Bangladesh

Controlled macroscopic assembly of carbon nanotubes (CNTs) while preserving their excellent optoelectronic properties still remain a key challenge. Here, we investigated the molecular dynamics of single-wall carbon nanotube (SWCNT) alignment inside various viscous media under electric fields. An analytical model based on dielectrophoresis induced torque considering the viscosity and conductivity of the medium was used to obtain molecular dynamics of the SWCNTs. An alternating current electric field was applied to a liquid solution of SWCNT containing several solvents/surfactants such as DIW, DMF, DPSF, SDS, and DOC. The time required for the SWCNTs to get aligned to the applied AC electric field was calculated for different initial conditions for all the solutions. The effects of CNT length, CNT diameter, and frequency of the electric field on the SWCNT network formation were theoretically studied. Longer and thinner SWCNTs prompted to faster alignment in the
SWCNT network. Furthermore, the effect of the concentration of surfactant on arrangement time was examined. Slower SWCNT alignment was observed in medium with higher viscosity. The findings of this report will be helpful for establishing an effective technique of producing large-scale aligned CNT films for diverse applications.

SESSION S.CT07.04: Transfer Printing
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-CT07

5:00 AM *S.CT07.04.01
Transfer-Printed Microscale LEDs and ICs for High Performance Emissive Displays Christopher A. Bower; X-Celeprint Ltd, United States

Displays that use combinations of microscale LEDs and ICs within each pixel to control and direct light emission have the potential to be colorful, bright, fast and power efficient. High-throughput mass transfer technologies that accurately and cost-effectively integrate large arrays of wafer-fabricated microscale LEDs onto non-native display substrates with high yield are key enablers for microLED displays. Transfer-printing with elastomer stamps is a candidate mass transfer technology for making next generation displays. A variety of displays, including displays driven by transfer-printed microICs, have been designed and fabricated using transfer-printed microscale microLEDs.

5:30 AM S.CT07.04.02
Transfer Print Integration of InP to Si for Photonic Integrated Circuits Fatih Atar, Thomas S. Wilhelm, James O'Callaghan, Agnieszka Gocalinska, Emanuele Pelucchi and Brian Corbett; University College Cork, Ireland

Indium Phosphide based materials are essential for realisation of lasers, modulators and detectors operating in the 1300 nm to 1600 nm range enabling widespread applications in telecommunications, data communications and sensing. The material structure for different devices are different expensive resulting in expensive components. With the emergence of silicon photonics (SiPh) as a platform for integrated photonics there is an urgent practical need to identify a scalable integration technology that can combine the unique functionality provided by InP with the routing and electronic capability enabled by SiPh in a low cost manner. We have developed a heterogeneous integration approach by using micro-transfer printing of InP devices to Si using either direct bonding or by using a thin intermediate adhesive polymer layer. The performance of transferred lasers is equal or superior to those on the native substrate after transfer due to enhanced thermal dissipation through Si. The lasers are coupled to the silicon waveguides either by butt coupling or by evanescent coupling methods. Here, we perform an in-depth study on the adhesion properties of directly bonded InP coupons to Si. Coupons of 1 micron thick InP layer with lateral dimensions of 600 mm x 60 mm are formed by dry etching. The coupons are released from the InP substrate by selective undercut etching of an AlInAs release layer in a FeCl3 solution while being registered and held in place on the substrate by resist tethers. The coupons are picked and transferred to silicon wafers using a PDMS stamp. The silicon has been prepared with different surface treatments to make the surface hydrophobic (HF) or hydrophilic (H2SO4, O2 plasma). Additionally, coupons are transferred to gold coated silicon for potential electrical injection. Following transfer, the resist tethers are removed by an O2 plasma. A high pick and transfer yield is obtained for coupons to all surfaces. Post-print treatments include annealing in different atmospheric environments and under vacuum. The adhesion is assessed by scratch test, acoustic microscopy and Raman spectroscopy. Experiments to perform epitaxy on the transferred coupons will be described.

5:45 AM S.CT07.04.03
Heterogeneous Integration of Silicon Nanoneedles onto Diverse Soft Elastomer Substrates for Enhanced Interaction with Biological System Yale Jeon¹, Chi Hwan Lee²,² and Dong Rip Kim¹; ¹Hanyang University, Korea (the Republic of); ²Purdue University, United States

Enhanced interaction of nanoscale structures with soft and curvilinear biological systems requires to reduce their large mechanical mismatches at the interface. Recently, successful development of vertically-aligned silicon nanoneedle (SiNN) arrays integrated onto flexible substrates provides a mechanically elastic interface between SiNNs and biological systems to enable their effective interactions, resulting high-efficacy delivery of biomolecules. To create more versatile platforms, transfer printing methods to integrate vertically-aligned SiNN arrays onto diverse, soft and flexible substrates necessitates
further development. Here, we introduce two different transfer printing techniques to integrate vertically-aligned SiNN arrays onto diverse soft elastomer substrates for enhanced interaction between SiNNs and biological systems. First, we discuss the swelling-driven transfer printing technique which employs the volume expansion phenomena of elastomers soaked in solvents to controllably break the SiNNs for their transferring from rigid Si substrates to soft and flexible substrates. Second, we develop the double transfer printing method to realize the heterogeneous integration of the vertically-aligned SiNN arrays onto soft and flexible substrates vulnerable to dissolution in solvents. Both methods successfully transfer the targeted nanoscale structures to diverse, soft and flexible substrates that can benefit the enhancement of interaction between nanoscale devices and biological systems for wide applications.

Acknowledgement
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SESSION S.CT07.05: Heterogeneous Integration Roadmap
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-CT07

5:00 AM S.CT07.05.02
Integration of Inductor with Magnetic Thin Films in Substrate Hongbin Yu and Yanze Wu; Arizona State University, United States

With increasing demand for electronics System on Chip (SoC) and System in Package (SiP) design in many applications, including consumer electronics and automotive electronics, integrated inductor, which is an essential passive component, has been widely used in numerous integrated circuits (ICs) such as voltage regulators and RF circuits, and the pursuit of its heterogeneous integration into various platforms for intended use has attracted intense interest.

There are inductor in package demonstrations or even early product, however, they are either air core without magnetic core materials that render large size yet low inductance density. Other types using close to surface mount type that can incorporate magnetic core materials, that has larger thickness around 1mm, not suitable for low profile, high inductance density in -package applications, where each organic substrate layer can be much thinner in the tens of µm range. There are prior attempts to make low height profile magnetic core materials in in-package inductor applications, yet typically using ferrite that has low relative permeability, and other processing challenges such as temperature restriction.

There have been work of integrating magnetic core inductor on package substrate, without achieving high inductance increase and small foot print, typically with low inductance increase after incorporation of magnetic core materials, typically ferrite that has low permeability. We plan to use high performance magnetic core materials such as CoZrTaB to achieve high inductance density, and low cost integration process.

In this work, soft ferromagnetic core material, for e.g. amorphous Co-Zr-Ta-B, are incorporated into in-package inductors in order to scale down inductors and improve inductors performance in both inductance density and quality factor. Design of the select inductor structure are performed and optimized through electromagnetic simulation; while magnetic film screening and selection for in package application, deposition, as well as characterization of films in both DC and AC modes are carried out.

5:15 AM S.CT07.05.03
Open-Air Plasma-Deposited Silica Films in a Heterogenous Multilayer Barrier for Improved Stability of Moisture Sensitive Devices Oliver Zhao, Yichuan Ding, Ziyi Pan, Nicholas Rolston and Reinhold H. Dauskardt; Stanford University, United States

In order to maintain performance over multiyear lifetimes, many existing and emerging wearable, flexible devices require robust packaging strategies to inhibit water ingress and prevent premature failure. We report on a scalable, open-air plasma process to deposit highly transparent and dense SiO₂ thin film barriers to prevent moisture ingress. Our plasma process is
suitable for direct deposition on thermally sensitive devices and is compatible with flexible, polymeric substrates as shown by 100 cycles of bending tests with a 1.25mm bending radius. Additionally, the open-air plasma process is suitable for large area devices. We show that over a field of view of over 10cm², there is a pinhole density of only 2.67 pinholes/cm². Considering that the deposition process occurs in an open-air system, where there is no regulation of particles in the deposition environment, the low pinhole density confirms the high film quality and is a key reason for its excellent barrier functionality.

We then incorporate the SiO₂ film into a multilayer barrier design comprising heterogenous organic and inorganic layers—all of which are deposited using solely open-air processes—and achieve low water vapor transmission rates on the order of 10⁻³ g/m²/day at an accelerated aging condition of 38°C and 90% relative humidity (RH). When deposited directly onto devices, they retained over 80% of their initial performance for over 660 hours in a 50°C 50%RH accelerated aging environment. The ability of the multilayer barrier to enable device resistance to humid environments is crucial towards realizing longer operating lifetimes of emerging biomedical devices and flexible/wearable electronics.

SESSION S.CT07.06: Advanced Integration and Applications
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
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5:00 AM *S.CT07.06.01
Extreme Miniaturization of Passive Electronic Components by Strain-Induced Self-Rolled-Up Membrane

Nanotechnology Zhendong Yang, Mark Kraman, Derek Wood, Jialiang Zhang, Julian Arthur Michaels, Apratim Khandelwal and Xiuling Li; University of Illinois at Urbana-Champaign, United States

Complex 3D structures enable advanced functionalities that are otherwise out of reach. However, processing issues such as mechanical stability, conformity, alignment, as well as cost, are challenging to address. The overarching physical principle of the Self-Rolled-up Membrane (S-RuM) nanotechnology is strain-driven spontaneous deformation of 2D membranes into 3D architectures. It opens up a new paradigm to achieve 3D functional hierarchical architectures without the difficulties of processing in 3D, and promises to break the constraints of size, weight, and performance of many types of devices. In this talk, we demonstrate S-RuM inductors, transformers, capacitors, and filters with > 10X smaller footprint and unique performance characteristics, through global and local strain engineering and material hierarchical integration.

SESSION S.CT07.07: Heterogeneous Integration for Robotic Motion
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-CT07

5:00 AM *S.CT07.07.01
Electronically Integrated, Microscopic Robots Marc Miskin; University of Pennsylvania, United States

Fifty years of microelectronics scaling have opened up new opportunities for building complex robotic systems that are microscopic in size. Electronic, magnetic, and optical systems now offer an unprecedented combination of complexity, small size, and low cost, and could readily be appropriated to form the intelligent core robots that are too small to be resolved by unaided human vision. But one major roadblock exists: there is no micron-scale actuator system that seamlessly integrates with semiconductor processing and responds to standard electronic control signals. In this talk, I show how to overcome this barrier, enabling a new generation of microscale robots that utilize on-board, integrated silicon electronics. First, I will present a new class of voltage-controllable electrochemical actuators that operate at low voltages (200 mV), low power (10 nW), and are completely compatible with silicon processing. Next, I'll present a full process flow that uses lithographic fabrication and release techniques to build sub-hundred micrometer robots that walk. Every step in this process is performed massively in parallel, producing over one million robots per 4-inch wafer. I'll show that in spite of their small size, microscopic robots are remarkably robust: they can survive harsh chemistries, large changes in temperature, and can even be...
injected through hypodermic needles. Finally, I will close by showing our first steps towards transforming sophisticated CMOS circuitry into programmable, autonomous robots too small to be seen by the naked eye.

5:30 AM *S.CT07.07.02
Micro/Milli Robotic Assembly Using Diamagnetic Surfaces Allen Hsu, Annjoe Wong-Foy and Ronald Pelrine; SRI International, United States

As Moore’s law for digital computation reaches its inevitable limits, future advances in system level integration will lead to the next generation of electronics. Approaches such as heterogeneous integration will enable small and high-performance micro-systems (optical and electronic integration or System-In-Package) necessary for the growing consumer areas such as wearables, the Internet of Things, and Augmented Reality. Beyond electronics, tools and techniques for heterogenous micro-assembly can lead towards new smart materials (i.e. defect-free constructed materials, digitally tailored electro-mechanical active materials with micro-scale properties and macro-scale performance, etc.) and the micro-assembly of biological and soft components.

While there are many research approaches towards tackling heterogenous micro-assembly (i.e. self-assembly, transfer printing, etc.), in this work, we will discuss our approach of directed robotic assembly using micro/milli robots. Directed micro/milli-robotic assembly has some unique advantages over other methods, such as being relative task agnostic and generalizable to various assembly problems. Furthermore, unlike many batch processes that are open-loop, directed micro-robotic assembly can be closed-loop by integration of metrology and material validation during the assembly process. Thereby swarms of micro/milli-robots can parallelize not only micro-assembly but also micro-metrology, enabling a method of overcoming statistical and thermodynamic limitations of conventional approaches.

Inspired by massive swarms of ants or termites assembling macro-scale objects from micro-scale parts, we utilize arrays of magnetic actuators in conjunction with diamagnetic graphite to create a magnetic collective of levitated micro/milli sized magnetic robots with nm level motion precision for 3D micro-assembly. By leveraging diamagnetic levitation, we can reduce factors such as hysteresis and stiction to enable high-precision and repeatable motion of micro/milli-robots. These passively levitated, but electromagnetically steerable micro/milli-robotic platforms can serve many roles: (1) compact high-precision motion platform for the manipulation and delivery of micro-components, (2) high precision sensors, and (3) motion platform for other micro-scale MEMS sensors and actuators. We will discuss multiple independently controlled robots (mm-sized) with dexterous behavior for assembling carbon fiber trusses and performing micro-assembly and micro-manipulation of 3d microspheres and silicon microparts, as well as some of the control issues for coordinating parallel robotic swarms for micro-assembly. In addition, by using robots cooperatively, we also demonstrate how teams of micro/milli robots can achieve new functionality and enable extremely high densities of independent micro-manipulation as compared to conventional standard robotic solutions.

6:00 AM S.CT07.07.03
Scale-Free, Programmable Design of Morphable Chain Loops of Kilobots and Colloidal Motors Mayank Agrawal and Sharon C. Glotzer; University of Michigan-Ann Arbor, United States

Achieving robotics at the micron and nano scale enables building reconfigurable machines and metamaterials that will create an unprecedented impact on fields such as healthcare, manufacturing, and smart materials. These applications demand scale-free and material-agnostic systems that can morph into arbitrary but programmable target configurations with precision as controlled by external agents such as heat, light, electricity and chemical environment. Such diverse actuation can be accomplished using active colloids—propellers that harness environmental energy source—that can act as motors, triggered and powered by these stimuli. However, unlike macro-scale motors, self-propelled colloids lack memory and ability to compute required by the conventional swarm-based algorithms to program the organization of motors into prescribed configurations. Here we present a design strategy that is both programmable and compatible with the sub-micron scale physics. Our strategy is to connect these motors such that the interactions among the motors are purely mechanical. The sequence of forces on these motors causes the system to morph into a unique configuration. We show how to reverse engineer the system’s design given a target configuration using kilobot (centimeter-scale robot) experiments and Brownian dynamics simulations. We also discuss methods of navigation and reconfiguration of the system. We demonstrate designing complex behavior such as a dynamic gripper, a dynamic Pacmac, and the letter M.

6:15 AM S.CT07.07.04
Directed Assembly of Magnetic Particles in a Magnetic-Field Assisted Inkjet Printing Process Karam N. Al-Milaji1, Ravi L. Hadimani1, Shalabh Gupta2, Vitalij K. Pecharsky2,3 and Hong Zhao1; 1Virginia Commonwealth University, United
Unique properties of one-dimensional assemblies of particles have attracted great attention during the past decades, particularly with respect to the potential for anisotropic magnetism. We have demonstrated directed assembly of ferromagnetic particles of Gd$_5$Si$_4$ into one-dimensional chains in a magnetic field-assisted inkjet printing process. The chains exhibit anisotropic magnetic properties, and are much easier to manufacture than, for example, corresponding single crystals. We have shown that three characteristic times, namely, the critical time for solvent imbibition into the porous substrate ($t_{im}$), the time it takes for particles to form chains in the presence of the magnetic field ($t_{ch}$), and the time in which the particles reach the substrate in the direction normal to the substrate ($t_{pz}$), control the assembly process. The characteristic time ratios of $t_{pz}/t_{ch}>>1$ and $t_{pz}/t_{im}<<1$, favor particle chaining and uniform particle deposition, respectively. Such an ability to control magnetic particle deposition and assembly through inkjet printing is a promising approach for many engineering applications.

Work at Ames Laboratory is supported by the Division of Materials Science and Engineering of the Office of Basic Energy Sciences, Office of Science of U.S. Department of Energy (DOE). Ames Laboratory is operated for the U.S. DOE by Iowa State University of Science and Technology under Contract No. DE-AC02-07CH11358. Work at Virginia Commonwealth University (VCU) is partially supported by National Science Foundation (1357565 and 1726617) and VCU startup funds.

SESSION S.CT07.08: Micro and Nano Assembly

On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

S-CT07

5:00 AM S.CT07.08.01
Capillary Self-Assembly Challenges on Multichip 3D Stacking and Scaling Down Chip Size Takafumi Fukushima; Tohoku University, Japan

3D chip stacking approaches with TSV (thorough-silicon vias) are mainly classified into three categories: chip-to-chip, wafer-to-wafer, and chip-to-wafer 3D integration. The chip-to-chip technologies are widely used for traditional microelectronic packaging in which KGDs (known good dies) are assembled using one-by-one pick-and-place techniques. Although the assembly yield is high due to the use of KGDs, the assembly throughput is not sufficiently high, compared with wafer-to-wafer approaches. However, wafer-to-wafer technologies have a serious issue in total production yield that is exponentially decreased with the number of stacked layers because the failure dies cannot be removed from the wafers to be stacked. Therefore, chip-to-wafer 3D integration is thought to be a promising candidate to satisfy both the throughput and yield issues. However, chip-to-wafer 3D integration potentially has a trade-off between assembly throughput and alignment accuracies in the conventional robotic pick-and-place techniques. In order to address the problems, we have proposed and developed multichip-to-wafer 3D integration using liquid surface tension. From the technical point of view of chip-to-wafer bonding, we talk about the basic concept and recent studies of the self-assembly based 3D integration. These approaches using surface tension-driven multichip assembly are divided into two methodologies: one is non-transfer stacking without carrier wafers and the other one is transfer stacking with them. These carrier wafers are typically used for temporary wafer bonding in standard 3D integration processes. Here, we also introduce temporary multichip bonding technologies applicable to 3D integration with multichip transfer stacking in which an inorganic temporary adhesive and a debonding layer sensitive to near UV lasers are utilized. In this presentation, we introduce our multichip-to-wafer 3D integration studies with non-transfer and transfer stacking particularly focused on solder microbump bonding, oxide-oxide direct bonding, and hybrid bonding through a new material of Cu nano-pillars. Finally, I will show the massively parallel self-assembly works with tiny dies with the side of less than 100 μm for micro-LED display application.

5:15 AM S.CT07.08.02
Macroscopic Conjugated Polymer Fibers Assembled under Electric Field Song Guo; University of Southern Mississippi, United States

It is often desirable to assemble conjugated polymer molecules into highly ordered macroscopic structures to fully utilize their potentials in a variety of organo-electronic applications. However, due to their intrinsic flexibility, conjugated polymer chains tend to entangle and form disordered bundles in solution. Here we show that centimeter-long conjugated polymer
(poly(3-hexylthiophene) (P3HT)) fibers can be assembled under an external DC electric field. In general, assembly under external stimuli such as magnetic or electric fields provides a way to arrange samples without using template materials, leading to a relatively simple procedure. The electric field is chosen here because of its low cost and tunability of field strengths and orientation during the assembly process. In this work P3HT molecules are pre-aggregated into high aspect ratio nanowires, then these nanowires can be further aligned and bundled into macroscopic fibers in solution under the applications of external electric field. To fully understand the assembly process, its dependences on nanowire microstructure types, the DC electric field strength, and solvent polarity are investigated by characterization methods including UV-Vis, AFM, and GIWAXS. It is proposed that the electric field-induced dipole in the nanowires aligns the nanowires along the electric field direction, then the dipole-dipole interactions will lead to further assembly of the nanowires into larger bundles. The macroscopic fibers will retain its morphology in solution even after the electric field is removed. Furthermore, curved macroscopic fibers can also be prepared under curved electric field lines. This hierarchy method provides a general way to assemble flexible molecules into macroscopic fibers by pre-forming high aspect ratio secondary nanostructures, then align and bundle them under external fields to retain the anisotropic properties. We hope this method can be extended to other flexible molecules that are difficult to be directly fabricated into macroscopic structures under electric fields.

SESSION S.CT07.09: Directed Self-Assembling
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-CT07

5:00 AM *S.CT07.09.01
Heterogeneous Integration of Self-Assembled Materials and Nano/Micro Devices in Electronics Koji Asakawa; Institute of Memory Technology Research, Kioxia Corporation, Japan

The bottom-up approaches recently become quite attractive for nano-scale fabrication. For example, block copolymers, nano-colloidal particles, and anodized aluminum are known to form nano-scale patterns. In addition, these bottom-up self-assembly can be combined with conventional top-down lithography resulting large scale periodic pattern can be fabricated. Several applications to nano/micro-electronics have been reported. Such as patterned magnetic media for a hard disk drive (HDD), light extraction structures of light-emitting diodes (LEDs), organic light-emitting diodes (OLEDs), anti-reflection (AR) structures for displays, metal wire-grid polarizers (WGP), and transparent conductive film (TCF) using nano-meshed metal thin film were demonstrated by these manners. The guided, aligned, or directed self-assembly (DSA) is a key technique, that the larger guides are made by conventional top-down methods then bottom-up self-assembled structures are formed along the guides. The challenges are continuing to fabricate the semiconductor memories. We would explain these potential applications fabricated by self-assembly.

5:30 AM S.CT07.09.03
Directed Self-Assembly Technology with Block Co-Polymer/Metal Nanocomposites for Ultrafine-Feature Metallization Takafumi Fukushima; Tohoku University, Japan

In this work, a new metallization to form metal nano wires are studied with nanocomposite consisting of block co-polymer and metal compounds or metal nano particles by advanced directed self-assembly (DSA) technology. To evaluate the impact of the metals, we simply characterize the standard DSA behavior with block co-polymer alone. Si trenches with a length of 10 μm and width of 3 μm are fabricated by dry Si etch processes used for 3D integration with TSV (Though-Silicon Via) applications. This trench size is quite larger than that used for typical DSA works. Surprisingly, we have successfully formed lamella (multiple annular) and nano cylindrical structures in the large Si trenches by using polystyrene-block-poly(methacrylate) (PS-b-PMMA) with the PS:PMMA composition of 1:1 and 2:1, respectively. When we used PS-b-PMMA with a PS:PMMA molecular weight ratio of 15K:15K and 57K:25K, the resulting lamella and cylinder pitches are 20 nm and 40 nm. The pitches depend on the molecular weight of the nanostructure. We evaluate the impact of DSA parameters such as heating time and temperature on morphological behavior and the resulting nanostructure of the block copolymers. The nanostructures were formed even at below 200degreeC. In addition, it is found that the nanostructure can be controlled by adding the homo polymer of PS or PMMA into the block copolymers. From mean field approximation simulation based on Self-Consistent Field (SCF) theory, if a metal compound well interacted with the PMMA or PS block is added into PS-b-PMMA, the metal in the nanocomposite will be kept to be distributed into nanocylindrical PMMA or PS to fabricate lateral
or vertical ultrafine-pitch interconnection. Here, we employed a nanocomposite with an Fe compound and PS-b-PMMA for nano wire formation by DSA. According to Moore’s law limitation, metal nano wires are promising candidate to breakthrough the interconnect scaling. It was interesting to note that SEM observation revealed Fe nano wires were induced by the phase separation of the PS-b-PMMA in the Si microstructure. The EDX analyses confirmed the added metal was either attached or aligned near the PMMA of the block copolymer. In addition, another nanocomposite is prepared with PS-b-PMMA and PMMA-modified Au nano particles. By DSA processing with simple heating, the nanocomposite shows nano wires with a width of 30 nm and the length of 500 nm or more. The electrical characterization is done with a nano probing system, indicating the liner relationship between current and voltage although the resistance is relatively high. By using DSA with the block co-polymer/metal nanocomposite, this is the first time to show the ohmic behavior applicable to interconnection. In this presentation, another DSA approach without nanocomposites will be proposed and their feasibility works are introduced.

5:45 AM S.CT07.09.04
Boundary-Directed Epitaxy of Block Copolymers Robert M. Jacobberger1, Vikram Thapar2, Guangpeng Wu3, Tzu-Hsuan Chang4, Vivek Saraswat5, Austin J. Way1, Katherine R. Jinkins1, Zhenqiang Ma1, Paul Nealey1, Su-Mi Hur2, Shisheng Xiong6 and Michael Arnold1; 1University of Wisconsin-Madison, United States; 2Chonnam National University, Korea (the Republic of); 3Zhejiang University, China; 4National Taiwan University, Taiwan; 5University of Chicago, United States; 6Fudan University, China

Directed self-assembly of block copolymers (BCPs) provides a scalable route for rationally fabricating dense nanoscale patterns beyond the resolution of conventional lithography at highly precise locations on a surface. Historically, there have been two strategies—graphoepitaxy and chemoepitaxy—for directing the self-assembly of BCPs into useful patterns. We have recently discovered a third paradigm—termed “boundary-directed epitaxy”—in which templates consisting only of planar, low-resolution features are used to drive the formation of more complex BCP patterns with enhanced feature resolution. The templates are comprised of spatial boundaries separating regions on a surface with different composition, formed at the edges of isolated stripes on a background substrate.

Vertical BCP lamellae are pinned by chemical contrast at each stripe/substrate boundary, align parallel to the boundaries, selectively form on the stripes (whereas horizontal lamellae form on the background substrate), and register to wide and incommensurate stripes to multiply the feature density. Isolated BCP line arrays with half-pitch of 6.4 nm are demonstrated on stripes wider than 80 nm. Directed assembly of isolated line arrays, superstructures of isolated line arrays, and complex features such as T-junctions, jogs, and bends is demonstrated, which may be particularly useful for fabricating critical features in integrated circuits. Boundary-directed epitaxy circumvents the need for topographic structures used in graphoepitaxy or ultra-narrow guiding features used in chemoepitaxy to direct assembly of sub-10 nm BCP features, and provides an attractive path towards nanofabrication beyond the resolution of conventional lithography.

SESSION S.CT07.10: Novel Integration Strategies
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-CT07

5:00 AM S.CT07.10.01
Hetero-Integration of CdS Nanorods on Carbon Substrates for Enhanced Photoelectrocatalytic Performance Min Soo Jeon, Youngshik Cho and Dong Rip Kim; Hanyang University, Korea (the Republic of)

Cadmium sulfide (CdS) has been highlighted due to the excellent photoelectrocatalytic properties and activities. Hetero-integrated CdS nanoscale structures onto diverse substrates can bring more enhanced performances in wide photocatalytic applications. Herein, we demonstrate a facile strategy to synthesize CdS nanorods on three-dimensional conductive carbon structures with the enhanced photoelectrocatalytic performance by using hydrothermal methods. The hetero-integrated CdS nanorods with high uniformity on highly conductive carbon substrates not only exhibit the enhanced photocatalytic efficiency in reduction of organic pollutant, but also perform the excellent photoelectrochemical activity and photostability, compared to control samples. The superior performance of the hetero-integrated CdS nanorods on carbon substrates is attributed to the improved charge separation and transport of photo-generated electrons in highly crystalline CdS nanorods and the effective photo-generated electron transfer to carbon substrates from CdS nanorods. Finally, we demonstrate the hetero-integrated CdS
nanorods on three-dimensional carbon supports with a variety of shapes by using the developed method. Our strategy to integrate CdS nanoscale structures on diverse substrates can be utilized to achieve high performance photoelectrocatalytic systems in wide energy and environmental applications.

**Acknowledgement**

This research is supported by Basic Science Research Program (NRF-2018R1C1B6007938) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT of Korea. This study was also supported by the Intelligent Synthetic Biology Center of Global Frontier Project funded by the Ministry of Science and ICT of Korea (NRF2012M3A6A8054889)

**5:15 AM S.CT07.10.02**

**Freestanding Layers of Silicon Nanocrystals—Photoluminescence and Mechanical Properties** Cameron Papson, Alborz Izadi, Mayank Sinha, Sara Roccabianca and Rebecca J. Anthony; Michigan State University, United States

Silicon nanocrystals (SiNCs) have many applications in electronic devices due to their efficient and tunable optoelectronic properties. In the many methods for creating SiNCs, they are nearly always either embedded in an inorganic matrix or supported by a substrate. While this has not hindered their use in technologies such as light-emitting devices (LEDs) and solar photovoltaics, it also raises questions about SiNC properties in standalone layers. It is well-known that the local environment of nanocrystals can influence their optical properties, and many of the methods for testing the mechanical behavior of thin layers of SiNCs rely on substrate-supported techniques. Here we present our work on fabrication of freestanding layers of SiNCs, and their optical and mechanical behavior.

SiNCs were synthesized in a nonthermal radiofrequency plasma reactor using silane, argon, and hydrogen gases. Transmission electron microscopy (TEM) and x-ray diffraction (XRD) measurements indicate that the SiNCs are crystalline with an average diameter of 4-5 nm. We created freestanding layers by using inertial impaction of SiNCs directly out of the reactor onto sacrificial layers, such as NaCl and sucrose. We used thermal evaporation to deposit thin layers of NaCl onto substrates such as glass, silicon wafer, and polydimethylsiloxane (PDMS). We also used block-like substrates entirely from NaCl and sucrose, as well as other surface coatings of sucrose, as our sacrificial bolsters for the SiNCs. We deposited SiNC layers of varying thicknesses onto these substrates using the inertial impaction process. We then liberated the SiNC layers via dissolution in water at controlled temperature. The SiNCs, which are hydrophobic, rose to the surface of the water where we collected them. Our ongoing experiments include testing the SiNC layers' photoluminescence and mechanical properties without the support of a substrate beneath, helping to elucidate their properties as a single system rather than as a layer supported by a bolster.

**5:30 AM S.CT07.10.03**

**Enhanced High-Voltage Cycling Stability of Ni-Rich Cathode Materials via Self-Assembly of Mn-Rich and Li-Rich Shells** Jianqing Zhao; Soochow University, China

Ni-rich layered LiNi_{1-x,y}Mn_xCo_yO_{2} (NMC, x+y<0.5) oxides have been demonstrated to be dominant cathode materials for high-energy lithium ion batteries. However, NMC cathode materials with high Ni contents usually show unsatisfied capacity decay and voltage fading cycled at high voltages, owing to aggravated side reactions and electrochemical irreversibility during prolonged lithiation/delithiation cycles. Here, we report the Mn-rich Li_{10,65}Mn_{0,50}Ni_{0,12}Co_{0,13}O_{3} (marked as LMNCO) nanocomposite that is integrated of layered Li_2MnO_3 and spinel LiMn_{1,5}Ni_{0,5}O_4-type phases as a desired shell for improving high-voltage cycling stability of the Ni-rich LiNi_{0,8}Mn_{0,2}Co_{0,1}O_2 (marked as NMC811) cathode material. The core-shell NMC811@x% LMNCO nanostructure has been fabricated in satisfied structural conformity by using an initial sonofragmentation, followed by the solvent evaporation-induced self-assembly (EISA) and post-annealing processes. The optimized NMC811@5% LMNCO cathode material can deliver an initial discharge capacity of 150.0 mAh g^{-1} at 5 C (1 C=200 mA g^{-1}) in a voltage range of 2.7-4.6 V vs. Li+/Li with 83.4 % retention up to 500 cycles, significantly superior to 75.6 % of the bare NMC811 material. The Mn-rich shell also enables to effectively stabilize Ni-rich cathode materials for long-term cycles in such a high voltage range at 55 °C. In addition, the in-situ X-ray diffraction (XRD) has been carried out to probe structural evaluations of the Ni-rich NMC811 cathode material during charge/discharge processes. The operando XRD results demonstrate undesired structural irreversibility of the NMC811 cathode material in the first cycle. Enhanced structural stability for continuous phase transformations in next electrochemical cycles can be implemented via a self-assembly of the Li-rich Li_2MnO_3 coating. The optimized NMC811@LMO-3% cathode can retain initial discharge capacities of 92.9 % at 0.1 C after 100 cycles and 80.4 % at 1 C after 500 cycles, significantly superior to 73.8 % and 61.3 % of the bare NMC811 cathode. This work sheds lights on structural evaluations of Ni-rich cathode materials during lithiation/delithiation processes, and further offers a synthetic prototype for the conformal core-shell-structured fabrications, which could be
adopted for the surface modification of various functional materials to achieve enhanced performance in device applications.

5:45 AM S.CT07.10.04
Colloidal Self-Assembly in Nanostructured Tribo-Electrically Charged Templates Pratik Ray¹,², Qiang Li², Akshit Peer², Lopamudra Palodhi¹, In Ho Cho², Rana Biswas³,⁴ and Jaeyoun Kim²; ¹IIT-Ropar, India; ²Iowa State University, United States; ³Ames Laboratory, United States

It is of great scientific interest to integrate nanoscale materials onto non-native substrates to synthesize structured architectures with novel functionalities that cannot be achieved by traditional means. To achieve this, we explore the crystallization of nanoparticles on periodically nanostructured substrates.

For the structured substrate we utilize a periodic array of nanocups of pitch 750 nm formed on a poly(dimethylsiloxane) (PDMS) substrate through replication from a polymer mold [1]. The novel feature of the nanocup array is the existence of surface tribo-charge strongly localized at the rims of the nanocups in an annular ring pattern, which was confirmed through Kelvin probe force microscopy of the surface electric potential [1,2]. Dielectric nanoparticles may be polarized by the strong electric fields in the vicinity of the tribo-charge. We expect that such dielectric nanoparticles in a colloidal suspension may be preferentially attracted to the charged regions and driven into nucleation, forming unusual structural motifs, including ring-like patterns, that could not otherwise be produced in conventional nucleation experiments. We hypothesize that the tribo-charge provides a new control variable to fabricate novel colloidal structures within the existing nanostructure.

To test this hypothesis, a PDMS nanostructured array with annular tribo-charge was immersed in a colloidal alumina suspension (5% alumina by volume) for ten minutes and then removed from the suspension. The mean particle size of the suspension was ~50 nm. The array was slowly dried, allowing crystallization. The dried PDMS array was characterized by scanning electron microscopy (SEM). We observed a high density of colloidal nanoparticles crystallized within each nanocup. It is very probable that the charged template has attracted the colloidal nanoparticles to the nanocup wall in the initial phase of growth. This is followed by agglomeration of the nanoparticles within each nanocup. Certain regions of the nanostructure reveal agglomerates of alumina nanoparticles with nearly spherical agglomeration shapes, neatly filling the entire nanocup. There is negligible agglomeration on the flat top surface between the nanocups.

It will be necessary to tailor the microscale assembly conditions that nucleate the colloids or loading material in the first phase, but prevent further agglomeration within the nanocups. This may be achieved by i) using a lower density of nanoparticles in the solution and ii) increasing the concentration of dispersants to reduce agglomeration kinetics of crystallization will be discussed. These experiments will create a pathway for tailored growth of colloidal crystals and other drug coatings within these charged templates.

These can be biomedically utilized for loading of nano-arrays with drugs since it leads to complete filling of the nanocups with negligible coating left on the flat surface. Thus drug elution would require dissolution of nanoparticles from the nanocups, starting with outer nanoparticles in the outer shell of the agglomerated clusters. Microstructures created by bottom-up technologies can serve as 2-dimensional photonic crystals where strong diffractive effects can be present.


6:00 AM S.CT07.10.05
Using Defects to Reshape Colloidal Assemblies Bryan VanSaders and Sharon C. Glotzer; University of Michigan, United States

Directed assembly at the colloidal scale remains challenging despite advances in using optical forces to manipulate nanoparticles. Optical holography allows for precise positioning of components, but does not scale well to thousands or millions of particles. However in dense colloidal systems particle positions are highly correlated, and so not every particle need be controlled in order to enact reconfigurations of the dense assembly. In this work we use simulation to study how a small number of particles embedded within a colloidal monolayer can exert forces that lead to long-range permanent deformation of the monolayer edges. By framing the problem in terms of the creation and migration of mobile dislocation defects, we uncover design principles for the embedded cluster shapes that result in the accumulation of large shear deformations on lattice planes. We show that arbitrary control of shear deformation localized to a single plane is sufficient to carry out a variety of useful reshaping operations on crystalline colloidal monolayers. This work provides a method to increase the length scale of control achieved with optical forces without imposing additional complexity on the optical system required.
S.CT07.11.02
Optimization of Geometry and Edge Passivation for High-Performance Si Heterojunction (SHJ) Microcells Marjorie Potter¹, Megan E. Phelan², Pradeep Balaji³, Phillip Jahelka², Rebecca Glaudell², Michael Enright¹, André Augusto², Harry A. Atwater² and Ralph G. Nuzzo¹; ¹University of Illinois at Urbana Champaign, United States; ²California Institute of Technology, United States; ³Arizona State University, United States

Perimeter recombination in micron-sized III-V photovoltaic (PV) materials has been studied extensively for performance at high concentrations, but minimal work toward understanding and optimizing edge recombination for Si-based photovoltaics has been pursued. Here, through both modelling and microcell fabrication, we explore the performance of Si heterojunction (SHJ) solar cells with varying edge to total surface area ratios by examining performance characteristics at different micron-scale lateral dimensions (between 200 µm × 200 µm and 1000 µm x 1000 µm microns) and device thicknesses (80 - 200 microns). We explore edge passivation strategies by determining the impact of a-Si:H and oxide- and nitride-based passivation coating materials on recombination at the edges and consequently device open-circuit voltage, VOC. Finally, we compare the impact of deep reactive ion etching (DRIE) and micro-laser cutting for solar cell dicing on edge surface quality and process scalability. Modelling results indicate that microcell device short-circuit current, JSC, increases with device thickness (up to 35 mA/cm²) and is generally independent of lateral dimensions, while device VOC decreases with thickness and increases with lateral dimensions, exceeding 700 mV at most geometries with high quality edge passivation. Consequently, device power conversion efficiency (PCE) is largely independent of thickness and increases with lateral dimensions, with a maximum PCE of > 20% at the largest lateral sizes. Notably, we found that edge passivation quality, rather than device geometry, dictates performance via the magnitude of edge recombination and is therefore the most important variable in this study to optimizing performance; high-quality a-Si:H was determined to be the best passivation material by virtue of minimizing edge recombination velocity (as indicated by dark current measurements) and thus maximizing VOC. Corroboration of modelling results with that of fabricated and tested SHJ microcell devices will be discussed, along with DRIE and micro-laser cutting routes to fabrication of micron-sized SHJ PV devices and the associated high-level cost-benefit analyses. This work will contribute to understanding of micro-scale Si-based PV and provide a framework for optimizing device parameters for integration with large-scale energy-harvesting systems.

S.CT07.11.03
Surface Morphology-Directed Nanoparticle Assembly for Versatile Sensors Sayli Jambhulkar, Weiheng Xu, Dharmeedar Ravichandran and Kenan Song; Arizona State University, United States

Well-controlled 'pick-and-place' of nanoparticles has vast potential in technological applications such as sensing, energy harvesting and transport, data storage, light composites, interfacial and functional modifiers, as well as other applications. These nanoparticles are anisotropic, including two-dimensional (2D) (e.g., nanosheets, nanolayers, nanoplatelets, nanoribbons) and one-dimensional (1D) (e.g., nanorods, nanotubes, nanowhiskers, nanofibers) nanomaterials that are chemically composed of carbon, semiconductor, and metal elements. While the organization and alignment of anisotropic nanosomic materials have been explored in many pathways, each method has its strengths and weaknesses. For example, non-directed methods (e.g., casting and drying) are simple and quite elegant but are somewhat limited in the morphologies they can access. As well, non-directed methods can be susceptible to factors such as solution concentrations and drying thermodynamics. Surface modification significantly expands the versatility of anisotropic nanomaterial assembly, but often requires challenging surface chemistry to modulate nanomaterial properties. Traditional use of prefabricated templates can control both the positional and orientational orders but requires the potentially difficult fabrication of a template. Therefore, our research aims to develop improved assembly strategies at microscales, coherently implemented into additive manufacturing (AM) infrastructure, to readily and simultaneously achieve orientational and positional control of anisotropic nanomaterials over arbitrarily large areas and volumes. The AM proposed here is an in-house designed process supported by layer-by-layer deposition of polymers with alternative and selective addition of nanoparticles. The printing and deposition mechanisms from the two-step manufacturing are compatible on the same processing platform that can greatly improve the precision and throughput.

Our proposed 3D printing mechanism will control the processing and material parameters along the working path such that
each voxel of printed material itself can be a spatially varying architecture of particles giving rise to a response that differs locally from highly anisotropic to isotropic. Hence, this manufacturing enables the design and fabrication of composites with site-specific optimization of particle orientations, programmable surface morphology, and designable interfacial transitions. One-dimensional (1D) carbons, namely carbon nanofibers (CNF), will be demonstrated as an example here due to their superior anisotropic properties especially the higher conductivity or sensitivity along the fiber axis as compared to that along with the cross-section directions. We used 3D printing for surface morphologies controls and the CNFs were deposited via layer-by-layer self-assembly (LBL) techniques. The samples with different roughness and pattern features were compared for the efficiency of directed self-assembly. The solid-liquid-air interfaces were proven to be critical in determining the selective deposition of CNF for surface conductive paths and sensitivity degrees. The electricity characterizations showed a strong anisotropy along with the fiber alignment directions, showing resistivity of 0.27 kW/sqr along with the CNF band as compared to 1.21 kW/sqr along with the normal directions. This phenomenon was taken advantage of their sensing capabilities. We observed significantly improved sensitivity to strain, temperature, and chemical liquid/gas as compared to randomly distributed CNF microstructures. The high sensitivity with exposure to different volatile chemicals was obtained from our research and suggests the potential in health monitoring, human-robotics interactions, microelectronics design, and environmental sustainability.

**S.CT07.11.04**

**Self-Aligned Copper Oxide Passivation Layer? A Study on the Reliability Effect**  
Yue Kuo and Jia Quan Su; Texas A&M Univ, United States

Due to its high conductivity, copper is an important interconnect material for high density as well as large area electronic and optoelectronic products, such as ICs, TFT LCDs, and OLEDs. The reliability of the copper line is critical to these applications. In general, the copper interconnect line needs a bottom adhesion layer as well as a passivation layer. The adhesion layer effect on the line reliability has been well studied. The passivation layer is commonly formed by adding a CVD or sputter deposited dielectric or metallic layer. There are some studies on the influence of these passivation layers on the reliability of the copper line (1,2). However, there are few studies on the copper oxide passivation effect on the copper line's reliability.  
Since oxide can be easily formed on the copper pattern under a well-controlled condition, it can be an effective self-aligned passivation layer. In this paper, authors report the reliability study of the copper oxide passivated copper line that is etched with the plasma-based etch process (3,4,5). The copper oxide layer was formed from the oxygen plasma method. Copper lines of various thicknesses and widths with and without the oxide passivation layer were prepared. The line breakdown phenomena under the constant current density stress condition are discussed. The composition and structure of the passivation layer before and after the high current stress condition have been examined and discussed. In summary, copper oxide is a potentially important passivation layer for the copper interconnect line in many products.


**S.CT07.11.05**

**Design, Microfabrication and Characterization of Bismuth and Glassy Carbon Based Sensor for Heavy-Metal in Drinking Water**  
Ryan Butler and Sammuel Kassegne; San Diego State University, United States

In the past several decades, the US has experienced a rising concern over toxic pollution from heavy metal sources. For example, the pollution based natural disaster of Flint, Michigan garnered an abundance of media attention for its devastating impact on the lives of those in the local community. Although this negative press was rightly deserved, there are many places in America with much higher recorded heavy metal poisoning rates – three thousand to be exact. A big concern of much of this pollution comes in the form of water toxicity. Often, heavy metals find their way into water supplies for local communities which results in the indirect poisoning of citizens. Therefore, there is great need for a commercially available and portable device which would provide an easy method to test the level of poisonous elements in community water supplies.  
Herein, the creation of a novel microfluidic device for the measurement of trace heavy metal ions is described. The work presented within focuses on these ions due to their health hazards and low concentration limits lending to an interesting challenge in detection.
The first effort in this project revolved around determining the form factor of a MEMS device which would act as an environmental sensor for minute concentrations of lead. Much background research into similar devices was performed before starting to conceptualize the preliminary design. Taking the equipment of the San Diego State University Clean Room facility into consideration, a rough model was presented and refined over several weeks. A final design then followed with a basic 3D model and fabrication process presented.

After much time testing and redesigning, results were generated for the measurements of trace heavy metal ions in solutions of water. Additional results were then obtained by altering various parameters within the experiment such as the analyte concentration. They were then compared to other experimental and commercial devices to determine the efficacy and practicality of the device. Finally, a study was performed to determine future work and technological extensions of the tool presented within.

S.CT07.11.07
Mass Analysis of Neuropeptides in Salty Environment Using Hydrophilic Ring-Shaped Anchors

Sook Yoon and Chang Young Lee; Ulsan National Institute of Science and Technology, United States

For more than a decade, researchers have studied cell-to-cell signaling peptides using various analytical methods. Signaling peptides have been known to have important role in the physiological mechanisms. Currently available approaches for analyzing peptides have drawbacks such as loss of peptides and complicated steps for sample preparation. We developed an efficient platform for mass analysis of neuropeptides that simultaneously concentrates and desalts the analytes via coffee ring effect. Our approach is to use C18-Au coated patterned substrate. When peptide solution with high salt content is dropped onto the patterned C18-Au surrounded by donut-shaped hydrophilic anchors, salts are removed by outward flow generated during evaporation, while peptides are collected onto the central C18-Au region. Our approach greatly simplifies the sample preparation for matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). We also found that our patterns can be regenerated and used 5 times or more without any performance degradation. We have developed a simple kinetic model that describes the correlation between the evaporation rate and the surface coverage of peptides. Moreover, the performance could be dramatically increased by concentrating absorbed peptides into a crystal using PDMS contact printing. Applying these drop-dry methods to MALDI-MS sample preparation potentially enables high-throughput analyses, including time-lapse mass analysis. Our approach is easily accessible to researchers who do not have special expertise in mass spectrometry, so it is possible to contribute to bringing new ideas to neuropeptide analysis.

S.CT07.11.11
Preparation of Nano Raspberry Particles Using Chemically Adsorbed Monolayers

Teruyoshi Sasaki, Kazufumi Ogawa and Yoshifumi Suzuki; Kagawa University, Japan

Since the nano world can be observed with SEM and SPM, nanomaterials have been actively developed. Among them, nanoparticles are often used for both metals and non-metals, such as cosmetics, home appliances / electrical electronic products, paints / inks, etc. In general, nanoparticles are produced by a vaper phase method or a liquid phase method. However, it is still difficult to produce nanoparticles with a desired shape such as raspberry particles. For example, the prototype raspberry particles are on the order of the micro level at the minimum.

In this study, the surface of two kinds of large and small nano level silica nanoparticles were coated with different reactive chemically adsorbed monomolecular film. Thereafter, the particles were bonded to each other by the interaction of the functional groups at the ends of the chemically adsorbed monomolecular film on the surface of each particle to produce nano sized raspberry particles. As an application example of nano raspberry particles, the nano raspberry particles were coated on the surface of a glass substrate to form a nano fractal surface structure. Furthermore, a light transmitting super water repellent glass substrates could be produced by forming a fluorocarbon based chemical adsorbed monomolecular film on the surface without damaging the surface of the fractal structure.

S.CT07.11.12
Nano-Engineering in Confined Spaces—Size- and Shape-Controlled Growth of Functional Nanostructures in Self-Assembled Block Copolymer Nanoreactors

Naman Arora1, Anna Perdikaki2, Paschalis Alexandridis3, T. J. (Lakis) Mountziaris4 and Georgios Karamikoles1,1; 1Khalifa University, United Arab Emirates; 2Demokritos National Research Center, Greece; 3University at Buffalo, The State University of New York, United States; 4University of Massachusetts Amherst, United States

Self-Assembly of amphiphilic block copolymers in selective solvents can yield a variety of organized structures at the nanoscale of different sizes, shapes, and interfacial characteristics. Such rich structural polymorphism has been tuned and subsequently utilized in this work to controllably prepare a variety of colloidal systems of nanoparticles by templated growth.
in the self-assembled nanodomains. Nanomaterials spanning compound semiconductors with 0-, 1-, and 2-D morphologies to metallic nanostructures grown in poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) assemblies will be presented. The metallic systems in particular were applied as antibacterial agents exhibiting enhanced and sustainable performance due to the block copolymer colloidal configuration.

S.CT07.11.13
Characterization of Device Edge Illumination of Si Heterojunction (SHJ) Microcells for Luminescent Solar Concentrator (LSC) Applications

Megan E. Phelan1, Maggie Potter2, Pradeep Balaji3, André Augusto3, David Needell1, Ralph G. Nuzzo2, and Harry A. Atwater1; 1California Institute of Technology, United States; 2University of Illinois at Urbana-Champaign, United States; 3Arizona State University, United States

In dense urban environments, with limited rooftop space, communities must look towards new photovoltaic (PV) technologies that can be integrable into the existing building envelope. Luminescent solar concentrators (LSCs), which sustain performance in both direct and diffuse lighting conditions and boast tunable transparencies, present an attractive option for building integrated (BI) PV. In this talk, we report performance optimization and characterization for varied illumination conditions of Si heterojunction (SHJ) microcells embedded within an LSC for BIPV applications. For this design, we propose a grid-like array of SHJ microcells, beneath a poly-lauryl methacrylate (PLMA) waveguide that has embedded InAs/InP/ZnSe quantum dots as the luminophore. Given the proposed architecture, the microcell can be illuminated from the top surface of the cell as well as each of its device edges; this illumination results from each direct sunlight and from quantum dot photoluminescence (PL) within the LSC waveguide, respectively.

In this talk, we compare SHJ microcell performance when illuminated on each: i) the top surface, ii) one device edge, and iii) all four device edges simultaneously. We present both simulated and experimental measurements to corroborate our results around photonic interactions at each surface, and preform the following characterizations and measurements: light current-voltage (LIV), dark current-voltage, photocurrent mapping, external quantum efficiency (EQE), and internal quantum efficiency (IQE). By varying the dimensions (width and length) of the SHJ micro cell (from 400um to 800um), we further report how cell performance for each surface illumination (top vs. edge) varies for different sized devices. Results of these measurements show that Jsc increases when illuminating the microcell on the edge (in comparison to top surface illumination) due to an increased absorption depth. However, Voc drops for edge illumination vs. top illumination, due to an additional darkness factor and increased recombination. The mechanisms and photonics behind the contrasting microcell performance at each of these surfaces will be discussed during this talk. By understanding microcell performance at each interface, we are able to better design a SHJ/LSC integrated device, with optimized luminophore PL to match the edge illumination performance, for BIPV applications.

SYMPOSIUM S.CT08

Crystallization via Nonclassical Pathways in Synthetic, Biogenic and Geologic Environments
November 21 - November 29, 2020

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* Invited Paper
SESSION S.CT08.05: Live Lightning/Flash I: Crystallization via Nonclassical Pathways in Synthetic, Biogenic and Geologic Environments
Session Chairs: Qian Chen and Xiaoqing Pan
Saturday Afternoon, November 28, 2020
S.CT08

5:00 PM OPENING COMMENTS

5:03 PM *S.CT08.01.02
Direct Imaging of Nucleation and Growth of Colloidal Nanoparticle Superlattices Qian Chen; University of Illinois at Urbana-Champaign, United States

We use liquid-phase transmission electron microscopy to directly image a series of crystallization pathways of colloidal nanoparticles into superlattices. We find that there exist similarities to the prevalent model system of micron-sized colloids, such as a non-classical two-step crystallization pathway, where amorphous intermediates in the form of nanoparticle clusters exist preceding the nucleation. Capillary wave theory can be used to describe the fluctuation and energy of the surfaces. But there are also differences, in particular, a universal layer-by-layer growth mode that we observe consistently for diverse nanoparticle shapes. Single particle tracking, trajectory analysis, and simulations combined unravel the energetic and kinetic features rendering this crystal growth mode possible and universal at the unexplored nanoscale, enabling advanced crystal engineering.

5:12 PM *S.CT08.01.10
How Do Additives “Get the Job Done” During Nanoparticle-Mediated Crystallization? Alexander E. Van Driessche; CNRS - Univ. Grenoble-Alpes, France

Crystallization from solution follows either a single or a multistep pathway. The latter case involves the formation, aggregation and transformation of precursor/intermediate particles to the final crystalline phase. This has been observed for several important minerals, such as CaCO₃, CaPO₄, CaSO₄ or CSH [e.g. 1-3], but also for macromolecular crystals [e.g. 4,5]. Moreover, this particle-mediated crystallization pathway can be “fossilized” in the structure of the final crystals [e.g. 6]. In the idealized laboratory environment pure solutions are often studied, but in real-world natural and engineered crystallization processes soluble additives, e.g. inorganic or organic molecules, are omnipresent. In fact, they frequently play a key role in the formation of crystalline phases and are a central part of biomineralization, functional material synthesis and anti-scaling strategies [e.g. 7]. Traditionally, models of additive-controlled crystallization have considered a single step nucleation with additives adsorbing on the surface of nuclei, impeding their further growth. Hence, to advance our understanding and gain a better control of multistep crystallization processes, the interaction of additives with the precursors and/or intermediate particles needs to be unraveled.

To achieve this, we constructed a holistic nanoscopic view of a particle-mediated crystallization pathway in an additive free system [e.g. 5-8], based on in situ nanoscale observations. Subsequently, we conducted macroscopic and microscopic observations of additive-controlled crystal formation. Opposing the classical view, we found that the inhibition of nucleation can be ascribed to additives that hinder the formation of precursor species and/or their aggregation/transformation by prevailing in their vicinity and thereby reducing their interaction probability [e.g. 7, 10-11].


5:21 PM *S.CT08.01.07
Synthesis, Phase Transformation and Structural Development in Magnetic Biocomposites Taifeng Wang¹, Anna Pohl¹, Steven Herrera¹, Yuka Narahara², Michiko Nemoto² and David Kisailus¹; ¹University of California, Riverside, United States; ²Okayama University, Japan

There is an increasing need for the development of multifunctional lightweight materials with high strength and toughness.
Natural systems have evolved efficient strategies, exemplified in the biological tissues of numerous animal and plant species, to synthesize and construct composites from a limited selection of available starting materials that often exhibit exceptional mechanical properties that are similar, and frequently superior to, mechanical properties exhibited by many engineering materials. These biological systems have accomplished this feat by establishing controlled synthesis and hierarchical assembly of nano- to micro-scaled building blocks. This controlled synthesis and assembly require organic that is used to transport mineral precursors to organic scaffolds, which not only precisely guide the formation and phase development of minerals, but also significantly improve the mechanical performance of otherwise brittle materials.

Here, we investigate an organism that have taken advantage of hundreds of millions of years of evolutionary changes to derive structures, which are not only strong and tough, but also demonstrate abrasion resistance. All of this is controlled by the underlying organic-inorganic components. Specifically, we discuss the formation of heavily crystallized radular teeth the chitons, a group of elongated mollusks that graze on hard substrates for algae.

Our investigation of the formation of a fully mature radular tooth from *Cryptochiton stelleri* found in the eastern Pacific, occurs over a series of more than 40 teeth. The initial stage of tooth formation begins with the synthesis of a three-dimensional fibrous α-chitin organic matrix, prior to the onset of crystallization. Microscope analysis of early stage teeth shows ferrihydrite mineral particles growing on α-chitin fibers. Synchrotron x-ray, combined with TEM analyses show that ferrihydrite exists as randomly oriented aggregates, but undergoes a phase transformation to magnetite within a few rows of teeth. We discuss potential mechanisms of nucleation of ferrihydrite, its transformation to magnetite as well as its subsequent mesoscale ordering, crystal growth and the resulting mechanical properties. From the investigation of synthesis-structure-property relationships in these unique organisms, we are now developing and fabricating multifunctional engineering materials for energy and water purification based applications.

5:30 PM S.CT08.01.03
*Direct Imaging of Atom-Mimicking Oriented Attachment of Nanoparticle Superlattices by Liquid-Phase TEM* Chang Liu and Qian Chen; University of Illinois at Urbana-Champaign, United States

We utilize nanoparticle superlattice as a model system to study the fundamental laws of order emergence and evolution from a dispersion of nanosized entities. Liquid-phase TEM makes it possible to directly conduct single-particle level imaging in real time and real space, to reveal pathways of nanoparticle crystallization. To be specific, we observe how different types of diffusion events (e.g., surface and volume diffusion) involved in the layer-by-layer growth of a nanoparticle superlattice, where the high spatiotemporal resolution enables us to identify single particles throughout the whole process and to map out their trajectories sampling the energy landscape. Furthermore, oriented attachment of different nanoparticle lattice domains is observed, where fast translational and rotational diffusions of the domains drive the neck formation. The single-particle analysis aids correlating order evolution to differently ranged interactions. Such crystallization behavior is distinct from that of micron-sized colloids, resembling more the faceted crystals formed from atoms. Our study provides new dynamic information on the superlattice development at high spatial and temporal resolution, which can serve as a general guideline for bottom-up material design.

5:35 PM S.CT08.01.04
*Unraveling Nonclassical Crystallization Pathways of Nanoparticle Superlattices via In Situ TEM Imaging* Zihao Ou and Qian Chen; University of Illinois at Urbana-Champaign, United States

Nucleation and growth are universally important in systems from the atomic to the micrometer scale as they dictate structural and functional attributes of crystals. However, at the nanoscale, the pathways toward crystallization have been largely unexplored owing to the challenge of resolving the motion of individual building blocks in a liquid medium. Here we address this gap by directly imaging the full transition of dispersed nanoparticles to a superlattice at the single-particle level. We utilize liquid-phase transmission electron microscopy at low dose rates to control nanoparticle interactions without affecting their motions. Combining particle tracking with Monte Carlo simulations, we reveal that positional ordering of the superlattice emerges from orientational disorder. Otherwise elusive parameters including line tension and phase coordinates are measured, charting the nonclassical nucleation pathway involving a dense, amorphous intermediate. We elucidate the origin of this two-step crystallization by experimentally measuring the energy barrier for nucleation, which is lower in the presence of the amorphous precursor. We demonstrate the versatility of our approach via crystallization of different nanoparticles, pointing the way to more general applications. Our real space nanoscopic imaging platform not only offers new understanding on the crystallization kinetics, but also opens opportunities to other nanoscale fluctuating systems, from biofouling, lubrication, melting, phonon transport, to dendrite formation.
Hypoxia-Induced Biosynthesis of Gold Nanoparticles in the Living Brain

Elena A. Rozhkova1, Byeongdu Lee1, Judy A. Prasad2, Yuzi Liu1 and Elena Shevchenko1; 1Argonne National Laboratory, United States; 2The University of Chicago, United States

Biosynthesis of NPs is a striking phenomenon in nature. Inspiring examples include storage and transport of iron atoms in a non-toxic form of a ferric oxyhydroxide cluster in the ferritin protein cage, using metal salts as terminal sinks in electron transfer pathways and formation of metal particles by bacteria, and biomineralization of magnetite nanocrystals in specific organelle magnetosome that enables coordinated movement of magnetotactic bacteria. Under certain experimental conditions, metal complexes and nanoclusters can be obtained in mammalian cells or in a whole animal, mainly for use in imaging. However, the mechanisms of this biosynthesis are often spontaneous, poorly understood and, therefore, difficult to control. In our approach, a pathological process, namely hypoxia of the brain accompanied by changes in the NADH/NAD+ co-enzymes ratio, initiates and controls the biosynthesis of biocompatible Au nanoparticles from precursor salts in the immediate vicinity of the hypoxia site, thereby restoring the redox status of the brain.


Supercluster-Coupled Crystal Growth in Metallic Glass Forming Liquids

Yujun Xie1,2, Jan Schroers1 and Judy Cha1,2; 1Yale University, United States; 2Yale West Campus, United States

Crystallization induced microstructure plays a central role in tailoring materials properties, yet our understanding of its formation process is limited due to its complexity. Classical crystallization theories assume that nucleation and growth are separate processes and growth ought to be temperature-dependent only. Local thermodynamically unstable clusters are considered to fluctuate in the nucleation stage but do not participate in the later growth. Here, we apply in-situ transmission electron microscope (TEM) to nanostructured metallic glasses (MGs) and directly probe crystallization kinetics at the unprecedented time and spatial resolution1, 2, 3, 4. In particular, the growth kinetics of single crystalline Pt57.5Cu14.6Ni5.3P22.5 MG nanorods were studied in situ by observing isothermal crystallization at the atomic level. We found that the crystal growth rates of heated metallic glass are much higher than those of cooled metallic liquid despite the same isothermal crystallization temperature. The observation is in direct contrast to one would expect from classical growth models. We, therefore, propose a supercluster-coupled growth model and hypothesize that structural ordering can strongly enhance the crystal growth. The asymmetric growth upon heating is thus attributed to the higher degree of structural ordering and a greater number of clusters in the MGs nanorods. The structure-coupled growth is further supported by manipulating the density of the small clusters through nanoscale confinement and thermal treatment of the MG nanorods. In addition, molecular dynamics simulations of binary Lennard-Jones glasses quenched at different cooling rates show a growth rate trend that agrees with experimental observations. The present results demonstrate the inadequacy of the classical crystallization model on modern complex materials systems.

Reference
Interfacial Structure, Interparticle Forces and Assembly Dynamics During Crystal Growth by Oriented Attachment

James J. De Yoreo1,2, Lili Liu1, Guomin Zhu1, Xin Zhang1, Dongsheng Li1, Sebastien Kerisit1, Maria Sushko1, Jaehun Chun1, Elias Nakouzi1, Chongmin N. Wang1, Gregory Schenter1, Kevin Rosso1 and Chris Mundy1; 1Pacific Northwest National Laboratory, United States; 2University of Washington, United States

Crystallization by assembly of primary nanocrystals is a widespread phenomenon in synthetic and natural environments. In mineral systems, this process exhibits diverse styles ranging from oriented attachment of like phases to mis-oriented aggregation of disparate phases followed by coarsening to single crystals. While descriptions of these systems must share a commonality with continuum-based DLVO-type theories for simple colloids, mineral systems present additional complexities, including face-specificity of dielectric properties, inherent diopolar interactions, structured nanoscale interfaces, and solvent-responses of a length scale comparable to particle size. To understand the relationship between nanocrystal structure, interparticle forces and assembly dynamics, we are investigating colloidal assembly of titanium, iron and zinc oxides. For ZnO, in situ TEM demonstrates that direction-specific forces align diffusing particles at distances far in excess of what is expected based on DLVO theory. Particles approach one another in a diffusion limited regime and then attach lattice matched via a sudden jump to contact unopposed by any significant energy barrier. Direct AFM-based measurements of the forces between both TiO2 and ZnO surfaces reveal orientation dependent attractive interactions that enforce alignment even in the absence of solvation-defined orientation dependent forces. Addition of organic ligands, like oxalate, to the FeOOH system produces a dramatically different pathway and outcome: Nanoparticles of Fe2O3 nucleate sporadically from the FeOOH and, once formed, are covered with oxalate, which drives all new Fe2O3 particles to nucleate within about 1 nm of the interface, after which they jump to contact. The oxalate inhibits growth and coarsening of the particles, leading to spindle-shaped aggregates of coaligned particles with a fixed and constant aspect ratio. Thus the random assembly process seen in the pure FeOOH system is replaced with one that is deterministic.

6:02 PM *S.CT08.01.11

Reaction Pathway and Assembly of Pt Nanostructures Revealed with Low-Dose In Situ Microscopy

Wenpei Gao, Peter Tieu, Christopher Addiego and Xiaoqing Pan; University of California, Irvine, United States

The progress of energy and electronic industry relies on the design and engineering of new nanostructures with fine control in the atomic scale. Examples include the use of twisted two-dimensional materials for the tuning of electronic structure, the surface engineering to create surface steps in metal nanowires that show enhanced catalytic activity. Manipulation of the nanostructures with more precise control requires the understanding of how atoms interplay with various stimuli, which must be characterized by advanced imaging tools that can not only reveal the materials behavior during growth and use, but also provides insights on the change of composition and bonding. Recent development of aberration-corrected transmission electron microscopy (TEM) or scanning transmission electron microscopy (STEM) allows the combination of low-dose imaging with in situ methods to study the materials dynamics at high spatial resolution, when coupled with high-speed direct electron detectors, the electric potential and field that can influence the materials interaction can also be imaged. Here we first demonstrate the atomic resolution imaging of a Pt precursor compound and the dynamics of its transformation to Pt nanoclusters.[1] Specifically, under an ultra-low electron dose, the atomic structure of pristine K2PtCl4 crystallite is resolved in the image captured by the CMOS-based direct electron detector. With further electron beam irradiation, the dynamics of staged reduction of Pt compound and nucleation of Pt cluster are captured and identified. Results show that the ionic bond between K+ and PtCl42- is first broken, which is followed by PtCl42- forming PtCl2; reduction of the dual-valent Pt then leads to the formation of Pt clusters. The solid-state transition is deciphered in real time and real space. Later, using a gas cell, we show that the sintering process of Pt clusters can be modified by gas adsorbates:[2] in H2, the Pt nuclei approach and attach to each other only along specific orientations, and gradually form short nanowires. In ex situ experiment, we successfully synthesized extended long Pt and PtNi nanowires in solid state assisted by H2. Compared to the Pt-based NWs grown by other methods, our catalysts showed both enhanced mass specific activity and stability in ORR. We will also show our four-dimensional STEM study at the interface of complex oxides that reveals the penetration of electric field from the ferroelectric BiFeO3 into the insulating SrTiO3,[3] and discuss how advanced electron microscopy can further our study of nanostructures.

Multi-Step Crystallization of Self-Organized Spiral Eutectics

Saman Moniri and Ashwin J. Shahani; University of Michigan, United States

A novel method for the solidification of metallic alloys involving spiral self-organization is presented as a new strategy for producing large-area chiral patterns with emergent structural and optical properties, with attention to the underlying mechanism and dynamics. This study reports the discovery of a new growth mode for metastable, two-phase spiral patterns from a liquid metal. Crystallization proceeds via a non-classical, two-step pathway consisting of the initial formation of a polytetrahedral seed crystal, followed by ordering of two solid phases that nucleate heterogeneously on the seed and grow in a strongly coupled fashion. Crystallographic defects within the seed provide a template for spiral self-organization. These observations demonstrate the ubiquity of defect-mediated growth in multi-phase materials and establish a pathway towards bottom-up synthesis of chiral materials with an inter-phase spacing comparable to the wavelength of infrared light. Given that liquids often possess polytetrahedral short-range order, our results are applicable to many systems undergoing multi-step crystallization.

Temperature Induced Strain Relaxation in Epitaxially Connected Quantum Dot Superlattices Probed by In Situ STEM

Michelle A. Smeaton, Daniel M. Balazs, Tobias Hanrath and Lena F. Kourkoutis; Cornell University, United States

The self-assembly of quantum dots (QDs) into epitaxially connected superlattices called quantum dot solids (QDSs), made possible by a growing library of synthesis methods for precisely controllable QD building blocks, represents exciting opportunities for advancing optoelectronic devices and realizing exotic electronic phenomena. However, the myriad complex interactions at play during the assembly and oriented attachment processes lead to imperfections in epitaxial connections between QDs. Such imperfections affect electronic coupling between QDs and lead to local translational disorder, which propagates through the film and hinders tunable miniband formation. Heating QDSs is a promising method for annealing out defects, thus improving electronic properties. Understanding the nuanced effects on epitaxial connections, however, requires visualization of atomic-scale structure over large enough fields of view to access a statistically meaningful number of QDs.

Here, we use in situ MEMS heating in combination with aberration-corrected HAADF-STEM and image analysis to assess the effects of heating on epitaxial connections in QDSs over extended fields of view. We analyze PbS QDs self-assembled into square SLs and epitaxially connected along the <100> directions. Localized heating provided by the MEMS device maintains stage stability such that a region of interest can be tracked throughout a heating cycle and images can be acquired at atomic-resolution over ~100 nm. We identify four distinct strain states in epitaxial connections: tension, shear, bending and torsion, noting that they appear concurrently in some cases. Using a local sine wave fitting technique similar to the phase lock-in method, we visualize the tension, shear and bending strain states. Given the limitation of STEM to projection imaging, torsion is investigated indirectly by identifying the out-of-plane orientation of each QD, nearest neighbor mismatches in which indicate torsion and out-of-plane bending strain states between connected QDs. The orientation data, in combination with wave fitting analysis, reveal that mild annealing between 150 and 200°C causes dramatic relaxation of tensile, shear and torsional strains, while bending strain is more persistent. These results give insight into the energetics of the types of defects present in epitaxial connections and represent a path toward improved carrier delocalization and miniband formation.

Real Time Imaging of the 3D-2D Transformations of Nanocrystals through Liquid Cell Transmission Electron Microscopy

Haimei Zheng1,2; 1Lawrence Berkeley National Laboratory, United States; 2University of California, Berkeley, United States

In recent years, significant achievements have been made in the synthesis of various colloidal nanostructures. The anisotropic nanostructures, such as nanowires or two-dimensional (2D) materials have attracted a lot of attention due to their unique properties. However, their formation mechanisms have not been fully understood. They seem to be contradictory to the
predictions based on the conventional crystal growth theories. And, it adds to the complexity that nanocrystals often change structure and morphology during growth. We explore the growth mechanisms of anisotropic nanocrystals using in situ liquid cell transmission electron microscopy (TEM). In this talk, I will show the growth of 2D transition metal oxide nanosheets, e.g. cobalt oxide and cobalt nickel oxide. The 2D nanosheets have been achieved in a liquid cell, which resemble those synthesized in flasks. Our direct observations reveal that 3D nanoparticles are initially formed from the molecular precursor solution and then transform into 2D nanosheets. Ab initio calculations show that a small nanocrystal is dominated by positive edge energy, but when it grows to a certain size, the negative surface energy becomes dominant, driving the transformation of the 3D nanocrystal into a 2D structure. Uncovering these growth pathways, including the 3D-to-2D transition, provides opportunities for the future design and solution synthesis of novel materials.

References:

Acknowledgements:
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6:48 PM OPEN DISCUSSION

6:53 PM S.CT08.02.07
Gypsum—Anhydrite Phase Transformation and Crystal Growth Induced by Microorganisms Living in the Atacama Desert
Wei Huang1, Emine Ertekin2, Taifeng Wang1, Luz Cruz1, Jocelyne DiRuggiero2 and David Kisailus1; 1University of California, Riverside, United States; 2Johns Hopkins University, United States

Microorganisms have been found living in one of the driest and oldest deserts on the earth, the Atacama Desert in Chile. In this hyper-arid environment, microbial communities colonize the interior of rocks and obtaining water is critical for their survival. Gypsum (CaSO4●2H2O) is one of the main components in rocks from the Atacama Desert and is a main source of water for these communities, which are mainly constituted of cyanobacteria and heterotrophic bacteria. We report that these microorganisms extract crystalline water from the gypsum rock, inducing a phase transformation from gypsum (CaSO4●2H2O) to anhydrite (CaSO4). Cyanobacteria cultures were inoculated on gypsum rock samples to investigate and validate the water extraction and phase transformation mechanisms found in the geological environment. It is shown that cyanobacteria attach on high surface energy crystal planes and generate a thin biofilm on the gypsum samples. Due to the acidic nature of the biofilm, gypsum dissolution is observed, accompanied with water extraction and subsequent transformation to anhydrite via reprecipitation and oriented attachment of mesocrystals. This is the first time showing gypsum – anhydrite phase transformation and non-classical crystal growth induced by microorganisms. The results in the present work not only shed light on how these organisms survive in such extreme environments, but also can provide insight into potential life in xeric environments such as Mars as well as offer strategies for advanced water storage methods.

6:58 PM CLOSING COMMENTS
Engineering of Chiral Inorganic Nanostructures

Nicholas A. Kotov; University of Michigan, United States

The early observation of strong circular dichroism for individual nanoparticles and their assemblies have developed into a rapidly expanding field of chiral inorganic nanostructures. The chiral inorganic nanostructures encompass sophisticated constructs from metals, semiconductors, ceramics, and nanocarbons with multiple chiral geometries with characteristic scales from Ångströms to microns. Such versatility enables their functional engineering over a broad range of physical and chemical properties but the relationship between the chirality of surface ligands, NP cores, and resulting assemblies remains obscure. Similarly, the relationship between their chiral geometries and their chiroptical properties. This talk will address (1) the origin of the uniquely high values of optical anisotropy; (2) the mechanisms of chirality transfer in inorganic materials; and (3) differences/similarities with chiral supramolecular, liquid crystal, and biological assemblies. Long-range correlations and critical phenomena in chiral nanoassemblies leading to the emergence of geometrically complex structures will be demonstrated. The novel venues for practical realizations of chiral nanoassemblies included in the talk will be photocatalytic C-C coupling in biomimetic chiral supraparticles and polarization spectroscopy in terahertz (THz) spectral window with chiroplasmonic kirigami composites.

Cluster-Coupled Crystallization of Metallic Glasses at the Nanoscale

Judy Cha; Yale University, United States

Common growth models assume a structure-less liquid composed of atomic flow units and describe crystal growth as a phenomenon of transferring atoms at the interface between a growing solid and a structure-less liquid. However, for liquid metals and polymers, structural ordering has been shown, raising the possibility of structure-coupled crystal growth. By performing in situ transmission electron microscopy (TEM) crystallization experiments on Pt-based metallic glass nanorods, we show that local structural order of the glass strongly affects crystal growth, in contrast to assumptions from conventional growth models [1].

Metallic glasses serve as a good model system to study crystallization due to their non-directional metallic bonds, relatively slow crystallization kinetics, and moderate crystallization temperatures, which readily allow direct visualization of crystallization events at the atomic scale via in situ TEM experiments. At the nanoscale, we have observed crystallization phenomena that deviate greatly from the macroscopic behaviors due to the geometrical confinement effects. These include suppression of crystallization for very small metallic glass nanorods [2], emergence of a metastable, single crystalline phase out of multi-component metals [3], and the structure-coupled crystallization [1]. The structure-coupled crystallization was inferred from the asymmetric growth rates of a heated metallic glass versus a cooled metallic liquid. We demonstrate that thermodynamically unstable structural ordering in the glass state can be kinetically stable enough to enhance crystal growth during crystallization. Thus our works highlight crystallization via non-classical pathways.

References:
(* indicates equal contributions)

The Diverse and Complex Nonclassical Pathways of Nanoporous Aluminosilicate Crystallization

Jeffrey D. Rimer; University of Houston, United States

The unique properties of nanoporous aluminosilicates (zeolites) are exploited in a variety of applications spanning from ion exchange and separations to catalysis and drug delivery. The ability to selectively control zeolite synthesis to achieve desired physicochemical properties relies upon detailed understandings of the thermodynamic and kinetic factors regulating crystal nucleation and growth, which are generally lacking. Designing innovative approaches to tailor zeolite crystallization and elucidate structure-performance relationships has the potential to produce materials with superior properties beyond what is achievable by conventional routes. In this talk, I will discuss efforts to characterize the complex mechanisms of zeolite crystallization, which occur by nonclassical pathways involving the self-assembly and structural evolution of amorphous precursors. There is still much that we do not understood regarding the role of precursors in nucleation and the influence of growth conditions on the selection of crystal topology, which underscores the need for molecular-level studies of zeolite...
crystallization. Our group addresses these challenges using a broad range of techniques that include the use solvothermal atomic force microscopy to capture time-resolved images of growing zeolite surfaces in real time. This technique has led to the first in situ characterization of zeolite growth with the capability of resolving surface dynamics at the spatiotemporal scales necessary to elucidate mechanistic pathways of crystallization. Based on our findings, we observe that growth occurs via multiple (cooperative) pathways that differ from one material to the next. In this talk, we will summarize our findings for several zeolite structures.

References

10:54 AM S.CT08.03.16
Slow-Injection Synthesis of Indium Phosphide Quantum Dots as a Route to Large Size and Low Size Dispersion
Odin B. Achorn and Moungh G. Bawendi; Massachusetts Institute of Technology, United States

The color purity of indium phosphide (InP) quantum dots (QDs) lags behind that of cadmium selenide (CdSe) QDs, especially at their largest sizes and reddest wavelengths. In order to improve the quality of InP QDs, we have developed a new synthetic method that features a slow precursor injection rate in contrast to the rapid injection rates that have worked so well for CdSe QD syntheses and that have traditionally been applied to InP. The absorption features of the InP QD batches produced by our method are redder than those of batches of comparably-disperse InP QDs and narrower than those of batches of comparably-sized InP QDs that are produced by other methods. We prepared InP QDs with first excitonic absorption peaks that are redder than 630 nm and have half widths at half maximum less than 85 meV. After adding a zinc selenide shell, we achieved core/shell QDs that are redshifted slightly with respect to the core and have photoluminescence full widths at half maximum under 55 nm. Our method also allows us to synthesize even larger InP cores with defined first excitonic absorption peaks that are redder than 660 nm. We used MALDI mass spectrometry to characterize the size and size dispersity of the QDs and to investigate the presence of low molecular weight clusters and secondary populations. Lastly, we find that the concentration of QDs increases throughout the entire course of the reaction, and we propose a nucleation and growth model to explain our observations.

10:59 AM S.CT08.03.05
Non-Centrosymmetric Metal Tetrel-Pnictides—Synthesis, Structure and Properties
Georgiy Akopov1,2, Juyeon Won2, Justin Mark2,1 and Kovnir Kirill2,1; 1Ames Lab, United States; 2Iowa State University of Science and Technology, United States

A scarcely investigated class of compounds, tetrel-pnictides of rare-earth and transition metals, R(M)-T-Pn (M = transition metal; T = Si, Ge; Pn = P, As), possess complex structural chemistry and potentially interesting properties. By combining rare-earth and transition metals, new quaternary tetrel-pnictide phases (R-M-T-Pn), both doping phases and new structural types, can be formed. The synthesis of these compounds is a challenge and it prompted us to look for new approach. Due to the volatility of phosphorus and arsenic, it is not possible to directly melt the reactants without strong depleting of sample with pnictogen due to evaporation. Target phases decompose peritectically below 1000°C, below this temperature Si and Ge are inert. Multicomponent nature of the target phase prevents effective use of molten flux reactions due to different solubility
and dissolution rates of constituent components, Pn>R>M>>T. Gas transport reactions also appeared to be ineffective for quaternary systems. As such, a synthesis using pre-reacted \{R, M, and T\} quasi- or true ternary compositions with phosphorus or arsenic becomes very appealing. Although R-M-T binaries and ternaries typically have melting points above 1000°C, our in-situ X-ray diffraction studies show that they are reactive in the presence of a pnictogen-rich atmosphere at temperatures as low as 650°C, thereby forming desired tetrel-pnictide compounds. Therefore, careful optimization of the starting reactant ratios can yield phase-pure single-phase compounds, where excess P and As can be sublimed away from the phase of interest. Furthermore, this method can generate single crystals for structural characterization due to the P and As acting as transport agents in addition to being reactants. The structural chemistry, polymorphism, and properties of the family of \{R,T\}-Si-Pn compounds will be discussed.

11:09 AM BREAK

11:12 AM *S.CT08.03.09
Non-Classical Crystallization of Thin Films and Nanostructures in the Chemical Vapor Deposition Process Nong-Moon Hwang; Seoul National University, Korea (the Republic of)

Although non-classical crystallization has been studied extensively in the solution growth, not much attention has been paid to the non-classical crystallization in the gas phase synthesis of thin films and nanostructures by chemical vapor deposition (CVD). Extensive studies were made in CVD processes and the non-classical crystallization was shown to be a general growth mechanism of thin films and nanostructures [1], where the charged nanoparticles become the building block. Generation of charged nanoparticles was confirmed in most CVD processes, including the growth of films and nanostructures of diamond, carbon nanotubes, ZrO2, Si, ZnO and GaN. Small charged nanoparticles are favorable for epitaxial growth whereas large ones are favorable for nanostructure growth.

Understanding made from the non-classical crystallization behaviour in the CVD process can provide the valuable information as to the non-classical crystallization in solution. For example, building block of nanoparticles are electrically charged in the CVD process and the presence of charge plays a critical role in the growth of thin films and nanostructures. The charge is responsible for not only self-assembly but also liquid-like coalescence, which result in the evolution of dense films and nanostructures. The role of charge could be clearly revealed by comparing the deposition behavior of silicon charged nanoparticles between electrically floating and grounded silicon substrates. Single crystalline silicon nanowires grew on the floating substrate whereas nanoparticles grew on the grounded substrate. In other processing conditions, a dense silicon film grew on the floating substrate whereas a porous silicon film grew on the grounded substrate. The fact that charged nanoparticles can be a building block of films and nanowires without leaving any void behind indicates that charged nanoparticles are quasi-solid, having a liquid-like property in diffusion. This means that the charge enhances the atomic diffusion, which is a newly discovered physical phenomenon. The charge-enhanced kinetics could be analyzed by comparing the behavior of Au nanoparticles on conducting and insulating membranes during transmission electron microscopy (TEM) observation. Au nanoparticles on insulating membranes were actively changing their orientation during TEM observation whereas those on conducting membranes were not. Also plasma dewetting behavior of sputtered Sn films was compared between grounded and floating conditions. The dewetting kinetics of Sn films in the floating condition was much higher than that in the grounded condition. Both experimental results support charge-enhanced kinetics. In this presentation, some important aspects of the non-classical crystallization in the CVD process would be introduced, emphasizing that the non-classical crystallization occurs not only in solution but also in the gas phase synthesis.


11:21 AM *S.CT08.03.01
How Solution-Phase Additives Control the Shapes of Metal Nanocrystals in Solution Kristen A. Fichthorn; The Pennsylvania State University, United States

Metal nanocrystals have gained tremendous attention due to their superior performance in various applications, ranging from selective catalysis to electronic devices to plasmonic applications, such as photovoltaics and sensing. The properties of nanocrystals are highly sensitive to their size and shape. To this end, solution-phase synthetic protocols have been highly successful at producing a variety of nanocrystal structures. However, great challenges remain in achieving high selectivity to particular nanostructures. A significant difficulty lies in understanding and controlling shape evolution in these systems.

A common adage is that solution-phase additives, such as capping molecules, can direct the shapes of colloidal nanocrystals by adsorbing selectively to certain facets. Though our first-principles-based studies indicate that capping molecules alone can...
direct the formation of nanocrystal shapes in certain systems, experiments demonstrate that more robust syntheses can be achieved in the co-presence of halide additives. We use DFT-based ab initio thermodynamics calculations to probe the influence of chloride on Ag nanoshapes. Consistent with experiment, these calculations indicate that chloride adsorption alone can lead to truncated Ag cubes. We find that adsorbed chlorine works synergistically with PVP, a common capping agent for Ag, to enhance the tendency for Ag cubes. We also demonstrate that adsorbed Cl works synergistically with HDA capping molecules to facilitate the growth of Cu nanowires via a kinetic pathway - consistent with experiment. These studies indicate that halides and capping molecules can be a powerful combination to create selective nanoshapes in solution-phase syntheses.

11:35 AM S.CT08.03.03
The Role of Carbon and SiC Crystallinities in the Oxidation and Mechanical Property Improvement of Hybrid Nano-Fibers Saja M. Al-ajrash; University of Dayton, United States

In this study, electrospinning was successfully used to fabricate hybrid Carbon-Silicon Carbide (C-SiC) fibers using polyacrylonitrile (PAN) and Silicon (Si) nanoparticles as precursors. Silicon-to-carbon precursor ratios and heat treatment were optimized to fabricate hybrid nano-fibers with high oxidation resistance. After heat treatment, the nano-fibers showed two-dimensional ordered carbons and SiC nano-phases formation. As a result, a noticeable improvement in mechanical and thermal properties was achieved. Samples with 90wt% PAN/10wt% Si showed about four-time improvements in char yield as compared with 100 wt % PAN. In addition, after the heat treatment of the fiber at 1250 °C, SiC was formed. The carbon and SiC crystallinities had a great impact on the oxidation and mechanical property improvement of hybrid nanofibers. The determination of crystal size was carried out using X-ray results obtained at different temperatures and holding times. The SiC grain growth was predicted using kinetic models and its exponent was found to be around n = 4 with activation energy around 35 KJ/mol.K. For such growth, the dominant grain growth mechanism was grain boundary diffusion.

11:40 AM S.CT08.03.08
Fabrication of High-Performance Carbon Fibers Using Template Induced Crystallization Rahul Franklin, Weiheng Xu, Dharneedar Ravichandran and Kenan Song; Arizona State University, United States

Carbon fibers have broad applications in aerospace, automobiles, wind turbines, medical devices, and implants, among many others. Carbon fibers with high-end applications have previously been manufactured from precursor fibers of rayon, pitch, and polyacrylonitrile (PAN) fibers. New precursor fibers have been conventionally fabricated by homogenously mixing the reinforcement/nanofiller and polymer matrix mechanically and spinning the dope into a coagulation bath, such as PAN processing in the case of dry-jet wet spinning followed by the drawing stage and heat treatment at different temperatures. Mechanical properties of this fiber are dependent on the continuity, density and interfacial action of the hierarchical graphitic structures. The presence of voids formed during crystallization due to the random dispersion of reinforcement/nanofiller in pre-carbon fibers (pCFs) deteriorates these properties.

In this project, a specialized templating graphene channel was developed via an in-house designed spinneret. This channel containing graphene and varied PAN solutions running along the axial direction of the fiber was parallel to the outer and inner PAN channels. On drawing the as-spun fibers the GNP was aligned in the axial direction. This channel then allowed for crystallization along the axial direction and minimizes the formation of voids leading to enhanced mechanical properties. The mechanical test showed the composite as-spun fiber with GNP templating channel has 18.5% and 51.4% increased Young’s modulus and tensile strength, respectively, as compared to the pure PAN fiber. The thermodynamics and kinetics of the heat-treatment procedures were analyzed to correlate the microstructure features and mechanical/thermal properties of obtained carbon fibers.

11:45 AM S.CT08.03.10
Liquid Phase TEM Study of 2D Indium Chloride Nanosheets Growth at Various Temperatures Junyi Shangguan1,2, Xinxing Peng1 and Haimei Zheng1,2; 1Lawrence Berkeley National Laboratory, United States; 2University of California, Berkeley, United States

Two-dimensional (2D) materials have attracted significant attention due to their unique structure and fascinating properties. However, our understanding of their growth mechanisms in solution is still limited. Here, using indium chloride (InCl₃) as a model system, we performed liquid phase transmission electron microscopy (TEM) study of the 2D growth in situ. We combined the low temperature techniques with liquid phase TEM. The nucleation and growth of 2D nanosheets in solution via both classical and non-classical pathways were observed with the atomic resolution in real time at room temperature as well as low temperature (e.g. 1-2 °C). We found the drastically decreased growth kinetics at the low temperature compared to that at the room temperature. Observation also showed that the fast growth induced the high density of crystal defects (e.g.,
nanotwins). Comparatively, perfect 2D nanocrystals were obtained through the low temperature growth. In addition, we did the atomic structural analysis of the nanosheets and chemical mapping of the reaction front at the Cryogenic temperature using the same liquid cell sample. The results revealed the growth mechanisms of InCl$_3$ 2D nanosheets and the formation of nanotwins in solution. And, the liquid phase TEM with variable temperature control opens many opportunities for future depth study of nanoscale materials growth and transformations.

11:50 AM  S.CT08.03.11
**Leveraging Pourbaix Diagrams for Design and Understanding of Hydrothermal Synthesis**
Lauren N. Walters, Chi Zhang, Vinayak Dravid, Kenneth R. Poeppelmeier and James M. Rondinelli; Northwestern University, United States

Synthesis design remains a paramount problem in materials science. Significant research has been dedicated to advancing tools to predict and aid in synthesis development. Here we describe an ab-initio approach to evaluate water-based synthesis processes such as hydrothermal synthesis. We show how to use electrochemical Pourbaix diagram, constructed from first principles density functional theory (DFT) calculations, to understand thermodynamic forces of complex Cu oxides and Cu oxychlorogenides in aqueous environments. We discuss how to construct these complex diagrams consisting of many degrees-of-freedom, including multiple elemental species, compounds, and complexes as well as nonstandard state conditions. We describe how the driving forces for the products evolve with changes in pH, oxidation state, and the activity of reactants; this understanding is then used to justify successful experimental synthesis of the targeted phase. Scale dependent nucleation is also examined. Last, we propose Pourbaix diagrams are a useful synthesis-processing design tool for accelerated discovery.

12:00 PM CLOSING COMMENTS

SESSION S.CT08.01: Particle Mediated Crystal Growth and Self-Assembly
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

S-CT08

5:00 AM *S.CT08.01.01
**Interfacial Structure, Interparticle Forces and Assembly Dynamics During Crystal Growth by Oriented Attachment**
James J. De Yoreo$^{1,2}$, Lili Liu$^1$, Guoming Zhu$^1$, Xin Zhang$^1$, Dongsheng Li$^1$, Sebastien Kerisit$^1$, Maria Sushko$^1$, Jaehun Chun$^1$, Elias Nakouzi$^1$, Chongmin N. Wang$^1$, Gregory Schenter$^1$, Kevin Rosso$^1$ and Chris Mundy$^1$; $^1$Pacific Northwest National Laboratory, United States; $^2$University of Washington, United States

Crystallization by assembly of primary nanocrystals is a widespread phenomenon in synthetic and natural environments. In mineral systems, this process exhibits diverse styles ranging from oriented attachment of like phases to mis-oriented aggregation of disparate phases followed by coarsening to single crystals. While descriptions of these systems must share a commonality with continuum-based DLVO-type theories for simple colloids, mineral systems present additional complexities, including face-specificity of dielectric properties, inherent diopolar interactions, structured nanoscale interfaces, and solvent-responses of a length scale comparable to particle size. To understand the relationship between nanocrystal structure, interparticle forces and assembly dynamics, we are investigating colloidal assembly of titanium, iron and zinc oxides. For ZnO, in situ TEM demonstrates that direction-specific forces align diffusing particles at distances far in excess of what is expected based on DLVO theory. Particles approach one another in a diffusion limited regime and then attach lattice matched via a sudden jump to contact unopposed by any significant energy barrier. Direct AFM-based measurements of the forces between both TiO$_2$ and ZnO surfaces reveal orientation dependent attractive interactions exhibiting the symmetry of the underlying lattice. MD simulations for both systems predict that solvation forces are responsible for the orientation dependence, creating solvent separated minima and barriers to contact. However, classical density functional theory applied to ZnO predicts that ion correlation forces lead to generally attractive interactions with little or no barrier, enabling random attachment, which is not observed. The long range nature of the forces and torques in the ZnO system are shown to be a consequence of the inherent dipole moments of ZnO particles and it is these dipole-dipole interactions that enforce alignment even in the absence of solvation-defined orientation dependent forces. Addition of organic ligands, like oxalate, to the FeOOH system produces a dramatically different pathway and outcome: Nanoparticles of Fe$_3$O$_4$ nucleate sporadically from the FeOOH and, once formed, are covered with oxalate, which drives all new Fe$_3$O$_4$ particles to nucleate within about 1 nm of the interface, after which they jump to contact. The oxalate inhibits growth...
and coarsening of the particles, leading to spindle-shaped aggregates of coaligned particles with a fixed and constant aspect ratio. Thus the random assembly process seen in the pure FeOOH system is replaced with one that is deterministic.

5:30 AM *S.CT08.01.02
Direct Imaging of Nucleation and Growth of Colloidal Nanoparticle Superlattices Qian Chen; University of Illinois at Urbana-Champaign, United States

We use liquid-phase transmission electron microscopy to directly image a series of crystallization pathways of colloidal nanoparticles into superlattices. We find that there exist similarities to the prevalent model system of micron-sized colloids, such as a non-classical two-step crystallization pathway, where amorphous intermediates in the form of nanoparticle clusters exist preceding the nucleation. Capillary wave theory can be used to describe the fluctuation and energy of the surfaces. But there are also differences, in particular, a universal layer-by-layer growth mode that we observe consistently for diverse nanoparticle shapes. Single particle tracking, trajectory analysis, and simulations combined unravel the energetic and kinetic features rendering this crystal growth mode possible and universal at the unexplored nanoscale, enabling advanced crystal engineering.

6:00 AM S.CT08.01.03
Direct Imaging of Atom-Mimicking Oriented Attachment of Nanoparticle Superlattices by Liquid-Phase TEM Chang Liu and Qian Chen; University of Illinois at Urbana-Champaign, United States

We utilize nanoparticle superlattice as a model system to study the fundamental laws of order emergence and evolution from a dispersion of nanosized entities. Liquid-phase TEM makes it possible to directly conduct single-particle level imaging in real time and real space, to reveal pathways of nanoparticle crystallization. To be specific, we observe how different types of diffusion events (e.g., surface and volume diffusion) involved in the layer-by-layer growth of a nanoparticle superlattice, where the high spatiotemporal resolution enables us to identify single particles throughout the whole process and to map out their trajectories sampling the energy landscape. Furthermore, oriented attachment of different nanoparticle lattice domains is observed, where fast translational and rotational diffusions of the domains drive the neck formation. The single-particle analysis aids correlating order evolution to differently ranged interactions. Such crystallization behavior is distinct from that of micron-sized colloids, resembling more the faceted crystals formed from atoms. Our study provides new dynamic information on the superlattice development at high spatial and temporal resolution, which can serve as a general guideline for bottom-up material design.

6:15 AM S.CT08.01.04
Unraveling Nonclassical Crystallization Pathways of Nanoparticle Superlattices via In Situ TEM Imaging Zihao Ou and Qian Chen; University of Illinois at Urbana-Champaign, United States

Nucleation and growth are universally important in systems from the atomic to the micrometer scale as they dictate structural and functional attributes of crystals. However, at the nanoscale, the pathways toward crystallization have been largely unexplored owing to the challenge of resolving the motion of individual building blocks in a liquid medium. Here we address this gap by directly imaging the full transition of dispersed nanoparticles to a superlattice at the single-particle level. We utilize liquid-phase transmission electron microscopy at low dose rates to control nanoparticle interactions without affecting their motions. Combining particle tracking with Monte Carlo simulations, we reveal that positional ordering of the superlattice emerges from orientational disorder. Otherwise elusive parameters including line tension and phase coordinates are measured, charting the nonclassical nucleation pathway involving a dense, amorphous intermediate. We elucidate the origin of this two-step crystallization by experimentally measuring the energy barrier for nucleation, which is lower in the presence of the amorphous precursor. We demonstrate the versatility of our approach via crystallization of different nanoparticles, pointing the way to more general applications. Our real space nanoscopic imaging platform not only offers new understanding on the crystallization kinetics, but also opens opportunities to other nanoscale fluctuating systems, from biofouling, lubrication, melting, phonon transport, to dendrite formation.

6:30 AM S.CT08.01.05
Temperature Induced Strain Relaxation in Epitaxially Connected Quantum Dot Superlattices Probed by In Situ STEM Michelle A. Smeaton, Daniel M. Balazs, Tobias Hanrath and Lena F. Kourkoutis; Cornell University, United States
The self-assembly of quantum dots (QDs) into epitaxially connected superlattices called quantum dot solids (QDSs), made possible by a growing library of synthesis methods for precisely controllable QD building blocks, represents exciting opportunities for advancing optoelectronic devices and realizing exotic electronic phenomena. However, the myriad complex interactions at play during the assembly and oriented attachment processes lead to imperfections in epitaxial connections between QDs. Such imperfections affect electronic coupling between QDs and lead to local translational disorder, which propagates through the film and hinders tunable miniband formation. Heating QDSs is a promising method for annealing out defects, thus improving electronic properties. Understanding the nuanced effects on epitaxial connections, however, requires visualization of atomic-scale structure over large enough fields of view to access a statistically meaningful number of QDs.

Here, we use in situ MEMS heating in combination with aberration-corrected HAADF-STEM and image analysis to assess the effects of heating on epitaxial connections in QDSs over extended fields of view. We analyze PbS QDs self-assembled into square SLs and epitaxially connected along the <100> directions. Localized heating provided by the MEMS device maintains stage stability such that a region of interest can be tracked throughout a heating cycle and images can be acquired at atomic-resolution over ~100 nm. We identify four distinct strain states in epitaxial connections: tension, shear, bending and torsion, noting that they appear concurrently in some cases. Using a local sine wave fitting technique similar to the phase lock-in method, we visualize the tension, shear and bending strain states. Given the limitation of STEM to projection imaging, torsion is investigated indirectly by identifying the out-of-plane orientation of each QD, nearest neighbor mismatches in which indicate torsion and out-of-plane bending strain states between connected QDs. The orientation data, in combination with wave fitting analysis, reveal that mild annealing between 150 and 200°C causes dramatic relaxation of tensile, shear and torsional strains, while bending strain is more persistent. These results give insight into the energetics of the types of defects present in epitaxial connections and represent a path toward improved carrier delocalization and miniband formation.

6:45 AM S.CT08.01.07
Synthesis, Phase Transformation and Structural Development in Magnetic Biocomposites Taifeng Wang1, Anna Pohl1, Steven Herrera1, Yuka Narahara2, Michiko Nemoto2 and David Kisailus3; 1University of California, Riverside, United States; 2Okayama University, Japan

There is an increasing need for the development of multifunctional lightweight materials with high strength and toughness. Natural systems have evolved efficient strategies, exemplified in the biological tissues of numerous animal and plant species, to synthesize and construct composites from a limited selection of available starting materials that often exhibit exceptional mechanical properties that are similar, and frequently superior to, mechanical properties exhibited by many engineering materials. These biological systems have accomplished this feat by establishing controlled synthesis and hierarchical assembly of nano- to micro-scaled building blocks. This controlled synthesis and assembly require organic that is used to transport mineral precursors to organic scaffolds, which not only precisely guide the formation and phase development of minerals, but also significantly improve the mechanical performance of otherwise brittle materials.

Here, we investigate an organism that have taken advantage of hundreds of millions of years of evolutionary changes to derive structures, which are not only strong and tough, but also demonstrate abrasion resistance. All of this is controlled by the underlying organic-inorganic components. Specifically, we discuss the formation of heavily crystallized radular teeth the chitons, a group of elongated mollusks that graze on hard substrates for algae.

Our investigation of the formation of a fully mature radular tooth from Cryptochiton stelleri found in the eastern Pacific, occurs over a series of more than 40 teeth. The initial stage of tooth formation begins with the synthesis of a three-dimensional fibrous α-chitin organic matrix, prior to the onset of crystallization. Microscope analysis of early stage teeth shows ferrihydrite mineral particles growing on α-chitin fibers. Synchrotron x-ray, combined with TEM analyses show that ferrihydrite exists as randomly oriented aggregates, but undergoes a phase transformation to magnetite within a few rows of teeth. We discuss potential mechanisms of nucleation of ferrihydrite, its transformation to magnetite as well as its subsequent mesoscale ordering, crystal growth and the resulting mechanical properties. From the investigation of synthesis-structure-property relationships in these unique organisms, we are now developing and fabricating multifunctional engineering materials for energy and water purification based applications.

7:15 AM S.CT08.01.08
Multi-Step Crystallization of Self-Organized Spiral Eutectics Saman Moniri and Ashwin J. Shahani; University of Michigan, United States

A novel method for the solidification of metallic alloys involving spiral self-organization is presented as a new strategy for
producing large-area chiral patterns with emergent structural and optical properties, with attention to the underlying mechanism and dynamics. This study reports the discovery of a new growth mode for metastable, two-phase spiral patterns from a liquid metal. Crystallization proceeds via a non-classical, two-step pathway consisting of the initial formation of a polytetrahedral seed crystal, followed by ordering of two solid phases that nucleate heterogeneously on the seed and grow in a strongly coupled fashion. Crystallographic defects within the seed provide a template for spiral self-organization. These observations demonstrate the ubiquity of defect-mediated growth in multi-phase materials and establish a pathway towards bottom-up synthesis of chiral materials with an inter-phase spacing comparable to the wavelength of infrared light. Given that liquids often possess polytetrahedral short-range order, our results are applicable to many systems undergoing multi-step crystallization.

7:30 AM S.CT08.01.09
Supercluster-Coupled Crystal Growth in Metallic Glass Forming Liquids Yujun Xie¹², Jan Schroers¹ and Judy Cha¹; ¹Yale University, United States; ²Yale West Campus, United States

Crystallization induced microstructure plays a central role in tailoring materials properties, yet our understanding of its formation process is limited due to its complexity. Classical crystallization theories assume that nucleation and growth are separate processes and growth ought to be temperature-dependent only. Local thermodynamically unstable clusters are considered to fluctuate in the nucleation stage but do not participate in the later growth. Here, we apply in-situ transmission electron microscope (TEM) to nanostructured metallic glasses (MGs) and directly probe crystallization kinetics at the unprecedented time and spatial resolution¹, ². In particular, the growth kinetics of single crystalline Pt₅₇.₅Cu₁₄.₆Ni₅.₃P₂₂.₅ MG nanorods were studied in situ by observing isothermal crystallization at the atomic level. We found that the crystal growth rates of heated metallic glass are much higher than those of cooled metallic liquid despite the same isothermal crystallization temperature. The observation is in direct contrast to one would expect from classical growth models. We, therefore, propose a supercluster-coupled growth model and hypothesize that structural ordering can strongly enhance the crystal growth. The asymmetric growth upon heating is thus attributed to the higher degree of structural ordering and a greater number of clusters in the MGs nanorods. The structure-coupled growth is further supported by manipulating the density of the small clusters through nanoscale confinement and thermal treatment of the MG nanorods. In addition, molecular dynamics simulations of binary Lennard-Jones glasses quenched at different cooling rates show a growth rate trend that agrees with experimental observations. The present results demonstrate the inadequacy of the classical crystallization model on modern complex materials systems.

Reference

7:45 AM *S.CT08.01.10
How Do Additives “Get the Job Done” During Nanoparticle-Mediated Crystallization? Alexander E. Van Driessche; CNRS - Univ. Grenoble-Alpes, France

Crystallization from solution follows either a single or a multistep pathway. The latter case involves the formation, aggregation and transformation of precursor/intermediate particles to the final crystalline phase. This has been observed for several important minerals, such as CaCO₃, CaPO₄, CaSO₄ or CSH [e.g. 1-3], but also for macromolecular crystals [e.g. 4,5]. Moreover, this particle-mediated crystallization pathway can be “fossilized” in the structure of the final crystals [e.g. 6]. In the idealized laboratory environment pure solutions are often studied, but in real-world natural and engineered crystallization processes soluble additives, e.g. inorganic or organic molecules, are omnipresent. In fact, they frequently play a key role in the formation of crystalline phases and are a central part of biomineralization, functional material synthesis and...
anti-scaling strategies [e.g. 7]. Traditionally, models of additive-controlled crystallization have considered a single step nucleation with additives adsorbing on the surface of nuclei, impeding their further growth. Hence, to advance our understanding and gain a better control of multistep crystallization processes, the interaction of additives with the precursors and/or intermediate particles needs to be unraveled.

To achieve this, we constructed a holistic nanoscopic view of a particle-mediated crystallization pathway in an additive free system [e.g. 5-8], based on in situ nanoscale observations. Subsequently, we conducted macroscopic and microscopic observations of additive-controlled crystal formation. Opposing the classical view, we found that the inhibition of nucleation can be ascribed to additives that hinder the formation of precursor species and/or their aggregation/transformation by prevailing in their vicinity and thereby reducing their interaction probability [e.g. 7, 10-11].


8:15 AM S.CT08.01.11
Reaction Pathway and Assembly of Pt Nanostructures Revealed with Low-Dose In Situ Microscopy Wenpei Gao, Peter Tieu, Christopher Addiego and Xiaqoing Pan; University of California, Irvine, United States

The progress of energy and electronic industry relies on the design and engineering of new nanostructures with fine control in the atomic scale. Examples include the use of twisted two-dimensional materials for the tuning of electronic structure, the surface engineering to create surface steps in metal nanowires that show enhanced catalytic activity. Manipulation of the atomic scale. Examples include the use of twisted two-dimensional materials for the tuning of electronic structure, the electron microscopy (TEM) or scanning transmission electron microscopy (STEM) allows the combination of low-dose imaging with in situ methods to study the materials dynamics at high spatial resolution, when coupled with high-speed direct electron detectors, the electric potential and field that can influence the materials interaction can also be imaged. Here we first demonstrate the atomic resolution imaging of a Pt precursor compound and the dynamics of its transformation to Pt nanoclusters. [1] Specifically, under an ultra-low electron dose, the atomic structure of pristine K2PtCl4 crystallite is resolved in the image captured by the CMOS-based direct electron detector. With further electron beam irradiation, the dynamics of staged reduction of Pt compound and nucleation of Pt cluster are captured and identified. Results show that the ionic bond between K+ and PtCl42- is first broken, which is followed by PtCl42- forming PtCl2; reduction of the dual-valent Pt then leads to the formation of Pt clusters. The solid-state transition is deciphered in real time and real space. Later, using a gas cell, we show that the sintering process of Pt clusters can be modified by gas adsorbates: [2] in H2, the Pt nuclei approach and attach to the formation of Pt clusters. The solid-state transition is deciphered in real time and real space. Later, using a gas cell, we show that the sintering process of Pt clusters can be modified by gas adsorbates: [2] in H2, the Pt nuclei approach and attach to


8:45 AM S.CT08.01.12
Hypoxia-Induced Biosynthesis of Gold Nanoparticles in the Living Brain Elena A. Rozhkova1, Byeongdu Lee1, Judy A. Prasad2, Yuzi Liu1 and Elena Shevchenko1; 1Argonne National Laboratory, United States; 2The University of Chicago, United States

Biosynthesis of NPs is a striking phenomenon in nature. Inspiring examples include storage and transport of iron atoms in a
non-toxic form of a ferric oxyhydroxide cluster in the ferritin protein cage, using metal salts as terminal sinks in electron transfer pathways and formation of metal particles by bacteria, and biomineralization of magnetite nanocrystals in specific organelle magnetosome that enables coordinated movement of magnetotactic bacteria. Under certain experimental conditions, metal complexes and nanoclusters can be obtained in mammalian cells or in a whole animal, mainly for use in imaging. However, the mechanisms of this biosynthesis are often spontaneous, poorly understood and, therefore, difficult to control. In our approach, a pathological process, namely hypoxia of the brain accompanied by changes in the NADH/NAD+ co-enzymes ratio, initiates and controls the biosynthesis of biocompatible Au nanoparticles from precursor salts in the immediate vicinity of the hypoxia site, thereby restoring the redox status of the brain.


SESSIO8 S.CT08.02: Crystal Nucleation, Growth and Phase Transformation

On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

5:00 AM *S.CT08.02.02

Engineering of Chiral Inorganic Nanostructures Nicholas A. Kotov: University of Michigan, United States

The early observation of strong circular dichroism for individual nanoparticles and their assemblies have developed into a rapidly expanding field of chiral inorganic nanostructures. The chiral inorganic nanostructures encompass sophisticated constructs from metals, semiconductors, ceramics, and nanocarbons with multiple chiral geometries with characteristic scales from Ångströms to microns. Such versatility enables their functional engineering over a broad range of physical and chemical properties but the relationship between the chirality of surface ligands, NP cores, and resulting assemblies remains obscure. Similarly, the relationship between their chiral geometries and their chiroptical properties. This talk will address (1) the origin of the uniquely high values of optical anisotropy; (2) the mechanisms of chirality transfer in inorganic materials; and (3) differences/similarities with chiral supramolecular, liquid crystal, and biological assemblies. Long-range correlations and critical phenomena in chiral nanoassemblies leading to the emergence of geometrically complex structures will be demonstrated. The novel venues for practical realizations of chiral nanoassemblies included in the talk will be photocatalytic C-C coupling in biomimetic chiral supraparticles and polarization spectroscopy in terahertz (THz) spectral window with chiroplasmonic kirigami composites.

5:30 AM S.CT08.02.04

Solid-State Phase Transformation and Self-Assembly of Amorphous Nanoparticles into Higher-Order Mineral Structures Stanislas Von Euw and Paul Falkowski; Rutgers, The State University of New Jersey, United States

Exerting control over non-classical pathways to crystallization to direct the growth, polymorphism, and self-assembly of inorganic nanoparticles into higher-order structures shapes the future of materials science [1]. To achieve this, the dominant strategy currently under development is directed towards our ability to govern the nucleation stage in a multitude of precipitation reactions occurring far from thermodynamic equilibrium [2]. These reactions share the common purpose of converting solution precursors into solid mineral materials, and, hence, are based on a number of different approaches that overcome the free-energy barrier to nucleation. We have examined the feasibility of an alternative approach that could not only overcome the limitations associated with the dominant strategy mentioned above, but also shape our way of manufacturing novel materials suitable for modern needs. We believe that future approaches will deliberately skip over the nucleation stage on which little control can be exercised, and will focus on the conversion of solid, metastable amorphous nanoparticles into their crystalline counterparts. Such metastable amorphous nanoparticles that latter transform into higher-order, hierarchical mineral structures have been observed across various biomineralizing taxa such as stony corals [3], but their use in synthetic systems remains extremely limited. Here we used Amorphous Calcium Magnesium Carbonate (ACMC) nanoparticles as models, and we monitored their pathway to crystallization in aqueous medium to show their potential usefulness in the development of novel materials. To this end, we applied a combination of ultrahigh-resolution three-dimensional imaging, and in situ, solid-state nuclear magnetic resonance (ssNMR) spectroscopy.

Our results reveal the underlying mechanism of the phase transformation of these Amorphous Calcium Magnesium Carbonate (ACMC) nanoparticles into crystals in wet conditions. First, they suggest that these amorphous nanoparticles are
coated by a rigid hydration shell of bound H2O molecules when soaked in water. Our results also show that fast chemical exchanges occur between hydrogens from the nanoparticles and those from the free H2O molecules of the surrounding aqueous medium. Crystallization spontaneously occurs after the amorphous nanoparticles were soaked in water. Using two-dimensional ssNMR spectroscopy, we especially show that the nascent crystalline environments, together with the starting amorphous materials, belong to the same particles. This is a clear spectroscopic evidence of a solid-state phase transformation of the starting amorphous nanoparticles into crystals. In addition, we reveal that the starting amorphous nanoparticles remain hydrated while crystallization progresses. There is also evidence of fast chemical exchanges between hydrogens from the amorphous nanoparticles partially converted into crystals, and those from the free H2O molecules of the surrounding aqueous medium. Hence, our results question the role played by these unceasing chemical exchanges towards crystallization. We imagine that they are likely to be associated with an enhanced mobility of the ions/molecules that compose the amorphous nanoparticles which, in turn, allows for rearrangement of these ions/molecules into crystalline domains. Lastly, using ultrahigh-resolution three-dimensional imaging, we show that these amorphous nanoparticles aggregate to form ordered crystalline structures through crystal growth by particle attachment; and this conclusion is further supported by our ssNMR results. As such, these metastable amorphous nanoparticles open new avenues to develop novel ceramic or inorganic-organic hybrid materials through strategies that are no longer limited by the nucleation stage.


5:45 AM *S.CT08.02.06
Real Time Imaging of the 3D-2D Transformations of Nanocrystals through Liquid Cell Transmission Electron Microscopy Haimei Zheng1,2; 1Lawrence Berkeley National Laboratory, United States; 2University of California, Berkeley, United States

In recent years, significant achievements have been made in the synthesis of various colloidal nanostructures. The anisotropic nanostructures, such as nanowires or two-dimensional (2D) materials have attracted a lot of attention due to their unique properties. However, their formation mechanisms have not been fully understood. They seem to be contradictory to the predictions based on the conventional crystal growth theories. And, it adds to the complexity that nanocrystals often change structure and morphology during growth. We explore the growth mechanisms of anisotropic nanocrystals using in situ liquid cell transmission electron microscopy (TEM). In this talk, I will show the growth of 2D transition metal oxide nanosheets, e.g. cobalt oxide and cobalt nickel oxide. The 2D nanosheets have been achieved in a liquid cell, which resemble those synthesized in flasks. Our direct observations reveal that 3D nanoparticles are initially formed from the molecular precursor solution and then transform into 2D nanosheets. Ab initio calculations show that a small nanocrystal is dominated by positive edge energy, but when it grows to a certain size, the negative surface energy becomes dominant, driving the transformation of the 3D nanocrystal into a 2D structure. Uncovering these growth pathways, including the 3D-to-2D transition, provides opportunities for the future design and solution synthesis of novel materials.

References:

Acknowledgements:
The project was funded by U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231 within the in situ TEM program (KC22ZH). Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

6:15 AM S.CT08.02.07
Gypsum—Anhydrite Phase Transformation and Crystal Growth Induced by Microorganisms Living in the Atacama Desert Wei Huang1, Emine Ertekin2, Taifeng Wang1, Luz Cruz1, Jocelyne DiRuggiero2 and David Kisailus1; 1University of California, Riverside, United States; 2Johns Hopkins University, United States

Microorganisms have been found living in one of the driest and oldest deserts on the earth, the Atacama Desert in Chile. In
this hyper-arid environment, microbial communities colonize the interior of rocks and obtaining water is critical for their survival. Gypsum (CaSO₄•2H₂O) is one of the main components in rocks from the Atacama Desert and is a main source of water for these communities, which are mainly constituted of cyanobacteria and heterotrophic bacteria. We report that these microorganisms extract crystalline water from the gypsum rock, inducing a phase transformation from gypsum (CaSO₄•2H₂O) to anhydrite (CaSO₄). Cyanobacteria cultures were inoculated on gypsum rock samples to investigate and validate the water extraction and phase transformation mechanisms found in the geological environment. It is shown that cyanobacteria attach on high surface energy crystal planes and generate a thin biofilm on the gypsum samples. Due to the acidic nature of the biofilm, gypsum dissolution is observed, accompanied with water extraction and subsequent transformation to anhydrite via reprecipitation and oriented attachment of mesocrystals. This is the first time showing gypsum – anhydrite phase transformation and non-classical crystal growth induced by microorganisms. The results in the present work not only shed light on how these organisms survive in such extreme environments, but also can provide insight into potential life in xeric environments such as Mars as well as offer strategies for advanced water storage methods.

SESSION S.CT08.03: Materials Synthesis and Processing
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-CT08

5:00 AM *S.CT08.03.01
How Solution-Phase Additives Control the Shapes of Metal Nanocrystals in Solution Kristen A. Fichthorn; The Pennsylvania State University, United States

Metal nanocrystals have gained tremendous attention due to their superior performance in various applications, ranging from selective catalysis to electronic devices to plasmonic applications, such as photovoltaics and sensing. The properties of nanocrystals are highly sensitive to their size and shape. To this end, solution-phase synthetic protocols have been highly successful at producing a variety of nanocrystal structures. However, great challenges remain in achieving high selectivity to particular nanostructures. A significant difficulty lies in understanding and controlling shape evolution in these systems.

A common adage is that solution-phase additives, such as capping molecules, can direct the shapes of colloidal nanocrystals by adsorbing selectively to certain facets. Though our first-principles-based studies indicate that capping molecules alone can direct the formation of nanocrystal shapes in certain systems, experiments demonstrate that more robust syntheses can be achieved in the co-presence of halide additives. We use DFT-based ab initio thermodynamics calculations to probe the influence of chloride on Ag nanoshapes. Consistent with experiment, these calculations indicate that chloride adsorption alone can lead to truncated Ag cubes. We find that adsorbed chlorine works synergistically with PVP, a common capping agent for Ag, to enhance the tendency for Ag cubes. We also demonstrate that adsorbed Cl works synergistically with HDA capping molecules to facilitate the growth of Cu nanowires via a kinetic pathway - consistent with experiment. These studies indicate that halides and capping molecules can be a powerful combination to create selective nanoshapes in solution-phase syntheses.

5:30 AM S.CT08.03.03
The Role of Carbon and SiC Crystallinities in the Oxidation and Mechanical Property Improvement of Hybrid Nano-Fibers Saja M. Al-ajrash; University of Dayton, United States

In this study, electrospinning was successfully used to fabricate hybrid Carbon-Silicon Carbide (C-SiC) fibers using polyacrylonitrile (PAN) and Silicon (Si) nanoparticles as precursors. Silicon-to-carbon precursor ratios and heat treatment were optimized to fabricate hybrid nano-fibers with high oxidation resistance. After heat treatment, the nano-fibers showed two-dimensional ordered carbons and SiC nano-phases formation. As a result, a noticeable improvement in mechanical and thermal properties was achieved. Samples with 90wt% PAN/10wt% Si showed about four-time improvements in char yield as compared with 100 wt % PAN. In addition, after the heat treatment of the fiber at 1250 °C, SiC was formed. The carbon and SiC crystallinities had a great impact on the oxidation and mechanical property improvement of hybrid nanofibers. The determination of crystal size was carried out using X-ray results obtained at different temperatures and holding times. The SiC grain growth was predicted using kinetic models and its exponent was found to be around n = 4 with activation energy around 35 KJ/mol.K. For such growth, the dominant grain growth mechanism was grain boundary diffusion.
The unique properties of nanoporous aluminosilicates (zeolites) are exploited in a variety of applications spanning from ion exchange and separations to catalysis and drug delivery. The ability to selectively control zeolite synthesis to achieve desired physicochemical properties relies upon detailed understandings of the thermodynamic and kinetic factors regulating crystal nucleation and growth, which are generally lacking. Designing innovative approaches to tailor zeolite crystallization and elucidate structure-performance relationships has the potential to produce materials with superior properties beyond what is achievable by conventional routes. In this talk, I will discuss efforts to characterize the complex mechanisms of zeolite crystallization, which occur by nonclassical pathways involving the self-assembly and structural evolution of amorphous precursors. There is still much that we do not understood regarding the role of precursors in nucleation and the influence of growth conditions on the selection of crystal topology, which underscores the need for molecular-level studies of zeolite crystallization. Our group addresses these challenges using a broad range of techniques that include the use solvothermal atomic force microscopy to capture time-resolved images of growing zeolite surfaces in real time. This technique has led to the first in situ characterization of zeolite growth with the capability of resolving surface dynamics at the spatiotemporal scales necessary to elucidate mechanistic pathways of crystallization. Based on our findings, we observe that growth occurs via multiple (cooperative) pathways that differ from one material to the next. In this talk, we will summarize our findings for several zeolite structures.

References
starting reactant ratios can yield phase-pure single-phase compounds, where excess P and As can be sublimed away from the phase of interest. Furthermore, this method can generate single crystals for structural characterization due to the P and As acting as transport agents in addition to being reactants. The structural chemistry, polymorphism, and properties of the family of {R,T}-Si-Pn compounds will be discussed.

6:30 AM *S.CT08.03.08
Fabrication of High-Performance Carbon Fibers Using Template Induced Crystallization Rahul Franklin, Weiheng Xu, Dharneedar Ravichandran and Kenan Song; Arizona State University, United States

Carbon fibers have broad applications in aerospace, automobiles, wind turbines, medical devices, and implants, among many others. Carbon fibers with high-end applications have previously been manufactured from precursor fibers of rayon, pitch, and polyacrylonitrile (PAN) fibers. New precursor fibers have been conventionally fabricated by homogenously mixing the reinforcement/nanofiller and polymer matrix mechanically and spinning the dope into a coagulation bath, such as PAN processing in the case of dry-jet wet spinning followed by the drawing stage and heat treatment at different temperatures. Mechanical properties of this fiber are dependent on the continuity, density and interfacial action of the hierarchical graphitic structures. The presence of voids formed during crystallization due to the random dispersion of reinforcement/nanofiller in pre-carbon fibers (pCFs) deteriorates these properties. In this project, a specialized templating graphene channel was developed via an in-house designed spinneret. This channel containing graphene and varied PAN solutions running along the axial direction of the fiber was parallel to the outer and inner PAN channels. On drawing the as-spun fibers the GNP was aligned in the axial direction. This channel then allowed for crystallization along the axial direction and minimizes the formation of voids leading to enhanced mechanical properties. The mechanical test showed the composite as-spun fiber with GNP templating channel has 18.5% and 51.4% increased Young’s modulus and tensile strength, respectively, as compared to the pure PAN fiber. The thermodynamics and kinetics of the heat-treatment procedures were analyzed to correlate the microstructure features and mechanical/thermal properties of obtained carbon fibers.

6:45 AM *S.CT08.03.09
Non-Classical Crystallization of Thin Films and Nanostructures in the Chemical Vapor Deposition Process Nong-Moon Hwang; Seoul National University, Korea (the Republic of)

Although non-classical crystallization has been studied extensively in the solution growth, not much attention has been paid to the non-classical crystallization in the gas phase synthesis of thin films and nanostructures by chemical vapor deposition (CVD). Extensive studies were made in CVD processes and the non-classical crystallization was shown to be a general growth mechanism of thin films and nanostructures [1], where the charged nanoparticles become the building block. Generation of charged nanoparticles was confirmed in most CVD processes, including the growth of films and nanostructures of diamond, carbon nanotubes, ZrO₂, Si, ZnO and GaN. Small charged nanoparticles are favorable for epitaxial growth whereas large ones are favorable for nanostructure growth. Understanding made from the non-classical crystallization behaviour in the CVD process can provide the valuable information as to the non-classical crystallization in solution. For example, building block of nanoparticles are electrically charged in the CVD process and the presence of charge plays a critical role in the growth of thin films and nanostructures. The charge is responsible for not only self-assembly but also liquid-like coalescence, which result in the evolution of dense films and nanostructures. The role of charge could be clearly revealed by comparing the deposition behavior of silicon charged nanoparticles between electrically floating and grounded silicon substrates. Single crystalline silicon nanowires grew on the floating substrate whereas nanoparticles grew on the grounded substrate. In other processing conditions, a dense silicon film grew on the floating substrate whereas a porous silicon film grew on the grounded substrate. The fact that charged nanoparticles can be a building block of films and nanowires without leaving any void behind indicates that charged nanoparticles are quasi-solid, having a liquid-like property in diffusion. This means that the charge enhances the atomic diffusion, which is a newly discovered physical phenomenon. The charge-enhanced kinetics could be analyzed by comparing the behavior of Au nanoparticles on conducting and insulating membranes during transmission electron microscopy (TEM) observation. Au nanoparticles on insulating membranes were actively changing their orientation during TEM observation whereas those on conducting membranes were not. Also plasma dewetting behavior of sputtered Sn films was compared between grounded and floating conditions. The dewetting kinetics of Sn films in the floating condition was much higher than that in the grounded condition. Both experimental results support charge-enhanced kinetics. In this presentation, some important aspects of the non-classical crystallization in the CVD process would be introduced, emphasizing that the non-classical crystallization occurs not only in solution but also in the gas phase synthesis.

[1] N.M. Hwang, Non-Classical Crystallization of Thin Films and Nanostructures in CVD and PVD Processes, vol. 60,
Two-dimensional (2D) materials have attracted significant attention due to their unique structure and fascinating properties. However, our understanding of their growth mechanisms in solution is still limited. Here, using indium chloride (InCl₃) as a model system, we performed liquid phase transmission electron microscopy (TEM) study of the 2D growth in situ. We combined the low temperature techniques with liquid phase TEM. The nucleation and growth of 2D nanosheets in solution via both classical and non-classical pathways were observed with the atomic resolution in real time at room temperature as well as low temperature (e.g., 1-2 °C). We found the drastically decreased growth kinetics at the low temperature compared to that at the room temperature. Observation also showed that the fast growth induced the high density of crystal defects (e.g., nanotwins). Comparatively, perfect 2D nanocrystals were obtained through the low temperature growth. In addition, we did the atomic structural analysis of the nanosheets and chemical mapping of the reaction front at the Cryogenic temperature using the same liquid cell sample. The results revealed the growth mechanisms of InCl₃ 2D nanosheets and the formation of nanotwins in solution. And, the liquid phase TEM with variable temperature control opens many opportunities for future depth study of nanoscale materials growth and transformations.

Synthesis design remains a paramount problem in materials science. Significant research has been dedicated to advancing tools to predict and aid in synthesis development. Here we describe an ab-initio approach to evaluate water-based synthesis processes such as hydrothermal synthesis. We show how to use electrochemical Pourbaix diagram, constructed from first principles density functional theory (DFT) calculations, to understand thermodynamic forces of complex Cu oxides and Cu oxychalcogenides in aqueous environments. We discuss how to construct these complex diagrams consisting of many degrees-of-freedom, including multiple elemental species, compounds, and complexes as well as nonstandard state conditions. We describe how the driving forces for the products evolve with changes in pH, oxidation state, and the activity of reactants; this understanding is then used to justify successful experimental synthesis of the targeted phase. Scale dependent nucleation is also examined. Last, we propose Pourbaix diagrams are a useful synthesis-processing design tool for accelerated discovery.

Metallic glasses serve as a good model system to study crystallization due to their non-directional metallic bonds, relatively slow crystallization kinetics, and moderate crystallization temperatures, which readily allow direct visualization of crystallization events at the atomic scale via in situ TEM experiments. At the nanoscale, we have observed crystallization phenomena that deviate greatly from the macroscopic behaviors due to the geometrical confinement effects. These include suppression of crystallization for very small metallic glass nanorods [2], emergence of a metastable, single crystalline phase out of multi-component metals [3], and the structure-coupled crystallization [1]. The structure-coupled crystallization was inferred from the asymmetric growth rates of a heated metallic glass versus a cooled metallic liquid. We demonstrate that thermodynamically unstable structural ordering in the glass state can be kinetically stable enough to enhance crystal growth during crystallization. Thus our works highlight crystallization via non-classical pathways.
8:15 AM S.CT08.03.15
Strain Localization and Dynamic Recrystallization in Polycrystalline Metals—Thermodynamic Theory and Simulation Framework
Charles Lieou1, Hashem Mourad1 and Curt Bronkhorst2,1; 1Los Alamos National Laboratory, United States; 2University of Wisconsin–Madison, United States

We describe a theoretical and computational framework for adiabatic shear banding (ASB) and dynamic recrystallization (DRX) in polycrystalline materials. The work is based on the thermodynamic dislocation theory (TDT) by Langer et al., to which we add the grain boundary density as an internal state variable. TDT provides a convenient and thermodynamically consistent way to represent the viscoplastic and thermal behavior of the material, with minimal ad-hoc assumptions regarding the initiation of yielding or onset of shear banding. Within the TDT framework, dynamic recrystallization emerges as an entropic effect arising from the competition between dislocation creation and grain boundary formation, and contributes to material weakening and failure. We implement the TDT-DRX theory in conjunction with a finite-element computational framework. Favorable comparison to experimental measurements on a top-hat AISI 316L stainless steel sample compressed with a split-Hopkinson pressure bar suggests the accuracy and usefulness of the TDT-DRX framework, and demonstrates the crucial role of DRX in strain localization.

8:30 AM S.CT08.03.16
Slow-Injection Synthesis of Indium Phosphide Quantum Dots as a Route to Large Size and Low Size Dispersity
Odin B. Achorn and Moungi G. Bawendi; Massachusetts Institute of Technology, United States

The color purity of indium phosphide (InP) quantum dots (QDs) lags behind that of cadmium selenide (CdSe) QDs, especially at their largest sizes and reddest wavelengths. In order to improve the quality of InP QDs, we have developed a new synthetic method that features a slow precursor injection rate in contrast to the rapid injection rates that have worked so well for CdSe QD syntheses and that have traditionally been applied to InP. The absorption features of the InP QD batches produced by our method are redder than those of batches of comparably-disperse InP QDs and narrower than those of batches of comparably-sized InP QDs that are produced by other methods. We prepared InP QDs with first excitonic absorption peaks that are redder than 630 nm and have half widths at half maximum less than 85 meV. After adding a zinc selenide shell, we achieved core/shell QDs that are redshifted slightly with respect to the core and have photoluminescence full widths at half maximum under 55 nm. Our method also allows us to synthesize even larger InP cores with defined first excitonic absorption peaks that are redder than 660 nm. We used MALDI mass spectrometry to characterize the size and size dispersity of the QDs and to investigate the presence of low molecular weight clusters and secondary populations. Lastly, we find that the concentration of QDs increases throughout the entire course of the reaction, and we propose a nucleation and growth model to explain our observations.
(FCC), but how they nucleate and grow and transform from one to another remain largely unknown. In this work, we applied highly monodispersive magnetite nanocubes with an average side length of 12.5 nm, and controlled various assembly environments, and revealed the formation and growth of three major phases (SC, acute Rh and FCC). Taking advantage of synchrotron-based SAXS techniques, we also explored the structural correlations between three superlattices phases. With additional simulations and computations, we further discussed the driving forces and constructed a reasonable superlattice phase diagram of nanocube-based assembly. Our results not only dramatically expand our understanding on the shape-dependent phase behaviors of nanocrystal, but also provide insights for design and fabrication of novel functional materials.

S.CT08.04.02
DFT Study of Graphene Formation in Carbon Droplets Condensed in Stellar Atmospheres
Chathuri Silva, Philip Fraundorf, Eric H. Majzoub and Philip Chrostoski; University of Missouri-St. Louis, United States

Because macroscopic clusters of elemental carbon at low (ambient) pressure sublimate to vapor near 4000K, liquid carbon is seldom considered to play a role in nature even though quenched carbon droplets have been reported in laboratory laser ablation studies [1,2]. However, a subset of meteoritic carbon particles from red giant atmospheres show a “graphene-core”/graphite-rim structure [3,4], likely following condensation of super-cooled carbon droplets from the vapor phase, which nucleated graphene sheets on randomly-oriented 5-member rings before solidification and subsequent coating with a graphite rim. Similar core-rim particles can be formed by slow cooling of carbon vapor in the lab [5]. It remains a challenge to study the properties of liquid carbon in a lab due to the difficulty of experimentation under extreme conditions. Therefore, we investigated nucleation and growth of carbon rings and graphene sheets using density functional theory (DFT). We assume low pressure, with an experimental 1.8 g/cc density estimate, and relax randomized positions of liquid-like 13/20-carbon atom clusters in a cubic supercell. Inter-atom distances characteristic of covalent vs. metallic interactions (with a gap in 1.7-2.0 Å range) allow us to identify covalent “bonds” with small separation. Local energy minima at T = 0K show a mix of sp² and sp, plus few sp³ coordination numbers as in the literature which reports that liquid carbon favors sp coordination at lower densities, sp³ coordination at higher densities, and a mix of sp and sp³ coordination at intermediate densities [6-10]. Ring sizes vary from triangle to heptagon, but pentagons are more abundant than hexagons, also consistent with previous reports [9,10]. Further work remains to see if such ab initio studies can confirm that abundant pentagonal rings at this density, during slow cooling of the liquid, can nucleate the growth of faceted pentacones as suggested by electron phase-contrast imaging of the presolar cores [11].

In summary DFT relaxation of random configurations of 13/20-atom clusters in a supercell, along with literature reports of the same, suggest that: (a) covalent bonds can be identified by interatom spacings below 1.85 Å, (b) sp³ coordination is expected at that density, and (c) pentagonal rings are more abundant than hexagonal rings as possible nucleation seeds. The properties of unlayered graphene sheets in a frozen liquid matrix, e.g. as a diffusion barrier, should be interesting to explore further both experimentally and computationally.

References

S.CT08.04.03
Fabricating Polystyrene Core-Shell Fibers
Dharmeedar Ravichandran, Weiheg Xu, Rahul Franklin, Namrata Kanth, Sayli Jambhulkar, Ali Alshami, Sumeeti Shukla and Kenan Song; Arizona State University, United States

Core/shell fibers have many broad applications in the biomedical field, such as drug delivery and tissue engineering, and are also used in environmental-related applications like water treatment and CO₂ absorption. This research demonstrated an alternative technique of gel-spinning for fabricating core/shell structures other than the traditionally used melt spinning or electrospinning technique. These fibers were porous in the shell and had capabilities to load particles in the core. Polystyrene (PS) and polyethylene glycol (PEG) were used as an example for demonstrating the feasibility of the core/shell fiber
A two-phase liquid-state microstructure was first achieved via the co-axial spinneret with the exterior layer composed of PS pellets (PSP)/PEG/organic solvent (e.g., xylene or dimethylformamide) solutions and the interior layer containing dispersed PS spheres (PSs)/PEG/water solutions. Procedures of coagulation, heat-treatment, and phase-separation-based selective dissolution were used to generate the porous-shell/particle-core fibers. The pore sizes and density were controlled by the porogen (i.e., PEG) concentrations and examined using scanning electron microscopy (SEM). The fiber formation dynamics and microstructural features were studied via rheology tests and gelation measurements, tensile tests, thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC).

**S.CT08.04.05**

**Hematite Mesocrystal Formation through Near Interface Nucleation and Oriented Aggregation** Guomin Zhu¹, Maria Sushko², John Loring², Miao Song², Benjamin Legg¹, Xiaopeng Huang², Kevin Rosso² and James J. De Yoreo²*,¹; ¹University of Washington, United States; ²Pacific Northwest National Laboratory, United States

A diverse class of materials exhibit characteristics of mesocrystals: single crystals constituting distinct nano-sized domains that are atomically aligned. The formation of such structures is often attributed to crystallization through oriented attachment. However, many questions about the fundamental drivers and dynamic progression of this phenomenon remain. And the process become more complexed when coupled with phase transformation. Here we focus on the crystallization of hematite (hm, Fe₂O₃) mesocrystals from ferrihydrite (fh) nanoparticles. In the oxalate-free solution, the resulting hm crystals are well faceted rhombohedron, while in the presence of oxalate, hm forms nanoporous spindle-shaped mesocrystals. We applied in situ liquid phase TEM with heating temperatures of 80 °C to investigate the formation. We directly observed both the dissolution of fh and the nucleation of new hm particles, which formed within close proximity (~ 1 nm) of the hm/solution interface. Immediately after nucleation, the hm particles attached to the nearby seed to form a hm mesocrystal. Post analyses using EDX mapping and electron diffraction after disassembling the liquid cell confirmed the growth of spindle-shaped hematite during the liquid phase TEM experiments. In addition, we utilized a quasi in situ approach of using indexed TEM grids to cycle samples between the growth reactor and the TEM in order to track the pathway of crystallization. The results were consistent with those of the in situ experiments and confirmed that the fh serves as a buffer and the Hm grow by creation of new particles in the solution near the hm interface. Based on ATR FTIR measurements, ion chromatography and classic DFT calculation we propose that oxalate plays the role of inhibiting classical monomer-by-monomer growth of the hematite particles while promoting the nucleation of new hm particles at the hm/solution interface by modifying the interfacial energy of hm close to the hm/solution interface. In this way, the oxalate ligands bias the growth process away from classical mechanisms and towards oriented attachment.

**SYMPOSIUM S.EL01**

Surfaces and Interfaces in Electronics and Photonics
November 21 - November 29, 2020

**Symposium Organizers**
Silvia Armini, imec
Santanu Bag, Air Force Research Laboratory
Mandakini Kanungo, Corning Incorporated
Hong Zhao, Virginia Commonwealth University

**Symposium Support**
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**Bronze**
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* Invited Paper
SESSION S.EL01.07: Live Keynote I: Surfaces and Interfaces in Electronics and Photonics
Session Chairs: Santanu Bag and Mandakini Kanungo
Saturday Morning, November 28, 2020
S.EL01

8:00 AM *S.EL01.01.01
Energy Storage Devices and Optoelectronic Sensors from Solution-Processed Polymers Kaiping Wang¹, Ning Li¹, Jason Azoulay² and Tse Nga Ng¹; ¹University of California, San Diego, United States; ²University of Southern Mississippi, United States

Conducting polymers are an important class of Faradaic materials for energy storage, as they present opportunities to create energy dense supercapacitors. The vast majority of conducting polymers are p-type cathodes and already operating at or close to the upper voltage limit of non-aqueous electrolytes. On the other hand, it is generally safe for electrolytes to operate down to -2 V vs Standard Hydrogen Electrode. Therefore, extending the operational voltage in the negative range is an attractive route to increase energy density. Here we present promising n-type polymers that retained 90% of initial capacitance after 5000 charge-discharge cycles. The polymers are processed with solution based methods to ensure that the devices are scalable to large area. The electronic and ionic transport in the conducting polymers are monitored in operando by current-voltage and spectroscopic measurements, where spatial variations of film absorption would be mapped to discern electronic versus ionic degradation. We infer the mechanisms that lead to capacitance fade and suggests structural and electrochemical strategies to realize high-endurance energy storage devices for flexible printed systems.

In addition to energy storage, the narrow bandgap polymers are used to realize photodetectors that is relevant to a variety of applications including environmental monitoring and medical diagnosis. Here we show how the infrared polymers are processed into bulk heterojunction photodiodes with photoresponse up to wavelength of 1.7 micron. The performances of devices with different polymer structures were compared through metrics including detectivity, quantum efficiency, response time and rectification ratio. Example applications including hemodynamics and tissue composition measurements will be demonstrated.

8:24 AM DISCUSSION TIME

8:48 AM *S.EL01.01.06
Solution Chemistry of Semiconducting Metal Oxides at the Atomic Scale Melissa A. Hines; Cornell University, United States

Semiconducting metal oxides, particularly transparent conducting oxides, have attracted a great deal of attention for a variety of applications. Nevertheless, the solution chemistry and solution functionalization of these materials has been much less explored than that of traditional semiconductors, such as silicon. One challenge in the stable functionalization of these materials is that their semiconducting nature enables efficient generation of long-lived photocarriers that can initiate chemical reactions that degrade the functionalization. This reactivity has typically been attributed to the undercoordinated metal cation sites at the surface, although direct evidence has been lacking. We have developed a new photochemical reaction that leads to the fluorination of all exposed metal cation sites on TiO₂. In contrast to approaches that use fluoride or HF-containing solutions, our method produces covalently bonded fluorine which is stable in aqueous solutions. To our surprise, these fluorine-terminated TiO₂ surfaces display higher photoreactivity than comparable “clean” surfaces. Possible origins of this behavior will be discussed.

We have also investigated the structure of solution-deposited monolayers on TiO₂ and demonstrated a rational approach to tuning intermolecular interactions and enabling long-range ordering. We show that simple electrostatic insights can be used to engineer away unfavorable intermolecular interactions, producing monolayers with exceptional long-range ordering. Quantitative measurements of the intermolecular interaction energies from molecularly resolved STM images are a factor of ~7 larger than those predicted by dispersion-corrected density functional theory (DFT). This finding suggests a new path to the production of highly ordered monolayers and superstructures of large molecules.

9:12 AM *S.EL01.01.07
Atomic Layer Deposition from Dissolved Precursors for the Preparation of Accurately Nanostructured
Heterojunctions Maïssa Barr1, Vanessa Koch1, Soheila Nadiri1, Ceyla Asker1, Dong-Hui Chen2, Peter G. Weidler2, Felix Hoga1, Tobias Stubhan1, Engelbert Redel2, Helmut Baumgart3, Christoph J. Brabec1 and Julien Bachmann1,4; 1Friedrich Alexander University, Germany; 2Karlsruhe Institute of Technology, Germany; 3Old Dominion University, United States; 4Saint Petersburg State University, Russian Federation

An interdigitated geometry of the interface between semiconductors remains a Graal in the photovoltaic field. Nanocylindrical solar cells based on a coaxial p-n or p-i-n junction have been generated in a small number of materials systems only so far, mostly among the classical semiconductors. The generalization of this interface geometry to alternative semiconductors, which are expected to profit of it most, has been hampered by the lack of appropriate deposition methods suited to coating complex three-dimensional structures in a conformal manner. Atomic layer deposition (ALD) provides this capability, but is limited by the necessity to use gaseous precursors in vacuum conditions. Modern classes of semiconductors such as the hybrid perovskites are not accessible by ALD due to their ionic nature.

In this perspective, we have transferred the principles of ALD to precursors dissolved in liquid solvents. The ‘solution ALD’ (sALD) method can be implemented in a variety of microfluidic or slot-die processing devices. We have demonstrated that the principles of classical, gas-based ALD—self-limiting surface reactions—are reproduced in sALD. Furthermore, sALD allows the experimentalist to design new, advantageous, reactions of known semiconductors (oxides, heavier chalcogenides), or to deposit materials otherwise inaccessible to ALD altogether, such as polymers, ionic solids, and metal-organic frameworks. They may be obtained in highly pure, crystalline form at room temperature, either as planar films or as conformal coatings of porous substrates. Based on these advances, we have been able to make the first sALD-derived hybrid perovskite cells.

9:36 AM *S.EL01.01.04
Activating Conductivity in Liquid Metal Particle Films by Laser and Thermal Sintering Rebecca Kramer-Bottiglio; Yale University, United States

Metallic inks with superior conductivity and printability are necessary for high-throughput manufacturing of printed electronics. In particular, gallium-based liquid metal inks have shown great potential in creating soft, flexible and stretchable electronics. Despite their metallic composition, as-printed liquid metal nanoparticle films are non-conductive due to the surrounding metal oxide shells which are primarily Ga2O3, a wide-bandgap semiconductor. Hence, these films require a sintering process to recover their conductivity. For conventional solid metallic nanoparticles, thermal and laser processing are two commonly used sintering methods, and the sintering mechanism is well understood. Nevertheless, laser sintering of liquid metal nanoparticles was only recently demonstrated, and to date, the effect of thermal sintering has rarely been investigated. In this talk, eutectic gallium–indium nanoparticle films processed separately by laser or thermal sintering in an ambient environment will be presented. Laser and thermally sintered films will be compared with respect to electrical conductivity, elemental composition, crystallinity and surface morphology. Both methods impart thermal energy onto the films and generate thermal stress in the particles, resulting in rupture of the gallium oxide shells and achieving electrical conductivity across the film. For laser sintering, extensive oxide rupture allows liquid metal cores to flow out and coalesce into conductive pathways. For thermal sintering, due to less thermal stress and more oxidation, the oxide shells only rupture locally and extensive phase segregation occurs, leading to non-liquid particle films at room temperature. Electrical conductivity is instead attributed to segregated metal layers and gallium oxide which becomes crystalline and conductive at high temperatures. This comprehensive comparison confirms the necessity of oxidation suppression and significant thermal stress via instantaneous laser irradiation to achieve conductive liquid metal patterns.

SESSION S.EL01.08: Live Keynote II: Surfaces and Interfaces in Electronics and Photonics
Session Chairs: Silvia Armini and Santanu Bag
Sunday Afternoon, November 29, 2020
S.EL01

2:45 PM *S.EL01.02.01
Understanding Area Selective Atomic Layer Deposition by a Comparative Study of Precursors Il-Kwon Oh1, Tzu-Ling Liu1, Tania Sandoval2, Ralf Tonne1er and Stacey F. Bent1; 1Stanford University, United States; 2Technical University Federico Santa Maria, Chile; 3Philipps-Universitat, Germany

The rapid growth of technologies such as machine learning and autonomous vehicles is fueling a need for more powerful
electronic devices requiring complex nanoscale structures. With the growing demands on nanostructure fabrication, selective deposition is gaining attention as a process to enable pattern features at the sub-10 nm length scale. This talk will focus on area selective atomic layer deposition (AS-ALD), a bottom-up growth strategy in which material is added only where desired, without the need for subsequent lithography and etch steps. ALD is a good choice for selective deposition because its chemical specificity provides a means to achieve selectivity on a spatially patterned substrate. One popular approach to AS-ALD uses inhibitory layers such as self-assembled monolayers (SAMs) to alter the native surface reactivity, allowing ALD selectivity to be achieved. There have been a number of studies demonstrating that different types of SAMs, including organosilanes, phosphonic acids and thiols, can successfully block ALD processes. However, the efficacy of the blocking varies strongly across different ALD processes. For example, for the same SAM system, the blocking selectivity of Al₂O₃ is limited to only ~6 nm whereas ZnO can be blocked for over ~30 nm. The difference in blocking highlights the importance of precursor chemistry for AS-ALD. In this work, we describe our studies to elucidate the mechanism of AS-ALD based on a comparative study of ALD precursors. Several precursors are studied, including trichloroaluminum (TCA), dimethylaluminum chloride (DMACl), trimethylaluminum (TMA), and triethylaluminum (TEA), each used for Al₂O₃ ALD, allowing comparison between polarity and steric effects of the precursors. Results of quantum chemical calculations of the reaction pathways show product energetics that are correlated with experimental observations, and Monte Carlo simulations address the role of sterics on surface coverage. AS-ALD of Al₂O₃ using octadecyltrichlorosilane SAMs as an inhibitor is also investigated; the blocking properties of the ALD precursors will be compared and the results discussed based on the growth mechanism. By pursuing first principles design of selective ALD processes, this work may enable new methods for additive nanoscale patterning.

3:09 PM *S.EL01.02.05
Nanoscale Proximity Effects in Selective Metal ALD Michael Breeden, Steven Wolf, Ashay Anurag, Victor Wang and Andrew C. Kummel; University of California, San Diego, United States

The atomic layer deposition of cobalt using Co(DAD)₂ and tertiary-butyl amine (TBA) has nearly infinite selectivity (>1000 cycles) on metal vs. insulator (SiO₂ or low-k SiCOH) planar samples. However, on patterned samples, selectivity under identical ALD conditions is limited, due to the diffusion of molecularly-adsorbed metal precursor from reactive to non-reactive surfaces. Three strategies have been found to improve Co ALD selectivity: adding a passivant to remove insulator defect sites, increasing the purge time, decreasing the precursor dose, and periodic annealing. The periodic annealing technique allows reabsorption of the Co nuclei from the insulator surface to the growth surface and is consistent with a low temperature reflow process. This technique has the added advantage of allowing a lower temperature for reflow, potentially allowing a scaling of the diffusion barrier between the Co and the SiCOH which is normally employed. Co ALD was performed using Co(DAD)₂ + TBA at 180°C on 85 nm wide Cu stripes on SiO₂. The planar structure of these stripes is used to demonstrate the effectiveness of passivation, as top-down SEM imagery and XPS quantification can be used to monitor growth and presence of unwanted Co nuclei on insulator. To control precursor dose, multiple precursor pulses were employed in each cycle to limit the maximum pressure. XPS is performed without breaking vacuum to prevent oxidation of Co. This work is supported by the Applications and Systems Driven Center for Energy-Efficient Integrated Nanotechnologies (ASCENT), a Semiconductor Research Corporation program sponsored by JUMP and DARPA.

3:33 PM *S.EL01.04.01
Electronic Structure of Technologically Important Interfaces and Heterostructures Richard Haight; IBM T.J. Watson Research Ctr, United States

From thin film solar cells to metal-oxide-semiconductor devices in leading edge integrated circuits, the electronic structure at and near the interfaces between component materials determines the most important fundamental operating characteristics of those devices such as turn-on voltage, power dissipation and off-state current leakage. Fermi level location at buried interfaces, semiconductor band-bending, charge transfer, oxide defects and work functions of the constituent materials all contribute to device performance. In this talk I will describe how these important parameters can be determined by employing femtosecond photovoltage spectroscopy (FPS)[1], an extension of ultraviolet photoelectron spectroscopy (UPS) using ultrafast lasers. While UPS is fundamentally a surface sensitive spectroscopy, I will describe how pump/probe techniques add a new dimension to this venerable spectroscopy, permitting the accurate extraction of the underlying band bending in Si. When combined with valence band edge location of the semiconductor and oxide, and determination of the system Fermi level, full characterization of the electronic structure of an MOS stack can be obtained providing key insights on device operating properties. I will describe the use of FPS to investigate device stacks ranging from Si and III-V based MOS structures to thin film solar cells formed from earth-abundant elements. In each case surprising new details were uncovered.
that led to performance optimization of these technologically important devices.


5:00 AM *S.EL01.01.01
Energy Storage Devices and Optoelectronic Sensors from Solution-Processed Polymers Kaiping Wang1, Ning Li1, Jason Azoulay2 and Tse Nga Ng1; 1University of California, San Diego, United States; 2University of Southern Mississippi, United States

Conducting polymers are an important class of Faradaic materials for energy storage, as they present opportunities to create energy dense supercapacitors. The vast majority of conducting polymers are p-type cathodes and already operating at or close to the upper voltage limit of non-aqueous electrolytes. On the other hand, it is generally safe for electrolytes to operate down to -2 V vs Standard Hydrogen Electrode. Therefore, extending the operational voltage in the negative range is an attractive route to increase energy density. Here we present promising n-type polymers that retained 90% of initial capacitance after 5000 charge-discharge cycles. The polymers are processed with solution based methods to ensure that the devices are scalable to large area. The electronic and ionic transport in the conducting polymers are monitored in operando by current-voltage and spectroscopic measurements, where spatial variations of film absorption would be mapped to discern electronic versus ionic degradation. We infer the mechanisms that lead to capacitance fade and suggests structural and electrochemical strategies to realize high-endurance energy storage devices for flexible printed systems.

In addition to energy storage, the narrow bandgap polymers are used to realize photodetectors that is relevant to a variety of applications including environmental monitoring and medical diagnosis. Here we show how the infrared polymers are processed into bulk heterojunction photodiodes with photoresponse up to wavelength of 1.7 micron. The performances of devices with different polymer structures were compared through metrics including detectivity, quantum efficiency, response time and rectification ratio. Example applications including hemodynamics and tissue composition measurements will be demonstrated.

5:30 AM S.EL01.01.02
Correlating Hansen Solubility Parameters to Morphology for Printable Organic Electronics Natalie P. Holmes1,2, Matthew Marcus2, Jan van Stam1, Paul Dastoor2 and Ellen Moons3; 1Karlstad University, Sweden; 2University of Newcastle, Australia; 3Advanced Light Source, Lawrence Berkeley National Laboratory, United States

Printed organic electronics is an expanding field with numerous advantages, including scalability, solution processability of the organic semiconductors, biocompatibility, mechanical flexibility, semi-transparency, color-tunability and low-cost manufacture.1 Transitioning to eco-friendly printing inks for the large-scale manufacture of printed organic electronics is the next step on the horizon, as the use of halogenated solvents is environmentally hazardous, harmful to the health of workers, and will increase the cost of production.2 Our recent work involves applying Hansen solubility theory, based on solution thermodynamics, to propose a Hansen solubility parameters (HSP)-based method that is a general platform for the rational design of ink formulations for solution-based organic electronics.3 Which will facilitate the green solvent transition of organic photovoltaics (OPV), in particular. A series of bulk heterojunction films were spin coated from green solvent ink formulations and X-ray spectromicroscopy was utilised to measure donor–acceptor domain size and domain composition. This seminar demonstrates that we can now engineer a nanostructured donor–acceptor thin film from green solvents, with donor and acceptor domain sizes closely matched to the exciton diffusion length in organic semiconductor systems.3,4 The HSP approach is versatile for different organic semiconducting material systems, and we have detailed the pathway for using the HSP semi-empirical tool to predict morphologies, screen suitable ink formulations, and importantly design nanostructured donor–acceptor thin film morphologies for efficient OPV device production. By carefully considering HSP and choosing solvent blends with relative solubilities for the two materials, donor and acceptor can be driven to precipitate in the necessary
order for forming a nano-structured interdigitated network morphology.


5:45 AM S.E.01.04
**Activating Conductivity in Liquid Metal Particle Films by Laser and Thermal Sintering** Rebecca Kramer-Bottiglio; Yale University, United States

Metallic inks with superior conductivity and printability are necessary for high-throughput manufacturing of printed electronics. In particular, gallium-based liquid metal inks have shown great potential in creating soft, flexible and stretchable electronics. Despite their metallic composition, as-printed liquid metal nanoparticle films are non-conductive due to the surrounding metal oxide shells which are primarily Ga2O3, a wide-bandgap semiconductor. Hence, these films require a sintering process to recover their conductivity. For conventional solid metallic nanoparticles, thermal and laser processing are two commonly used sintering methods, and the sintering mechanism is well understood. Nevertheless, laser sintering of liquid metal nanoparticles was only recently demonstrated, and to date, the effect of thermal sintering has rarely been investigated. In this talk, eutectic gallium–indium nanoparticle films processed separately by laser or thermal sintering in an ambient environment will be presented. Laser and thermally sintered films will be compared with respect to electrical conductivity, elemental composition, crystallinity and surface morphology. Both methods impart thermal energy onto the films and generate thermal stress in the particles, resulting in rupture of the gallium oxide shells and achieving electrical conductivity across the film. For laser sintering, extensive oxide rupture allows liquid metal cores to flow out and coalesce into conductive pathways. For thermal sintering, due to less thermal stress and more oxidation, the oxide shells only rupture locally and extensive phase segregation occurs, leading to non-liquid particle films at room temperature. Electrical conductivity is instead attributed to segregated metal layers and gallium oxide which becomes crystalline and conductive at high temperatures. This comprehensive comparison confirms the necessity of oxidation suppression and significant thermal stress via instantaneous laser irradiation to achieve conductive liquid metal patterns.

6:15 AM S.E.01.05
**Understanding the Contact of Screen-Printable Cu Paste for Si Solar Cells through One-Step Atmospheric Firing** Keming Ren1, Krishnamraju Ankireddy2, Thad Druffel2, Sandra Huneycutt1 and Abasifeke Ebong1; 1University North Carolina at Charlotte, United States; 2Bert Thin Films, LLC, United States

Screen-printing and fire through the anti-reflective coating of the front gridline for crystalline silicon solar cell is cost-effective due to the high throughput and simplicity. Silver is the metal of choice because of high conductivity and the understanding that has been gained in decades of research. However, the cost of silver is high and it is the second most expensive layer of a solar cell. In order to penetrate the solar electricity, it is essential to fabricate cheaper solar cells and one of the feasible ways is to replace the expensive Ag front contacts by Cu which has been studied. However, despite the oxidation of copper in the atmosphere, it is challenging to have Cu directly contact with Si because (1) Cu diffuses into Si under high temperature and forms recombination sites; (2) Cu reacts with Si and form micro-sized Cu3Si to shunt the p-n junction; Thus, a diffusion barrier to block Cu from diffusion into Si is required for Cu front contacts on Si. Although people have used electroplating or two-step printing to fabrication diffusion barriers before fabricating Cu contacts, these methods include extra manufacturing steps and are too expensive to be commercialized. Thus, there is a need to replace the costly silver with copper and use the low-cost and high throughput process that will not require additional equipment in production. In this case, the most cost-effective method is using Cu to fully replace the Ag in the paste to make screen-printable pure Cu paste but it requires the paste to prevent the Cu from diffusing into the Si during the high-temperature sintering. According to our previous work, extra Cu in commercial Ag paste with glass frits results in increased transition temperature of glass frits and causes poor etching of SiNx layer, leading to low Voc. In this work, antimony is added into pure Cu paste without glass frits. Here, we are reporting the successful printing and sintering of metal gridlines with pure copper paste. After the one-step atmospheric firing process, the pure Cu fingers formed effective contacts on the Si emitter with Voc larger than 600 mV. In addition to the electrical output parameters of the solar cell, the microstructure analysis to elucidate the contact quality is reported. The preliminary studies showed that uniform pure Cu contacts were formed under < 800 °C with a low ratio of Cu2O and the antimony formed an effective diffusion barrier to prevent the Cu diffusion into the Si and ensured high Voc. The contact path should either through direct contact with Cu gridlines or tunneling through a thin glass layer.

6:30 AM S.E.01.06
Solution Chemistry of Semiconducting Metal Oxides at the Atomic Scale
Melissa A. Hines; Cornell University, United States

Semiconducting metal oxides, particularly transparent conducting oxides, have attracted a great deal of attention for a variety of applications. Nevertheless, the solution chemistry and solution functionalization of these materials has been much less explored than that of traditional semiconductors, such as silicon. One challenge in the stable functionalization of these materials is that their semiconducting nature enables efficient generation of long-lived photocarriers that can initiate chemical reactions that degrade the functionalization. This reactivity has typically been attributed to the undercoordinated metal cation sites at the surface, although direct evidence has been lacking. We have developed a new photochemical reaction that leads to the fluorination of all exposed metal cation sites on TiO₂. In contrast to approaches that use fluoride or HF-containing solutions, our method produces covalently bonded fluorine which is stable in aqueous solutions. To our surprise, these fluorine-terminated TiO₂ surfaces display higher photoreactivity than comparable “clean” surfaces. Possible origins of this behavior will be discussed.

We have also investigated the structure of solution-deposited monolayers on TiO₂ and demonstrated a rational approach to tuning intermolecular interactions and enabling long-range ordering. We show that simple electrostatic insights can be used to engineer away unfavorable intermolecular interactions, producing monolayers with exceptional long-range ordering. Quantitative measurements of the intermolecular interaction energies from molecularly resolved STM images are a factor of ~7 larger than those predicted by dispersion-corrected density functional theory (DFT). This finding suggests a new path to the production of highly ordered monolayers and superstructures of large molecules.

7:00 AM *S.ELO.01.07
Atomic Layer Deposition from Dissolved Precursors for the Preparation of Accurately Nanostructured Heterojunctions
Maïssa Barr¹, Vanessa Koch¹, Soheilla Nadiri¹, Ceyla Asker¹, Dong-Hui Chen², Peter G. Weidler², Felix Hoga¹, Tobias Stubhan¹, Engelbert Redel², Helmut Baumgart¹, Christoph J. Brabec¹ and Julien Bachmann¹,²; ¹Friedrich Alexander University, Germany; ²Karlsruhe Institute of Technology, Germany; ³Old Dominion University, United States; ⁴Saint Petersburg State University, Russian Federation

An interdigitated geometry of the interface between semiconductors remains a Graal in the photovoltaic field. Nanocylindrical solar cells based on a coaxial p-n or p-i-n junction have been generated in a small number of materials systems only so far, mostly among the classical semiconductors. The generalization of this interface geometry to alternative semiconductors, which are expected to profit of it most, has been hampered by the lack of appropriate deposition methods suited to coating complex three-dimensional structures in a conformal manner. Atomic layer deposition (ALD) provides this capability, but is limited by the necessity to use gaseous precursors in vacuum conditions. Modern classes of semiconductors such as the hybrid perovskites are not accessible by ALD due to their ionic nature.

In this perspective, we have transferred the principles of ALD to precursors dissolved in liquid solvents. The ‘solution ALD’ (sALD) method can be implemented in a variety of microfluidic or slot-die processing devices. We have demonstrated that the principles of classical, gas-based ALD —self-limiting surface reactions— are reproduced in sALD. Furthermore, sALD allows the experimentalist to design new, advantageous, reactions of known semiconductors (oxides, heavier chalcogenides), or to deposit materials otherwise inaccessible to ALD altogether, such as polymers, ionic solids, and metal-organic frameworks. They may be obtained in highly pure, crystalline form at room temperature, either as planar films or as conformal coatings of porous substrates. Based on these advances, we have been able to make the first sALD-derived hybrid perovskite cells.

SESSION S.ELO.01.02: ALD Enabled Nanopatterning
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN02

5:00 AM *S.ELO.01.02.01
Understanding Area Selective Atomic Layer Deposition by a Comparative Study of Precursors
Il-Kwon Oh¹, Tzu-Ling Liu¹, Tania Sandoval², Ralf Tonner³ and Stacey F. Bent⁴; ¹Stanford University, United States; ²Technical University Federico Santa Maria, Chile; ³Philipps-Universitat, Germany
The rapid growth of technologies such as machine learning and autonomous vehicles is fueling a need for more powerful electronic devices requiring complex nanoscale structures. With the growing demands on nanostructure fabrication, selective deposition is gaining attention as a process to enable pattern features at the sub-10 nm length scale. This talk will focus on area selective atomic layer deposition (AS-ALD), a bottom-up growth strategy in which material is added only where desired, without the need for subsequent lithography and etch steps. ALD is a good choice for selective deposition because its chemical specificity provides a means to achieve selectivity on a spatially patterned substrate. One popular approach to AS-ALD uses inhibitory layers such as self-assembled monolayers (SAMs) to alter the native surface reactivity, allowing ALD selectivity to be achieved. There have been a number of studies demonstrating that different types of SAMs, including organosilanes, phosphonic acids and thiols, can successfully block ALD processes. However, the efficacy of the blocking varies strongly across different ALD processes. For example, for the same SAM system, the blocking selectivity of Al2O3 is limited to only ~6 nm whereas ZnO can be blocked for over ~30 nm. The difference in blocking highlights the importance of precursor chemistry for AS-ALD. In this work, we describe our studies to elucidate the mechanism of AS-ALD based on a comparative study of ALD precursors. Several precursors are studied, including trichloroaluminum (TCA), dimethylaluminum chloride (DMACl), trimethylaluminum (TMA), and triethylaluminum (TEA), each used for Al2O3 ALD, allowing comparison between polarity and steric effects of the precursors. Results of quantum chemical calculations of the reaction pathways show product energetics that are correlated with experimental observations, and Monte Carlo simulations address the role of steric on surface coverage. AS-ALD of Al2O3 using octadecylchlorosilane SAMs as an inhibitor is also investigated; the blocking properties of the ALD precursors will be compared and the results discussed based on the growth mechanism. By pursuing first principles design of selective ALD processes, this work may enable new methods for additive nanoscale patterning.

5:30 AM *S.EL01.02.02
In Operando XPS Study of Atomic Layer Etching of Fe, Co and FeCoB Robert L. Opila, Zijian Wang, Omar Melton, David Angel and Bo Yuan; University of Delaware, United States

Etching of transition metals is one of the major challenges in magnetoresistive random-access memory (MRAM) device fabrication. In this work, atomic layer etching of iron and cobalt surfaces in sequential steps of exposure to halogen and an organic molecule was studied. We successfully performed etching of Fe Co, and FeCoB thin films through the formation of volatile metal complexes at low temperature with cyclic reactions of Cl2 and acetylacetone (acacH) or hexafluoroacetylacetone (hfacH). The etching reaction mechanism of acac and hfac reacting with chlorine-modified Fe, Co, and FeCoB surfaces was investigated: the surface was first activated with Cl2 gas, and subsequently, the top layer of chlorinated metal was removed by reaction with a diketone (acacH/hfacH) as shown in the photoemission spectra. The extent of Cl2 reaction determines the etching rate of the metal. At substrate temperatures lower than 135°C, acac could remove the chlorinated Fe metal layer from Fe surfaces, but not chlorinated Co from Co surfaces (Table 1 and 2). In-operando x-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) simulation shows that the reaction of acacH or hfacH with chlorinated Fe or Co surfaces is likely following a complex reaction pathway instead of a simple diketone substitution for the metal chloride. Reactions of FeCoB with Cl2 results in the removal of B. The atomic layer etching cycle described above results in enrichment of the surface in Co. Diketone decomposition likely plays an important role in the etching process on all these surfaces. Moreover, the surface morphology becomes smoother as etching proceeds. The mechanisms for all of these observations will be discussed.

6:00 AM *S.EL01.02.03
Passivation of Surfaces and Interfaces by Atomic Layer Deposited Oxide Nanolayers Erwin Kessels; Eindhoven University of Technology, Netherlands

Passivation of electronic defects on surfaces and interfaces is vital for many (opto)electronic devices in the field of electronics, photonics and photovoltaics. In the last decade it has been demonstrated that a high level of passivation of surface and interfaces can be achieved by nanolayers of oxides prepared by atomic layer deposition (ALD). This passivation can be achieved by termination of bonds of the semiconductor surface but also by shielding of charges from the interface by fixed or trapped charges in the oxide. In this presentation the growth of nanolayers by ALD on a variety of semiconductors (Si, Ge, InP, …) will be discussed, both for planar wafers and for nanowires as used in the aforementioned devices. Results will be presented for various oxides such as Al2O3, TiO2, Nb2O5, PO3, MoO2 and ZnO and including data as obtained with a wide set of analytical techniques for electrical and structural interface characterization.

6:30 AM *S.EL01.02.05
Nanoscale Proximity Effects in Selective Metal ALD Michael Breeden, Steven Wolf, Ashay Anurag, Victor
Wang and Andrew C. Kummel; University of California, San Diego, United States

The atomic layer deposition of cobalt using Co(DAD)₂ and tertiary-butyl amine (TBA) has nearly infinite selectivity (>1000 cycles) on metal vs. insulator (SiO₂ or low-k SiCOH) planar samples. However, on patterned samples, selectivity under identical ALD conditions is limited, due to the diffusion of molecularly-adsorbed metal precursor from reactive to non-reactive surfaces. Three strategies have been found to improve Co ALD selectivity: adding a passivant to remove insulator defect sites, increasing the purge time, decreasing the precursor dose, and periodic annealing. The periodic annealing technique allows reabsorption of the Co nuclei from the insulator surface to the growth surface and is consistent with a low temperature reflow process. This technique has the added advantage of allowing a lower temperature for reflow, potentially allowing a scaling of the diffusion barrier between the Co and the SiCOH which is normally employed. Co ALD was performed using Co(DAD)₂ + TBA at 180°C on 85 nm wide Cu stripes on SiO₂. The planar structure of these stripes is used to demonstrate the effectiveness of passivation, as top-down SEM imagery and XPS quantification can be used to monitor growth and presence of unwanted Co nuclei on insulator. To control precursor dose, multiple precursor pulses were employed in each cycle to limit the maximum pressure. XPS is performed without breaking vacuum to prevent oxidation of Co. This work is supported by the Applications and Systems Driven Center for Energy-Efficient Integrated Nanotechnologies (ASCENT), a Semiconductor Research Corporation program sponsored by JUMP and DARPA.

7:00 AM S.EL01.02.06
Area-Selective Deposition of Titanium Oxide and Titanium Nitride for Nanoscale Patterning Solutions Based on Self-Aligned Tone Reversal Scheme
Mikhail Krishtab¹², Li Zheng¹, Rob Ameloot², Silvia Armini³, Joey Hung³, Roy Koret⁴, Igor Turovets⁴, Kavita Shah³, Srinivasan Rangarajan³, Laxmi Warad³ and Vanessa Zhang³; ¹imec, Belgium; ²Katholieke Universiteit Leuven, Belgium; ³Nova Measuring Instruments, Inc., United States; ⁴Nova Measuring Instruments, LTD, Israel

Area-selective deposition (ASD)-driven processes gained recently a lot of attention from the microelectronics industry as a potential solution for the issues associated with top-down pattern formation at the nanoscale. However, the defectivity of typical ASD processes relying on delayed nucleation on a non-growth area is one of the key concerns for the adoption of this technology. Among the strategies addressing the defectivity issue, repetitive refreshment of the non-growth surface and selective etching of undesired nuclei are particularly promising.

This work is focused on the ASD of TiO₂ and TiN deposited by atomic layer deposition (ALD). In this respect, as an ALD inhibition route, we have been investigating both halogen plasma surface modification of amorphous carbon materials (non-growth area) and methyl-terminated monomolecular organic films on SiO₂ (non-growth area) substrates. On one side, on a-C non-growth area, we examined the possibility to combine the two defect-reduction strategies by employing low power Cl₂ or CF₄ plasmas for both surface functionalization/re-functionalization and for removal of nuclei. We employed prototypical water-based metal oxide process such as ALD TiOₓ (TiCl₄/H₂O) to demonstrate area-selective deposition on top of silicon oxide using both blanket films and 45-60 nm half-pitch patterns of a-C. At first, the plasma parameters were optimized to minimize etching of a-C and silicon oxide. Then the selectivity of the ALD processes under study was checked on the plasma halogenated a-C films using a standard ALD sequence and a sequence interrupted by the appropriate plasma treatment steps. On the other side, self-assembled monolayers (SAMs) derived from octadecyltrimethoxysilanes allow ASD of >10 nm of TiN (TiCl₄/NH₃) at temperatures as high as 325°C. Patterning of SAMs has been deployed to demonstrate successful selectivity and ASD surface dependency.

Special attention in this work is paid to the defectivity analysis of patterned a-C, which typically has surface composition deviating from that of the original coating as a result of employed dry etching. The efficiency of the proposed defect elimination strategy and its impact on resulting pattern quality are assessed using advanced wafer-level metrology including scatterometry and XPS.

SESSION S.EL01.03: Thin-Film Growth and Control
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN02

5:00 AM *S.EL01.03.03
Surface Functionalization for Area-Selective Atomic Layer Deposition
Adrie Mackus; Eindhoven University of Technology, Netherlands
Future nanoelectronics requires area-selective deposition to eliminate the alignment challenges in the fabrication of multilayered device structures. For example, area-selective atomic layer deposition (ALD) processes of both oxides and nitrides are currently being considered for various applications in interconnect technology, with especially the fabrication of fully self-aligned vias receiving much attention. Most work in the field of area-selective ALD relies on local deactivation of the ALD growth by selective functionalization of the non-growth area. Previous research predominantly focused on surface functionalization using self-assembled monolayers (SAMs), which so far is the most successful approach for achieving a high selectivity.

Our approach to area-selective ALD involves vapor-phase dosing of small molecule inhibitors in ABC-type (i.e. three-step) ALD cycles. One of the main merits of this alternative approach is that is compatible with industrial process flows, while it also allows for the use of a plasma as the co-reactant and therefore for area-selective ALD of a wider range of materials. It is however more challenging to block the ALD precursor adsorption using small molecules. In order to improve the selectivity of this approach, our current research aims at identifying and designing molecules that can effectively inhibit the ALD growth.

In this presentation, the requirements for the inhibitor molecules will be discussed, which will be illustrated with examples from our experimental and theoretical studies. Results for area-selective ALD of TiN, Al2O3, and SiO2 will be presented, with a focus on the mechanisms of precursor blocking. Special attention will be given on our recent work on using aromatic molecules as inhibitor on metal surfaces.


5:30 AM *S.EL01.03.04
Interface Control between Semiconductor and Gate Dielectric Layer for Highly Stable High Mobility Oxide TFT
Sang-Hee K. Park, Jong Beom Ko and Seung-Hee Lee; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The amorphous oxide thin film transistor (TFT) had been widely applied not only to the display but other electronics such as sensors and semiconductor devices. To secure long term stability of TFT, minimizing charge trapping defects in the interface and gate insulator (GI) would be the most important concern. In the case of amorphous oxide semiconductor, oxygen vacancy (Vo), cation interstitial, ionized Vo, oxygen interstitial (Oi), hydrogen interstitial (Hi), hydrogen substitutional are well known defects. Among these, Oi, which is known as oxygen excess, weakly bonded oxygen, peroxide, or metal vacancy is known to be major source of charge trapping center. Meanwhile, H, which is known as a shallow donor in oxide semiconductor, can passivate the Oi charge trapping center as does the dangling bonding Si. Therefore, optimization of Oi and H is one of the most important processes to secure the stability of oxide TFT. The charge trapping centers in the active and/or interface between active and GI are formed during the process generating oxygen related reactive species such as sputtering for active and PECVD or PEALD process for GI. Comparing these processes, PECVD generates less defects in the channel of TFT thus, top gate TFTs yield better PBTS stability than that of bottom gate TFT. Meanwhile, it still needs careful and precise control of O and H to result in high bias stability with proper Vth for the high mobility oxide TFT of which semiconductor has high concentration of carrier amount. It is because Vth of high mobility oxide TFT is more sensitive to the addition of H into the active layer than that of typical IGZO TFT. For these reasons, deposition of GI in top gate oxide TFT is carried out at relatively low temperature to minimize the H incorporation into the active layer, giving rise to the degrading stability than that of IGZO TFT. Therefore, optimization of GI process and controlling interface are very important in materialization of high mobility top gate structured oxide TFT with highly stability and proper Vth. Here, we scrutinize the effect of Oi and H on the formation of the interface of top gate structured high mobility Al: ITZO TFT with double GI consisting of ALD grown alumina (Al2O3) and PECVD deposited SiNx, film. Oxygen plasma treatment was conducted on the active surface and diffusion of H into the interface and/or active layer during thermal annealing was induced from the Al2O3, GI to inspect the effect of Oi and H, respectively. Here thermal ALD (T-ALD) Al2O3 provides H which plays as a passivator of the charge trapping centers in the interface as well as the shallow donor. To control the amounts of H and Oi in the active and/or interface, we did O2 and N2O plasma treatment prior to the Al2O3 deposition to yield TFTs with improved on/off characteristics. The TFTs with O2 and N2O plasma treatment showed 2.08V and 2.34V of Vth, respectively. We confirmed that both O2 and N2O plasma treatment increase the portion of M-O bonding and reduced the Vo. The O2 plasma-treated
TFTs with T-ALD GI yield high field-effect mobility over the 35.3 cm²/Vs with improved bias stability compared with that of TFT of which AlOₓ deposited by just PE-ALD. Therefore, we conclude that the T-ALD process for the thin GI deposition can be applied to fabricate even high mobility top-gate structured oxide TFTs by using O₂ or N₂O plasma treatment. The AlOₓ deposited by T-ALD can passivate extra trap sites generated during the supply of the oxygen for the carrier control process of high mobility oxide TFT. This enabled us to obtain high mobility TFTs with high stability and proper Vth. The TFTs fabricated by oxygen plasma treatment, followed by the T-ALD GI deposition resulted in excellent bias stability because of both fine defect control of interface and the carrier concentration.

6:00 AM *S.EL01.03.06
In situ Ellipsometry Study of Gallium Oxide Plasma-Enhanced Atomic Layer Deposition Florian Maudet¹, Soursih Banerjee¹, Hanno Kröncke¹, Mattia Mulazzi¹, Veeresh Deshpande¹ and Catherine Dubourdieu¹,²; ¹Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; ²Freie Universität Berlin, Germany

Gallium oxide has attracted renewed interest as an ultrawide band-gap transparent semiconductor. Monoclinic b-Ga₂O₃ is expected to be highly suitable for various applications such as high temperature and ultra-high voltage electronics, photon detectors, gas sensors as well as thin tunneling barriers in various devices. Amorphous gallium oxide has recently been shown to be an effective electron transport layer or an effective passivation layer in solar cells.

In this talk, we will discuss the growth and the characterization of amorphous gallium oxide thin films. The films were grown on (001) Si by plasma-enhanced atomic layer deposition (PE-ALD) using trimethyl gallium as the gallium precursor and oxygen plasma as the oxidizing agent. We will focus on the effects of the starting surface and of the oxygen plasma exposure time. In a temperature range of 100-360°C, the growth per cycle in the ALD growth regime is of ~ 0.67-0.70Å/cycle and the resulting films are amorphous. In situ characterization during the synthesis was performed by spectroscopic ellipsometry. By applying an expansion of the three-phase equation (air, thin film, substrate) in the thin film limit [1], we were able to determine unambiguously the optical properties (index and extinction coefficient) and the thickness of the thin film unlike with classic ellipsometry modelling that is limited by the non-uniqueness of the possible solutions. With this method, we could precisely determine the thickness evolution of each step of the ALD cycle. We evidenced the reduction of gallium oxide absorption for longer plasma times that can be attributed to a lower defect density. Finally, the leakage currents measured on MOS capacitors will be discussed as a function of the oxygen plasma exposure time. We will show that leakage current densities can be lowered by more than 3 orders of magnitude by adjusting this parameter.


6:30 AM S.EL01.03.07
Multi-Metal Coordination Polymers Deposition through a Ternary Hybrid Molecular Layer Deposition Process Nathaniel Richey, Shirin Borhan and Stacey F. Bent; Stanford University, United States

Atomic layer deposition (ALD) utilizes self-limiting surface reactions to deposit approximately one atomic layer of material per precursor exposure. As such, ALD is a promising technique for the deposition of highly conformal thin films for a wide variety of inorganic materials. Molecular layer deposition (MLD) is a related technique that also relies on self-limiting surface reactions but aims to deposit entire organic molecules instead of single atoms. Hybrid ALD/MLD combines these techniques to deposit coordination polymers in which metal atoms are connected through organic linkers which are typically referred to as “metalcones”. In this talk, we will discuss the deposition of metalcones comprised of more than one metal. We will specifically discuss ternary metalcones formed from mixtures of trimethylaluminum (TMA) and diethylzinc (DEZ) as well as from DEZ and tetrakis(dimethylamido)hafnium (TDMAHf). The growth properties of the multi metalcone films will be discussed, with a specific focus on the challenges these ternary films face due to transmetalation reactions which occur during the deposition and result in non-ideal compositions of the two metals.

6:45 AM *S.EL01.03.08
Growth of Inorganic Carboxylates as Thin Films Ola Nilsen; University of Oslo, Norway

The MLD technique could be considered as the ultimate in additive manufacturing where it builds materials one molecular layer at the time from the gas phase. It is based on chemistry and relies on availability of building units from the gas phase. The current presentation will focus on growth of such materials with emphasis on building units containing carboxylic acids. Inorganic carboxylates are mostly stable, offering high saturation of the metal centre’s coordination sphere, leading up to the plethora of such structures as metalorganic frameworks (MOF). Such materials can be grown via the gas phase, and examples
from growth of the UiO-66 series with variations in linker length and complexity will be given, in addition to alternative systems. This introduces concepts such as modulation of growth, reservoir effects, tuning of chemical reactivity, and amorphous porosity. The current contribution will provide highlights from such growth of organic- inorganic hybrid materials including MOF materials.

SESSION S.EL01.04: Advanced Characterization
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN02

5:00 AM *S.EL01.04.01
Electronic Structure of Technologically Important Interfaces and Heterostructures Richard Haight; IBM T.J. Watson Research Ctr, United States

From thin film solar cells to metal-oxide-semiconductor devices in leading edge integrated circuits, the electronic structure at and near the interfaces between component materials determines the most important fundamental operating characteristics of those devices such as turn-on voltage, power dissipation and off-state current leakage. Fermi level location at buried interfaces, semiconductor band-bending, charge transfer, oxide defects and work functions of the constituent materials all contribute to device performance. In this talk I will describe how these important parameters can be determined by employing femtosecond photovoltage spectroscopy (FPS)[1], an extension of ultraviolet photoelectron spectroscopy (UPS) using ultrafast lasers. While UPS is fundamentally a surface sensitive spectroscopy, I will describe how pump/probe techniques add a new dimension to this venerable spectroscopy, permitting the accurate extraction of the underlying band bending in Si. When combined with valence band edge location of the semiconductor and oxide, and determination of the system Fermi level, full characterization of the electronic structure of an MOS stack can be obtained providing key insights on device operating properties. I will describe the use of FPS to investigate device stacks ranging from Si and III-V based MOS structures to thin film solar cells formed from earth-abundant elements. In each case surprising new details were uncovered that led to performance optimization of these technologically important devices.


5:30 AM S.EL01.04.05
Imaging the Electronic Properties of Graphene with Photoemission Electron Microscopy (PEEM) Sujitra Pookpanratana, Steven W. Robey and Randolph E. Elmquist; National Institute of Standards and Technology, United States

The drive for high performance and lower power consumption compels the semiconductor industry to consider novel nanoscale device structures based on non-silicon-based materials. Continued innovation and progress towards novel nanoelectronic materials and devices in turn requires metrology sensitive to electronic properties at these length scales. The electronic properties of a material at length scales relevant to the nanoscale electronic devices define how it will be used and integrated into device functional form. Angle-resolved photoemission (ARPES) is the traditional work horse to determine the electronic band structure of crystalline solids, but typically requires crystalline uniformity on the scale of 1 mm². Tip-based scanning probe techniques provide electronic contrast with sub-nanometer resolution, and therefore is a local technique. Photoemission electron microscopy (PEEM) can be employed to allow access to this vital information, providing full-field imaging capabilities sensitive to a variety of electronic contrast mechanisms at 10’s of nanometers length scales. The new generation of PEEM has energy filtering capability which now allows for ARPES measurements at smaller length scales (100 μm²; known as μ-ARPES). Here, we will discuss the commissioning of a recently installed PEEM at NIST, using results of graphene to demonstrate imaging capability and energy resolution of this instrument.

Graphene was grown epitaxially on 4H-SiC (0001) in a custom vacuum furnace at NIST [1] and transferred into the PEEM vacuum chamber. The PEEM instrument is equipped with continuous wave excitation sources in the deep ultraviolet (UV) regime, and a magnetic prism array for electron energy filtering. The terraces due to the underlying SiC substrate can easily be discerned since the PEEM provides imaging contrast due to topography and electronic contrast, and the terrace edges can be resolved to 50 nm. There are three primary regions in PEEM images that we assign as the (i) interfacial layer, (ii) 1-2 layer graphene, and (iii) “bulk” graphite regions. The sample surface is mostly dominated by regions with 1-2 layers of graphene for which μ-ARPES was performed at 8 μm length scales. The electronic structure of these regions is consistent with...
previous reports (e.g., [2]), with the π band and σ band dispersions clearly resolved. The Dirac point lies below the Fermi energy, consistent with n-doping present in graphene grown on SiC. We will also use confocal laser microscopy to correlate with the PEEM results. Finally, we will discuss our plans on advancing the lab-based PEEM capability with coherent, monochromatic laser-based photon sources.


SEASON S.EL01.05: Interfaces in Emerging Technologies
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN02

5:00 AM S.EL01.05.03
Engineering Two-Phase and Three-Phase Structured Films from Colloidal Nanoparticles for Printed Electronics Natalie P. Holmes¹, David Kilcoyne² and Paul Dastoor¹; ¹University of Newcastle, Australia; ²Advanced Light Source, Lawrence Berkeley National Laboratory, United States

Colloidal nanoparticles of organic semiconductors have attracted increasing interest in recent years due to the eco-friendly fabrication of printed electronics afforded by colloidal ink technology,¹ including solar modules. Utilising the colloidal nanoparticle approach, it is now possible to engineer the microstructure of the light absorbing/charge generating layer of organic photovoltaics; decoupling film morphology formation from film deposition.² This seminar presents recent work on core-shell nanoparticle synthesis and single-component nanoparticle synthesis for printed organic electronics applications, via a miniemulsion synthesis route.²,³ Single-component nanoparticles of donor and acceptor materials are utilised to engineer two-phase structured films with control over domain size.³ Engineering a three-phase structured film is either via the synthesis of core-shell nanoparticles or via thermally annealing a two-phase structured film above the glass transition temperature (Tg) of the materials promoting the diffusion of the fullerene acceptor into amorphous polymer donor domains. Synchrotron-based X-ray spectromicroscopy and electron microscopy were used to characterize donor−acceptor domain size and domain composition. Donor-acceptor material systems studied span traditional polymer donor:fullerene acceptor systems and new polymer donor:non-fullerene acceptor systems, including poly(3-hexylthiophene) (P3HT) and poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1) donor materials and phenyl-C61 butyric acid methyl ester (PC61BM) and poly [(N,N'-bis[2-octyldodecyl]napththalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]alt-5,5'-(2,2'-bithiophene)] (N2200) acceptor materials. This seminar demonstrates the high level of control over donor−acceptor film morphology enabled by customizing nanoparticulate colloidal inks, where both two-phase and three-phase film architectures can be designed and engineered for new age printed electronics.⁴


5:15 AM S.EL01.05.04
Synthesis of Bright, Near Infrared Emissive Quantum Dots in Luminescent Solar Concentrators Michael Enright¹, Maggie Potter¹, Megan E. Phelan², Harry A. Atwater² and Ralph G. Nuzzo¹; ¹University of Illinois at Urbana-Champaign, United States; ²California Institute of Technology, United States

Luminescent solar concentrators (LSCs) are lumophore embedded waveguides capable of collecting sunlight across a wide area and concentrating it onto smaller cells for energy conversion. Unlike conventional solar cells, LSCs do not require solar tracking as they have omnidirectional absorption and demonstrate similar performance under diffuse and direct light conditions. However, LSCs with luminescence in the near infrared (NIR) have yet to realize their full potential. This is in part due to non-ideal lumophores; low photostability, large full width half maxes, poor quantum yields, and parasitic self-absorption are among the challenges that have plagued lumophore performance in LSCs over the past decades. This work explores the synthetic routes and post-synthetic improvement of highly emissive, NIR emissive quantum dot heterostructures. CsSnI₃ and InAs quantum dot based LSCs in particular have excellent potential in Si systems due to their narrow emission
near the band edge of a Si photovoltaic cell. Multishell luminophore systems with CsSnI3 and InAs cores are synthesized to improve luminophore quantum yield and to reduce parasitic self-absorption. The advantage of incorporation of these NIR emissive cores into shelled systems is multifaceted: (1) wider bandgap protective shells improve quantum yields through passivation of surface traps, (2) large shell to core volume ratios reduce parasitic self-absorption by separating the energies of absorbance by the shell and emission from the core, and (3) the surface of the outer shell can be post-synthetically modified to tune the luminophore’s aggregation properties and interactions with polymer waveguides without damaging the emissive properties of the core. Despite their clear potential role in LSCs, NIR emissive quantum dots have lagged behind their visible region fluorescent counterparts due to lower quantum yields and more limited precursor availability. This work develops synthetic and post-synthetic strategies for obtaining bright, near infrared emissive heterostructure quantum dots with a specific interest to incorporate them in LSCs with Si microcells.

5:30 AM S.EL01.05.05

Anisotropic emitters such as gold nanorods[1], quantum rods[2] and organic dye-doped rods[3] have been exploited as orientation probes. Their orientation analysis is based on comparing the emitted light intensities measured with different excitation and emission polarizations. However, the practical use of this technique requires overcoming several problems: (i) various sources of signal fluctuation: blinking and bleaching of emitters, unstable excitation power, instrumental noise… (ii) Polydispersity of emitter particles affecting the signal’s degree of polarization (DOP), (iii) complicated optical setup with multiple directions of excitation and emission.

Here we present a straightforward and accurate orientation analysis through a purely spectroscopic method using lanthanide luminescence. Nanocrystals doped with europium ions (Eu3+) exhibit unique photoluminescence (PL) spectra composed of a number of sharp peaks originating from the multiple 4f transitions and degenerate sub-levels due to the crystal-field splitting. Each of those sub-level peaks is polarized along a certain direction independent to others. Therefore, the orientation of a nanocrystal can be represented simply by the line shape of the polarized emission spectra regardless of its global intensity that can fluctuate due to other causes. This spectroscopic method enables three-dimensional (3D) orientation analysis on a single measurement plane not even taking into account the excitation polarization[4]. The polarization of Eu3+ emission is determined only by the crystal structure and not by the particle morphology, which makes the analysis reliable even with polydisperse particles. Moreover, the Eu3+ emission is highly photo-stable and free from photo-bleaching or blinking. We used Eu3+-doped monocrystalline NaYF4 nanorods as a proof of concept 3D orientation probes. The nanorods were solvothermally synthesized and randomly suspended in a polymer matrix (PVA - Polyvinylalcohol). By performing the conventional scanning confocal microscopy, polarized fluorescence spectra of single nanorods were obtained, from which the spherical angles (θ, φ) of rod orientation were calculated with high accuracy.

This new spectroscopic method to determine 3D orientation of nanoprobes offers a unique opportunity to unveil the complex dynamics of bio-molecular systems (e.g. rotating proteins) and also the ensemble behavior of nanoparticles (e.g. self-assembly).


5:45 AM S.EL01.05.07
Synthesis of Highly Luminescent CsPbX3 (X = Cl, Br, and I) Nanoplates via AlX3-Ligand Mediated Anion Exchange of CsPbCl3 Nanocubes at Room Temperature Md Aslam Uddin and Kenneth R. Graham; University of Kentucky, United States

Two-dimensional metal halide perovskite nanoparticles show great potential for use in optoelectronic devices because of blue-shifted absorption relative to their 3D counterparts, narrow emission line widths, high absorption cross sections, and high radiative recombination. Two-dimensional CsPbX3 nanoparticles have been synthesized using hot injection methods, solid state crystallization methods, microwave-assisted assisted methods, as well as high temperature-and-pressure methods. Herein, we show a different approach relying on rapid anion exchange between CsPbCl3 nanocubes and a mixture of dodecanethiol (DDT) & AlX3 (X = Cl, Br, I) to transform CsPbCl3 nanocubes into CsPbX3 nanoplates at room temperature. The combination of both DDT and AlX3 is necessary to facilitate nanoplate formation and maximize the photoluminescence quantum yield, ΦPL, and stability. Either DDT or AlX3 addition alone will result in improved ΦPL, but without the formation
of nanoplates and with lower $\Phi_{PL}$ and stability than when added together. The anion exchanged and surface modified nanoplates are highly emissive and stable due to the introduction of both an anion source and surface ligand. Nanoplates synthesized through DDT-AlX$_3$ ligand mediated anion exchange show photoluminescence quantum yields of 65% for violet-blue emitters (CsPbCl$_3$), near 100% for green emitters (CsPbBr$_3$), and 81% for red emitters (CsPbI$_3$), while retaining 80-90% of their maximum $\Phi_{PL}$ after 15-18 days of storage in ambient atmosphere. This combined approach of simultaneously adding a halide source and surface ligand provides an attractive route to simultaneously manipulate the optical properties and nanocrystal morphology of metal halide nanocrystals.

6:00 AM S.EL01.05.08
Electrical and Mechanical Characterization of Li-Ion Battery Electrode Using Pinpoint™ Scanning Spreading Resistance Microscopy
Byong Kim, John Paul Pineda, Cathy Lee and Keibock Lee; Park Systems, Inc., United States

Lithium ion batteries (LIBs) are key components of modern electronics and are regularly utilized as their primary power source. LIBs have become ubiquitous in a variety of applications ranging from portable devices to electric vehicles because of their high energy density, flexible and lightweight design, lower self-discharge, low cost and longer lifespan compared to other battery technologies. Despite these advantages, the reliability and performance of LIBs still need to be upgraded to meet the requirements of applications such as large-scale energy storage and hybrid electric vehicles. Extensive research has focused on the development of four cell materials in particular to achieve better performance: positive and negative electrode active materials as well as separators and electrolytes. Understanding the electrical and mechanical properties of electrode materials plays a major role in the performance improvement of LIBs. It has been shown that improved adhesion between electrode particles, electrode films and current collectors leads to better retention of discharge capacity during cycling, especially when electrode materials exhibit faster and/or larger volume expansion. Moreover, enhanced electronic conductivities and ionic diffusivities in electrodes also lead to LIB capacity improvements. As devices are becoming more compact, optimizing electrical and mechanical properties on a nanometer scale becomes more relevant and leads to improved interfaces.

There are several methods which can measure these local properties; the more common methods include impedance spectroscopy and nanoindentation. However, even using both methods, one cannot get the full local information about the aforementioned properties. Impedance spectroscopy needs an exact model and only distinguishes between interfaces, and therefore does not have local information for each interface. Nanoindentation is destructive and does not provide any electrical information. One of the more effective tools used to overcome the problems encountered in electrical property measurement is Scanning Spreading Resistance Microscopy (SSRM). This technique simultaneously measures both electrical properties and topography. However, SSRM has some disadvantages, such as rapid wearing of the tip, degradation of image resolution and low signal-to-noise ratio. These disadvantages stem from the high frictional force arising from continuous tip-sample contact during scanning. Recently, a new operational AFM mode developed by Park Systems called PinPoint™ can be coupled with SSRM to offer scientists and engineers an innovative solution to avoid the troublesome frictional forces during a scan. This method operates in an approach-retract manner ensuring a frictionless operation, which eliminates the lateral force from continuous tip-sample contact. In addition, the integration of these methods with AFM enables acquiring topography as well as electrical/mechanical property data simultaneously without changing the sample or tip. Here, we demonstrate that PinPoint™ SSRM effectively measures both electrical and mechanical properties of LIBs electrode surfaces at a much higher quality in high vacuum environment than in ambient condition using a Park NX-Hivac AFM system.

6:15 AM S.EL01.05.09
Approaching the Conductivity Limits of Aerosol Jet Printed Silver
Eva S. Rosker$^{1,2}$, Michael T. Barako$^3$, Rajinder Sandhu$^4$, Mark Goorsky$^1$ and Jesse Tice$^2$; $^1$University of California, Los Angeles, United States; $^2$Northrop Grumman Aerospace Systems, United States

Most efforts to directly write conductive metal traces have focused on nanoparticle ink suspensions that require aggressive sintering (>200°C) yet exhibit low density, small grains, and a maximum electrical conductivity of ~25% of bulk silver [1]. Here, we demonstrate an alternative approach to printing high conductivity metals using a reactive ink solution, where a molecular precursor reacts into a highly dense (>90%) silver film at a low temperature (80°C) compatible with conventional additive manufacturing processes. We show that by reducing porosity and transitioning from interface-rich sintered nanoparticles to dense solid metals, we achieve DC conductivities up to ~75% of bulk silver for aerosol jet printed conductive traces, which aligns with our predictive microstructural transport model. Furthermore, we show through an initial demonstration that the RF performance of these devices far exceeds that of standard printed transmission lines and competes with conventional electroplating techniques. This work demonstrates a path toward high performance printed RF passive components that are robust and reliable for disruptive opportunities in aerospace materials and manufacturing processes.
Ionic liquids (ILs) have gained considerable attention in the last two decades owing to their unique and tunable physico-chemical properties (e.g., low vapor pressure, and high thermal stability), which have made them potentially useful for a range of applications, including batteries, fuel cells, catalysis, and lubrication. Ionic liquids are particularly attractive in lubrication, since their properties make them suitable for components working under extreme conditions (e.g., high temperatures, low pressures), such as those found in engines, spacecraft, and micro-electromechanical systems. When ILs are used as lubricants, the interface between the IL and the surfaces of the components in relative motion plays a pivotal role in controlling the friction and wear response. Despite the scientific weight of published studies on the tribology of ILs, remarkably little is still known about the underpinning lubrication mechanism of ILs. The development of a fundamental understanding of the mechanism by which ILs reduce friction and/or wear requires shedding light on the processes occurring at nanoscale asperities within macroscale contacts. This constitute a significant challenge since observing and understanding the nanoscale mechanisms at play is inhibited by the hidden nature of the buried interface and the challenge of performing observations at the nanometer scale.

Here, we used atomic force microscopy (AFM) to visualize and quantify the processes occurring at sliding interfaces in situ, in single-asperity nanocontacts. In contrast to macroscale tribological experiments, where the multi-asperity nature of the contact does not allow for the accurate control of local contact stresses and geometries, in situ AFM studies, where the AFM tip mimics a single asperity in a multi-asperity macroscale contact, enable the precise control of critical parameters (e.g., contact stress) affecting mechano-chemical reactions, the visualization and quantification of phenomena occurring at tip/substrate interfaces (e.g., mechanically-induced nucleation and growth of films), and the local characterization of nanoscale properties (e.g., friction and adhesion). The AFM experiments, in which a diamond tip was slid on steel in phosphonium phosphate IL (PP-IL) at high contact pressure (>5 GPa), indicated a significant friction reduction only after the removal of the native surface oxide from steel. Even though the AFM experiments allowed for the identification of changes in topography and friction in situ while sliding in PP-IL, they could not provide any information about the composition and structure of the regions scanned by AFM. The analysis of these regions is a challenging surface science problem owing to their limited dimensions and the small thickness of the surface material modified by the mechanical action of AFM tips. To address this challenge and elucidate the origin of the friction reduction observed during AFM experiments, laterally-resolved ex situ analyses of the surface chemistry of steel were performed by synchrotron-based X-ray photoemission electron microscopy (X-PEEM), low energy electron microscopy (LEEM), and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The analytical results indicated that the mechanically-induced exposure of metallic iron during AFM tests carried out in PP-IL leads to an increase in surface coverage of adsorbed phosphate anions together with a change in surface potential. Based on these results and atomistic simulations of the configuration geometry of phosphate ions on metallic and oxidized iron, a simple phenomenological model is proposed to account for the observed lubrication behavior.

We demonstrate photovoltaic and photoconductive responses to near-infrared light in a new class of devices formed by depositing a film of gel permeation chromatography purified PbS quantum dots (QDs) on top of n-SiC epitaxial layers with natively grown, 10-15 monolayer thick epitaxial graphene (EG) Schottky contacts. The QD-film was removable by selective chemical etching, resetting the EG/SiC Schottky diode to its pristine state for multiple PbS-QD depositions. EG in these devices simultaneously forms Schottky contacts to SiC and ohmic contacts to PbS-QD, enabling electrical screening and isolation of these interfaces from each other. After PbS-QD deposition, the diodes exhibit photovoltaic and photoconductive response at photon energies far below the SiC bandgap, extending to the NIR gap of the QD film. Scanning photocurrent microscopy illustrates that this is due to charge transfer from the QD-film to the n-type 4H-SiC through a trap-limited, rectifying PbS-QD/SiC heterojunction with ideality n=2 in parallel with the EG/SiC Schottky diode. The photoconductive gain at this QD/SiC interface could be useful for IR detection in wide bandgap platforms. Response times as fast as 40 ms are suitable for imaging applications, although careful contact design is required to optimize work-function matching and spreading resistance.

S.EL01.06.13
A Review on Controlling Nano-Scale Chemically Modified Thin Films for CMP Processes Development
G. Bahar Basim; University of Florida, United States

As the microelectronics manufacturing faces the challenges related to the Beyond Moore’s Scale adaptation, Chemical Mechanical Planarization (CMP) process control becomes much more critical yet difficult simultaneously. The need for planarizing larger scale wafers at an atomic scale precision with superior removal rate selectivity and zero-defect focus demands a nano-scale control on the process performance. This study reviews the atomic-scale chemical and mechanical interactions on CMP as it applies to traditional as well as the next generation materials in microelectronics manufacturing. Once the behavior of the wafer surface is understood at an atomic level, the process control metrics can be tuned accordingly.

In an attempt to come up with the design criteria for the slurry chemistry, chemically modified layer formation is evaluated on conducting, semiconducting and insulating materials as a function of evaluating the nano-scale surface topography and change in surface energy. Metallic films are studied in terms of their corrosion and passivation behavior through macro-scale electrochemical evaluations as well as surface-sensitive characterization techniques such as XRR, XRD and FTIR [1, 2]. In addition, a modeling approach is introduced through Cahn Hilliard Equation (CHE) approximation to the surface energy minimization on the metal-oxide formation by nucleation [3]. Furthermore, removal rate selectivity properties of the semiconductor materials are discussed on conventional and III-V semiconductors and insulators as a function of chemically modified film alteration [4-5]. Some high-end applications such as (i) tungsten T-gate transistors, (ii) new liner/barrier materials [6], (iii) germanium based high-speed, shallow trench isolation transistors and (iv) high-power transistors and LED applications where III/V semiconductors are deliberated. As a new challenge, 3-D implementations of the CMP process, where the chemically modified nano-films impact the performance of the materials are also introduced.

CdSe_{1-x} alloys now used in state-of-the-art CdTe solar cell technology can be further characterized and optimized. Se alloying can significantly reduce the bandgap of the CdTe absorber due to the strong bandgap bowing between CdTe and CdSe. This has been demonstrated to enhance quantum efficiency in the infrared and boost the device short-circuit current (J_{sc}). Interestingly, despite having a lower bandgap, devices using Se have achieved open-circuit voltages (V_{oc}) on par with (unalloyed) CdTe-based devices. Recent time-resolved photoluminescence and cathodoluminescence data suggest that the CdSe_{1-x} materials have lower recombination rates and improved grain-boundary passivation relative to CdTe, and this appears to be making up for bandgap-related V_{oc} losses[1]. Further characterization studies should reveal additional relationships between absorber processing and the CdSe_{1-x} composition, current collection, recombination, etc., that can be used to optimize device performance.

There are two methods of CdSe_{1-x} growth. The first method creates a CdSe window layer for a CdTe device then allows diffusion to create a dopant gradient. The second processing method deposits a CdSe_{1-x} alloy layer and then a CdTe layer. Previous characterization studies have focused on the CdSe/CdTe device structure and the effects of changing window layer thickness and composition. A study by Poplawsky, et al. [2], indicated that, as CdSe window thickness increased, device performance increased then quickly decreased. Quantum efficiencies and correlative SEM/TEM analysis indicated that if the Se concentration was above 40 at%, grains could change phases from zinc-blende to wurtzite and stop contributing to the device photocurrent. In the CdSe_{1-x}/CdTe structure, the Se concentration can be kept below 40 at% to prevent the formation of the wurtzite phase.

To better understand the impact of Selenium concentration on device photo-collection, an Electron Beam Induced Current (EBIC) study is presented which studies the impact of Selenium on device collection for the CdSe_{1-x}/CdTe device structure. EBIC is an SEM-based characterization technique which uses an electron beam to locally excite carriers, which are subsequently collected and analyzed to understand microstructural effects on recombination. A current collection map can thus be created with sub-micron resolution. EBIC has been previously used to identify local variation in collection current which is correlated with a finite element device model. Using this model, it is possible to calculate the equilibrium band structure of the device and estimate the built-in potential between the junctions.

EBIC analyses of these alloy junctions indicate that the highest carrier collection was near the CdSe_{1-x}/CdTe interfaces with a second collection peak near the TCO/CdSe_{1-x} interface. This finding is indicative of a buried junction in the CdSe_{1-x}/CdTe device. Previous studies on the CdSe/CdTe structure have shown highest collection near the TCO contact with no buried junctions. The position and strength of this buried junction could decrease the impact of recombination at the TCO interface, but it could also decrease drift velocity, negatively impacting performance. These competing effects need to be better understood for the optimization of CdSe_{1-x}/CdTe device performance.

The presence of a buried junction in the CdSe_{1-x}/CdTe device implies a complex change in carrier concentrations and band structure within these devices. In order to better understand the implications of this observation, these results are correlated with a finite element device model. Using this model, it is possible to calculate the equilibrium band structure of the device and estimate the built-in potential between each junction.


S.E.L01.06.31
Experimental Study of Fundamental Material Properties of Alkali-Antimonide Photocathodes Pallavi Saha1, Oksana Chubenko1, Howard A. Padmore2 and Siddharth Karkare1; 1Arizona State University, United States; 2Lawrence Berkeley National Laboratory, United States

Alkali antimonides (such as CsSb, K_{2}CsSb and Na_{2}K_{2}Sb) constitute a rather interesting class of materials, exhibiting high quantum efficiency (>10%) and high brightness in visible light making them interesting materials for use in photon detectors and as photoemission based electron sources for large linear particle accelerators (used for X-ray Free Electron Lasers, Electron Colliders and Hadron Beam Coolers) and time resolved electron microscopes. Despite ongoing work on these extremely vacuum sensitive materials for the last several decades, there has been no conclusive understanding and little/no consensus on its opto-electronic properties like band gap, electron affinity, optical constants etc. Lack of knowledge of these vital properties has stood in the way of understanding the process of photoemission in these materials near the photoemission threshold. The objective of our work is to grow high quality alkali-antimonide films with smooth surfaces and perform different spectroscopic characterizations like photoluminescence, photoconductivity and ellipsometry on them, in order to explore their opto-electronic properties in ultra high vacuum. It is believed that this detailed experimental study will elucidate the exact process responsible for efficient photoemission from these materials and allow us to develop state-of-the-
art electron sources with maximized brightness.

S.E.L01.06.07
Comparative Study of Surface Energy Engineering for Low Temperature (< 453 K) Nanobonding™ of LiTaO₃ and LiNbO₃ to Si and α-Quartz SiO₂
Mohammed Sahal, Brian Baker, Nicole Herbots, Nikhil C Suresh, Shaurya Khanna, Amber A Chow, Saaketh R. Narayan, Aashi R. Gurijala, Robert J. Culbertson, Lauren Puglisi and Thilina N. Balasooriya; Arizona State University, United States

Opto-electronic integration yields high density and high complexity electronic devices by improving speed and reducing interconnection bottle-necks. Heteroepitaxy and wafer bonding are the main technologies to achieve monolithic integration of heterogeneous materials. However, heteroepitaxy is limited by the mismatches between dissimilar lattice constants and between different coefficients of thermal expansion (CTE).

Direct Wafer Bonding (DWB) is the fusion of two mirror-polished, flat wafers, which overcomes the limitations of heteroepitaxy. DWB can be applied to many materials including bonding III–V, II-IV semiconductors and piezoelectrics to Si.

In this work, low-temperature DWB via NanoBonding™ is investigated to bond LiTaO₃ and LiNbO₃ to Si(100) and α-quartz SiO₂(100). Low-temperature NanoBonding™ of piezoelectrics such as LiTaO₃ and LiNbO₃ on Si-based materials can avoid issues arising from their CTE mismatch, since conventional DWB requires anneal temperature > 673 K.

The highly anisotropic CTE of LiTaO₃ ranges from ~ 4 x 10⁻⁶ /K along the c-axis to up to ~ 16 x 10⁻⁶/K along the a-axis. Thus, the CTE for LiTaO₃ is 2-10 times larger than the CTE for Si, 2.6 - 2.77 x 10⁻⁶ /K, and 10-30 times larger than the CTE for fused SiO₂ and α-quartz SiO₂, which ranges 0.54 - 0.76 x 10⁻⁶ /K. Thus even a low T anneal at 473 K is found to shatter a 6” LiTaO₃/Si bonded pair. Nano-Bonding™ at T < 473 K uses Surface Energy Engineering (SEE) instead of high temperature anneal to bond surfaces. In addition, processing temperatures for LiTaO₃ are found to be limited by thermal decomposition LiTaO₃ into Ta₂O₅ at T ≥ 453 K due to Li out-diffusion, as much as by LiTaO₃ fractures due to CTE mismatch.

SEE is guided by surface energy and hydro-affinity measurements, using Three Liquid Contact Angle Analysis (3LCAA) and the Van-Oss-Chaudhury-Good theory. 3LCAA is conducted with high statistics, by mapping wafers for three surface interactions, namely van der Waals interactions, electron donors, electron acceptors interactions. Multiple metered 10-µl drops of three liquids, water, glycerin, and α-bromo-naphthalene are used. The contact angles are extracted from a large set of drops and their reflection via an automated, fast, accurate algorithm, DROP™. The “as received” surfaces are characterized at equilibrium, to yield insights for SEE into modifying the initial surface energy and hydro-affinity to a far-from-equilibrium state.

As received 6” Si(100) wafers are initially hydrophilic with a uniform average water contact angle of 37.7 ± 0.6°, and an average surface energy γT of 57.6 ± 0.5 mJ/m². As-received α-quartz SiO₂(100) wafers surface were hydrophobic with an average water contact angle of 66.7 ±1.7° and an average γT of 33.2 ± 0.8 mJ/m². 6” wafers of LiTaO₃ are initially mostly hydrophobic with an average water contact angle of 64.4 ± 2.7°, while water contact angle average 54.2 ± 8.1° LiTaO₃ and LiNbO₃ surface energies γT are low and very close: 38.8 ± 4 mJ/m² and 39 ± 2.5 mJ/m² respectively.

SEE via aqueous HF creates far-from-equilibrium Si surfaces by decreasing the initial γT of Si(100) from 57.6 ± 0.5 mJ/m² to 35 ± 0.03 mJ/m² and increasing the γT of α-quartz SiO₂(100) was increased from 33.2 ± 0.8 mJ/m² to 48.7 ± 1.5 mJ/m². Likewise, LiTaO₃ and LiNbO₃ were made hydrophilic via SC1(H₂O:NH₄OH:H₂O₂) solution (4:1:1) followed by aqueous HF etching.

Nano-contacting of LiNbO₃, LiTaO₃ on Si(100) and α-quartz SiO₂(100) and subsequent anneal at T < 453 K was performed to create a bonded interfacial phase. However, nano-contacting was only observed for hydrophobic LiTaO₃ and LiNbO₃ with hydrophilic Si-based surfaces. Results show that bonding hydrophobic LiTaO₃ and LiNbO₃ to hydrophilic Si or SiO₂ without anneal is much more effective than trying to bond hydrophilic LiTaO₃ to hydrophobic Si or SiO₂. This can be attributed to the modification of surface polarity and will be discussed based on the surface crystallography of LiTaO₃ and LiNbO₃.

S.E.L01.06.32
Enhancing Nucleation of Metal ALD by Pre-Dosing Small Organometallic Molecules Camila de Paula, Nathaniell Richey, Li Zeng and Stacey F. Bent; Stanford University, United States
The process of thermal atomic layer deposition (ALD) of metals on non-metal surfaces is sought for many applications, but often suffers from nucleation delays that result in poor-quality films. These growth delays can result from a lack of suitable chemisorption sites on the non-metal surface. Various strategies have been explored to improve nucleation in these systems. Vapor phase pre-treatments have proven to be an especially promising nucleation enhancement strategy due to the minimal substrate-modification induced, its robustness, and its uniformity.

In this work, we demonstrate that pre-functionalizing the surface with a sub-monolayer of small organometallic molecules such as ZnEt₂, AlMe₃ and AlMe₂Cl, from the vapor phase can lead to a significant increase in the surface coverage of the metal deposited by ALD at low cycle numbers. This process is demonstrated using Pt ALD as a model process, using (methylcyclopentadienyl)trimethylplatinum (MeCpPtMe₃) and O₂ as reactants. Pt coverage was enhanced by ~ 3-fold after 100 ALD cycles and even larger enhancements were observed at lower cycle numbers following the pre-treatment. We hypothesize that the high coverage of the small organometallic molecules provides an alternative chemisorption mechanism for the platinum precursor leading to increased MeCpPtMe₃ chemisorption during the first ALD cycle. This alternative chemisorption mechanism was investigated through in-situ X-ray photoelectron spectroscopy and mass spectrometry. Nanoparticle growth was monitored using grazing incidence small angle X-ray scattering and scanning electron microscopy. We determined that chemisorption of MeCpPtMe₃ on the treated substrate originates from a Brønsted acid-base reaction (i.e., proton transfer reaction), where the MeCpPtMe₃ acts as the Brønsted acid and the pre-treatment molecules serves as the Brønsted base. Growth analysis indicates that the pre-treatment leads to growth of highly dense, ordered Pt nanoparticles with improved wettability at low cycle numbers, leading to continuous and pinhole free Pt films.

S.EL01.06.11
Low Temperature c-Si/4H-SiC Heterojunction Growth Using Metal Induced Crystallization Fabian Triendl, Georg Pfusterschmied, Christopher Zellner, Sabine Schwarz, Werner Artner and Ulrich Schmid; Technische Universität Wien, Austria

Metal induced crystallization is a well-known technique to reduce the crystallization temperature of amorphous semiconductors like a-Si using a catalytic metal. Crystallization temperatures even below 200 °C have been realized making it compatible with organic materials or other applications where only a limited temperature budget is acceptable. A combination of the wide band gap semiconductor 4H-SiC and such a low temperature process is barely investigated, although the Si/4H-SiC heterojunction offers huge potential in the field of e.g. heterojunction diodes, bipolar junction transistors and optical detectors. Conventional growth methods like chemical vapor deposition (CVD) need temperatures well above 800 °C to achieve epitaxial growth of Si on SiC. A low temperature method could make this heterojunction more practical, also in combination with other materials and temperature sensitive processes.

We present the first results to achieve partially epitaxial c-Si/4H-SiC interfaces using Al as catalytic metal. Sputter deposited amorphous silicon has been successfully crystallized on 4H-SiC at temperatures ranging from 350 to 700 °C. Annealing led to an almost complete layer exchange of Al and Si as well as to a heteroepitaxial interface of crystallized Si islands and the SiC surface. Si <111> was found to be the dominating crystallographic orientation of the re-crystallized Si. X-ray diffraction measurements show the change in Si crystallinity and the crystallographic impact of the underlying SiC substrate in this temperature range. TEM and SEM imaging was performed to investigate the film microstructure and the interface quality, thus revealing a clean and abrupt interface of large Si grains and the SiC substrate.

S.EL01.06.87
Strongly Structure-Directed Phonon Dynamics in GaAs Observed by Ultrafast Electron Microscopy Elisah VandenBussche and David J. Flannigan; University of Minnesota Twin Cities, United States

The process by which strongly-photoexcited semiconductors return to their ground state consists of a series of complex, strongly-correlated many-body interactions which overlap in space and time, resulting in an evolution of behaviors that is both difficult to study and valuable, both for fundamental insights into the quantum nature of matter and for control of device and material behaviors in electronic and optoelectronic applications. Extensive work has been done in this regard, illuminating the sequence of hot carrier excitation, carrier-carrier scattering, carrier-lattice scattering and thermalization, recombination, and lattice heat diffusion. After strong photoexcitation creates a high-energy bath of “hot” carriers, electron-phonon coupling results in the emission of optical phonons, which decay into lower-energy phonons, either optical or acoustic. The resulting nonequilibrium phonon populations can in turn influence hot carrier relaxation and transport, an inextricability which has been demonstrated through transient Raman scattering [1-3]. The inseparable nature of structural behavior from that of excited electron-hole plasmas is further demonstrated by the result that when not in equilibrium, acoustic mode phase velocities change as a function of time due to residual Coulomb interaction caused by imperfect
screening by electrons [4]. Thus, a thorough understanding of ultrafast post-excitation structural dynamics is essential to a full comprehension of semiconductor behavior.

As electronic devices continue to shrink, the associated increased importance of device surfaces, interfaces, and defects add an additional layer of complexity to the structural behavior. Techniques typically employed to investigate post-excitation responses operate in reciprocal or momentum space and require spatial averaging, reducing real-space resolution. It is known that interfaces change the electronic structure in their surrounding regions, strongly influencing carrier dynamics, and it has been shown in our previous work that phonons are structure-directed, propagating specifically from interfaces and repeatably traveling perpendicularly to the launching interface [5]. In sum, electron-phonon coupling behaviors are known to be influenced by structure, making real-space information relevant to a complete picture of post-excitation behavior.

Here we use ultrafast electron microscopy (UEM) to image phonons in real space and thereby demonstrate the influence of both the meso-scale and atomic structure of GaAs on the post-excitation phonon behavior. Making use of combined picosecond-nanometer real-space resolutions, we have directly imaged excitation of GHz coherent strain waves propagating exclusively from specimen-vacuum interfaces with initial hypersonic velocities which decay over time to the speed of sound in GaAs. We also report the change in the properties of these waves upon laser annealing of the specimen, epitaxially crystallizing the focused-ion-beam-induced amorphous surface layer and resulting in measurable hardening of the specimen. This appears in the phonon behavior as an increase in the velocity of the phonons. By imaging the phonon interactions with both the specimen-vacuum interface and the amorphous-crystalline interface within the specimen, we demonstrate the importance of interfaces in fully understanding the phonon dynamics in photoexcited GaAs.


S.E1.01.06.16
Direct Write Waveguides Using Multiphoton Lithography

Michael Gallegos, Daryl Dagel, Amber Dagel, Andrew Pomerene, Allen Vawter, Erik Skogen and Bryan Kaehr; Sandia National Laboratories, United States

Abilities to capture, guide, and direct light into pixelated detectors (CCDs, CMOS sensors, FPAs, etc.) using free-form trajectories would be transformative for a range of technologies that currently use traditional optics (lenses, mirrors, prisms, etc.) for light coupling. However, few manufacturing techniques provide the appropriate scale and surface quality to address this task. In this work, we consider “free-form waveguides” using the high-resolution 3D printing technique of multiphoton lithography (MPL; also known as direct laser writing, DLW). First, we printed hollow and solid core vertical waveguide arrays spanning millimeters with single (5 micron) and multimode (30 micron) compatible cross-sections. Unsupported 5-micron diameter pillars generally succumbed to capillary forces during development and drying and thus sheathed waveguides were designed by anchoring fibers to a support scaffold. In addition, we examined direct printing onto active devices (coupling a source to a sensor) using an air-clad multimode design. Efficient light coupling was observed with scattering losses primarily from fabrication artifacts such as stitch lines. To address these issues, we considered stitch-free cores using a clad-only design resulting in encapsulated photoresist in the interior that is subsequently cured (UV, thermal) following development. These initial results, combined with the limitless design space afforded the MPL technique, provide a promising path forward to develop ultra-wide-field and highly compact imaging devices.

S.E1.01.06.40
Effect of Si Nanoparticles on Reflectance Spectra for Ge and Ge/Si Substrates

Sabina Abdul Hadi1, Ayman Z. Rezk2 and Ammar Nayfeh2; 1University of Dubai, United Arab Emirates; 2Khalifa University, United Arab Emirates

The continuous innovation in nano materials has allowed the development of new antireflective coats (ARCs) for optical lenses, solar cells, data storage, displays and others that require a reduced reflectance to increase efficiency. Multi-layered ARCs particularly have attracted attention lately for demonstrating low and tunable spectral reflectance.

This paper presents a simple approach for forming anti-reflective coating stacks on bulk Ge and PECVD Ge grown on Si employing colloidal dispersions of Si nanoparticles (NPs).

The Si NPs have a diameter of 2.85 nm and are prepared by chemical etching of crystalline Si wafers in HF and H2O2 using electrical or hexachloroplatinic acid catalyst. The nanoparticles are recovered by sonicating the wafers in isopropyl alcohol, forming a stable colloid with concentration of 10 µM [1].
Each antireflective coat is applied by the drop casting of monodispersed Si NPs on a 3 by 3 cm pieces of both Ge bulk and PECVD Ge grown on Si. A total of 5 drops are applied with each drop consisting of 100 µL. After each drop, the samples are left to dry for an hour and a half.

For bulk Ge, (110) Sb doped (n-type) Ge with a resistivity of 0.1–0.5 Ωcm were used, while for the PECVD Ge growth, (100) P doped (n-type) Si with a resistivity of 0.01–0.02 Ωcm are used as starting substrates. An Oxford Instrument System 100 PECVD activated by 13.56 MHz radio frequency signal is used to grow Ge layers on Si substrates. High purity germane (GeH₄), H₂, and Ar gases are used as precursors for Ge growth. The undoped Ge film was grown using the two-step approach, which has been described in detail in our previous work [2].

The impact of multiple drop casting of Si NPs on the antireflective properties of the Ge surfaces were investigated by the analysis of their reflection spectra. The reflectance of the coating was measured at four locations on each sample by a UV–VIS spectrophotometer (Lambda 850, PerkinElmer). The samples were qualified by controlling the reflectance at the four points within an error of 1.2%. The corresponding reflection spectra were captured as a function of the incident wavelength, ranging from 250 nm to 1500 nm.

For PECVD Ge grown on Si substrates, the average reduction in reflectance has shown to increase as the incident wavelength decreases, with a decrease of ~2% after each 100 µL coating. After 5 drops (100 µL ×5), the overall reflectance across the whole spectra is on average 9.35% lower compared to the uncoated samples. The minimum decrease in reflectance was of 2.49% at 1290 nm and the maximum of 34% at 250 nm.

For Bulk Ge, the average reduction in reflectance has shown to increase as the incident wavelength decreases from 1500 nm to 320 nm. At 500 µL, the reduction in reflectance had an average of 6.16% (Min.: 2.73% at 1500 nm, Max.: 13.75% at 320 nm and Median: 5.1%). At lower wavelengths range from 250 nm to 320 nm), the amount of reflectance reduction is less compared to wavelengths above 320 nm.

After 5 drops (100 µL ×5) on PECVD Ge samples, the incident wavelength where the minimum reflectance occurred (λ_{min}), shifted from 1050 nm where reflectance is lowered by 34.5%, to 410 nm with 25.2% reduction in reflectance. While for bulk Ge sample, λ_{min} shift occurs from ~1480 nm to ~420 nm with a decrease in reflectance of 37.9% and 28%, respectively.

Results demonstrate that it is feasible to deposit a coating of Si NPs with tunable reflectivity over a wide range by drop casting multiple layers of the nanoparticles.

References:

S.EL01.06.38
Towards Scalable Fabrication of Atomic Wires in Silicon by Nano-Patterning Self-Assembled Molecular Monolayers Chufan Zhang and Yaping Dan; Shanghai Jiao Tong University, China

Developing a scalable method to fabricate atomic wires is an important step for building solid-state semiconductor quantum computers. In recent years, self-assembled molecular monolayer doping (MLD) has attracted intensive research interests due to its capability of facilitating mass production and forming ultra-shallow junctions with atomic precision[1]. MLD is believed to have a great potential in controllable dopant manipulation at sub-10 nm scale[2]. However, there is still no general method for effectively patterning dopant-containing monolayer at nanoscale. In this work, a novel selective doping strategy is proposed by patterning self-assembled monolayer to a few nanometers using standard nanofabrication processes, which significantly improves the lateral doping resolution of monolayer doping from microscale to nanoscale.

We first found an effective way to remove the self-assembled monolayer via oxygen plasma followed by HF etching, which is confirmed by X-Ray photoelectron spectroscopy and Van der Pauw measurements. Electron beam resist HSQ (XR1541-002, Dow Corning) was used to create patterns that protect part of the self-assembled DVP monolayers from being oxidized by oxygen plasma, since HSQ will turn into amorphous SiO₂ after electron beam exposure. To increase the resistance of the HSQ SiO₂ against HF etching, a second time of high dosage exposure was performed on the HSQ structure. The high dosage electron beam exposure might induce a thin amorphous carbon layer covering the HSQ structures and dramatically improved the resistance of HSQ against HF etching.

Using this method, we further explore the possibility to fabricate phosphorus atomic wires in silicon by patterning self-assembled diethyl vinylphosphonate monolayers into lines with a width ranging from 500 nm to 10 nm. The phosphorus
dopants are driven into silicon by rapid thermal annealing, forming dopant wires. Four-probe and Hall effect measurements are employed to characterize the dopant wires. The results show that the conductance is linear with the width for the wires, showing the success of the monolayer patterning process to nanoscale. To fabricate atomic wires made of one or a few lines of phosphorus atoms, we need to shorten the thermal diffusion length and increase the dopant incorporation rate at the same time. Pulsed laser annealing may be a promising solution. The present work provides a promising pathway for mass fabrication of atomic wires in silicon that may find important applications in quantum computing.

References

S.EL01.06.17
Role of Carbon and Oxygen Coverage in the Modification of Surface Energy and Hydro-Affinity of GaAs and Si for Low Temperature Wafer Bonding

Aashi R. Gurijala1, Shaurya Khanna1, Amber A. Chow1, Nikhil Suresh1, Mohammed Sahal1, Sukesh Ram1,2, Nicole Herbots1, Thilina N. Balasooriya1, Robert J. Culbertson1 and Karen Kavanagh1; 1Arizona State University, United States; 2Yale University, United States

Native oxides increase electrical resistance and inhibit epitaxy on semiconductors. Their removal is key in opto-electronic integration for devices such as tandem solar cells. Besides heteroepitaxy, Direct Wafer Bonding (DWB) is a viable integration technology for GaAs and Si. NanoBonding™ is DWB conducted at low T (~200°C) by modifying surface energy and hydro-affinity to reach far-from-equilibrium states and activate cross-bonding and electron exchange between the surfaces.

Hence, the surface energy has to be increased (if it is initially low), or decreased (if it is high). One of the surfaces in the pair has to be made hydrophilic if it is initially hydrophobic, and the other one hydrophilic if it is initially hydrophobic. Moreover, the surfaces have to be modified in a complementary way so that electrons are transferred from electron donors from one surface to electron acceptors on the other.

To conduct Surface Energy Engineering (SEE) of GaAs and Si into a bonding pair, the initial surface energy, hydro-affinity, surface composition, and oxidation levels of as-received GaAs(100) and Si(100) are initially characterized. Next, the initial surface energies and hydro-affinities are modified not only by oxygen removal via chemical etching, but also to maximize cross-bonding. The characterization methods are Three Liquid Contact Angle Analysis (3LCAA) for surface energy and hydro-affinity, High Resolution Ion Beam Analysis (HR-IBA) for O coverage, and X-Ray Photoelectron Spectroscopy (XPS) for oxidation and C contamination.

In 3LCAA, the total surface energy, \( \gamma_T \), is determined by the van Oss-Chaudhury-Good theory using 3 components: Lifshitz-Van der Waals, electron donors, and acceptors. GaAs(100) native oxides are hydrophilic with a low surface energy (\( \gamma_T = 33.4 \pm 1.1 \) mJ/m²) while Si(100) native oxides are hydrophilic with a high surface energy (\( 59.7 \pm 1.7 \) mJ/m²). GaAs surfaces are then etched with NH4OH:H2O (1:10) to be highly hydrophilic, while their \( \gamma_T \) can be reproducibly increased by a factor of 2 to 65.5 \( \pm 1.4 \) mJ/m². HF:CH3OH (1:20) etching makes Si(100) hydrophobic and decreases its \( \gamma_T \) by 20% to 48.2 \( \pm 1 \) mJ/m². Nano-bonding™ of GaAs to Si does not occur between these surfaces. However, Si(100) etched by aqueous HF becomes even more hydrophilic with a 25% decrease in \( \gamma_T \) to 44.4 \( \pm 2.3 \) mJ/m². With this SEE of Si, GaAs nano-bonds to Si reproducibly.

O etching is measured by HR-IBA, while oxidation states and C-contamination are measured by XPS to correlate to nano-bonding. HR-IBA combines <111> channeling with O nuclear resonance to measure O coverage within \( \pm 0.2 \) Monolayers (ML) and analyzed via SIMNRA simulations. O coverage on GaAs is found to decrease by a factor 2 from 7.2\( \pm 0.5 \) ML to 3.6\( \pm 0.2 \) ML after etching.

The ratio of Ga and As is found to be unaffected by C-contamination, and remains \(~54:46\) within 1 atomic % by HR-IBA or \(~1.18\) within 10% by XPS. XPS shows that the relative ratio of Ga bound to GaAs versus Ga bound to Ga2O3 is initially 64:36 to within 1% with a slight increase in Ga bound to O. The relative ratio of As bound to GaAs versus As bound to O is much lower than Ga, 80:20 to within 1% and does not change with etching.

XPS analysis also shows that when C-contamination ranges between 12%-35% atomic %, the measured ratios of Ga and As bound to GaAs versus Ga and As bound to O vary less than 2%. After etching, Ga bound to Ga2O3 decreases with increasing carbon with a weak correlation factor of 0.4. C-contamination does not appear to significantly affect Ga oxidation. For As oxides, As2O5 shows a relative increase compared to As2O3 as C contamination increases with a strong correlation factor of 0.86 in native oxides before etching. After etching, the correlation factor is 0.55.
In summary, aqueous HF produces more hydrophobic Si(100) surfaces that can nano-bond to highly hydrophilic GaAs etched via dilute NH4OH while C contamination does not appear to modify GaAs surface composition nor oxidation.

S.EL01.06.24
Unraveling Vertical Inhomogeneity Effects in Vapor Phase Polymerized PEDOT:Tos Films Shangzhi Chen and Magnus P. Jonsson; Linkoping University, Sweden

Electrically conductive polymers are widely utilized in emerging electronic devices due to their excellent optoelectronic properties as a potential alternative to conventional conductors. Among them, Poly(3,4-ethylenedioxythiophene):Tosylate (PEDOT:Tos) thin films deposited by Vapor Phase Polymerization (VPP) exhibit electrical conductivity exceeding 3400 S/cm which is almost comparable to commercial ITO electrodes. [1] Systematic investigation on such films indicates a strong anisotropy in electrical and optical properties and this anisotropy is believed to be mostly caused by the preferential alignment of para-crystallines in the films. [2]

Here, I will present our recent study on the VPP PEDOT:Tos thin film system and reveal that vertical gradient could also be an important factor contributing to the electrical anisotropy. By examining the results from grazing-incidence wide-angle X-ray scattering and X-ray photo-electron spectroscopy, we observed significant differences of the top and bottom surfaces, including para-crystalline alignment preference and oxidation level (doping level). These show that the VPP PEDOT:Tos layer is not vertically homogeneous in terms of both “crystallization” fraction and charge carriers (doping level). To explain the origin of this inhomogeneity, we propose a growth mechanism for VPP based on diffusion-limiting transport of polymerization precursors. Conductive polymer thin films with certain gradient profile may find applications in functionally graded thermoelectrics, gradient-index optics, and optoelectronic devices with gradient doping.

References

S.EL01.06.48
Optimizing n-Type Dopant Incorporation in GaAsBi for Multijunction Photovoltaics Margaret A. Stevens, Kevin Grossklaus, Samuel Lenney, John H. McElearney and Thomas E. Vandervelde; Tufts University, United States

Multijunction photovoltaics employed in solar concentrator architectures can have theoretical efficiencies as high as 65% for a 4-junction cell [1]. For these devices, sub-cell band gaps of 0.96-1.18 eV are required. Epitaxially grown GaAsBi is of interest for this application due to (1) less lattice mismatch to GaAs than InGaAs for comparable band gaps [2] and (2) a proposed temperature-insensitive band gap and reduction in Auger recombination [3]. However, these materials are challenging to grow due to the surfactant-like nature and low solubility of bismuth (Bi) in this system. The low growth temperatures necessary for good bismuth incorporation is often at odds with good material quality. The need for depleted arsenic overpressure can often lead to challenging dopant incorporation [4], a critical requirement if these devices are to be employed in PN junctions.

In this work, we explore methods to improve dopant incorporation and carrier mobility in GaAsBi and GaAsBi for future photovoltaic devices. Samples were grown on a Veeco GENxplor MBE using a valved As source and a solid source effusion cell for group-III elements and Bi. Bismuth fraction and strain state were determined by high-resolution x-ray diffraction and absorption edge was measured by transmission spectroscopy. Select samples are grown lattice matched to InGaAs virtual substrates to decrease compressive strain which delays both Ga-Bi droplet formation and defect formation from strain relaxation [5]. Samples grown on GaAs and InGaAs substrates are doped with silicon or tellurium for n-type doping and beryllium for p-type doping. The benefits and challenges of using a group-IV n-type dopant versus using a group-VI n-type dopant in this materials system will be discussed. Mobility of GaAsBi as a function of dopant concentration was measured using Hall effect measurements and compared for the different choice of dopants. Temperature-dependent Hall measurements are utilized to explore scattering mechanisms. Additionally, the effects of ex situ thermal annealing at 500 °C on optical and electrical parameters will be discussed. Finally, mobility data will be fed into device simulations using Silvaco to evaluate best device architectures to use bulk GaAsBi films in photovoltaics.

Chalcopyrite materials based on CuInGaSe₂ is practically used for the commercially available high efficiency solar cells. The room temperature bandgap of AgGaTe₂ is about 1.3eV, hence the application of this material to the active layer of novel solar cells also attracted the attention. Among various film preparation methods, the closed space sublimation (CSS) method is suitable for the fabrication of mass production solar cells since it has various advantages toward the production cost reduction. The growth of crystallized AgGaTe₂ thin films utilizing this method on Si and Al₂O₃ substrates have performed in past, and it was discovered that the introduction of the two-step sequence was the key to realize high quality thin films. The Ag₂Te layer was deposited as the first step to avoid the melt-back etching related problems of Ga against substrate materials. Then, AgGaTe₂ thin films were formed using the mixed powder source of Ag₂Te and Ga₂Te₃. The AgGaTe₂ thin films could be also prepared using the powder source of Ga₂Te₃. The first Ag₂Te layer was disappeared during the high temperature growth process of the second sequence, and a single phase AgGaTe₂ of the uniform layer has formed once the growth parameter was optimized.

It was clarified from the X-ray diffraction (XRD) measurement that the inclusion of AgGa₅Te₈ compounds occurred when the fraction of Ga₂Te₃ in the deposits was greater than that of Ag₂Te. On the other hand, mixed crystal of AgGaTe₂ and Ag₂Te were formed when the fraction of Ga₂Te₃ was less than that of Ag₂Te. These results corresponded to the phase diagram of the Ag₂Te–Ga₂Te₃ system. A pn-heterojunction solar cell structure was prepared using the AgGaTe₂ layer on the n-Si substrate, and the photovoltaic properties were confirmed. The AgGaTe₂ layer was also prepared on the Mo/quartz substrate using the same growth sequence.

In case of the CuInGaSe₂ layer growth on the Mo electrode layer, Se diffusion was observed in the Mo electrode layer. The advantage and disadvantage were still discussed for this structure. In this study, the interfacial diffusion of elements at AgGaTe₂/Mo was studied to understand how the diffusion of Ga could be suppressed. High resolution cross sectional TEM images of the interfacial region was analyzed using the Z-contrast images of the high angle annular dark field (HAADF) mode and EDX-mapping mode.

When AgGaTe₂ layer was directly grown on the Si substrate, Si surface was etched and became very rough, and it was considered that Ga has damaged the Si substrate surface. By introducing the two step procedure, the interface quality was substantially improved and the roughening was vanished.

When the layer was grown on the Mo layer using the two step procedure, sharp interface was also observed. By careful analysis using the EDX mapping, it was confirmed that Ga was diffused into the Mo layer when the growth temperature was above 650 °C. Different from the conventional interdiffusion, Ga accumulation was also observed at the diffusion front. The diffusion depth was fairly uniform across the specimen. The diffusion of Te was also observed for samples grown at high temperatures as well as samples post annealed at the high temperature. Those samples exhibited Mo and Te condensation region with the size of around 0.2 to 0.5 micron within the AgGaTe₂ layer. It probably suggested that a part of Mo was reacted with Te, and formed the volatile MoTe₂ material, and it was migrated into the AgGaTe₂ layer.

Further investigation is ongoing to identify the diffusion characteristics at the AgGaTe₂/Mo layers. It is reconfirmed that the two step growth procedure is a very useful approach to achieve the high quality layer, but processing temperatures including the growth temperature and post growth annealing temperature are very critical parameters to achieve the high quality interface with the abrupt profile.

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Enhancement of Electrical Characteristics of Amorphous Indium-Gallium-Zinc-Oxide Thin-Film Transistors by Inserting Carrier Induced Interlayer

Chansic Yoon, Hyung Tae Kim, Min Seong Kim, Hyukjoon Yoo, Jeong Woo Park, Dong Hyun Choi, Dongwoo Kim and Hyun Jae Kim; Yonsei university, Korea (the Republic of)

Since the development of display technology, a new type of industry, such as augmented reality (AR), virtual reality (VR), and wide screen displays, has arrived. Requirements of performance standards on new type of displays have become more severe. Therefore, improving the mobility and stability of thin-film transistors (TFTs) for using in such devices have been actively conducted. To date, low temperature polycrystalline silicon (LTPS) with high field-effect mobility of about 100
cm²/Vs has been widely used as channel material for TFTs, but some problems remain, such as poor uniformity for large area, high leakage current, and high fabrication costs. To resolve the issues mentioned above, amorphous oxide semiconductor (AOS) has been attracted attention due to low off current, large area uniformity, and relatively low fabrication cost. Especially, amorphous Indium-Gallium-Zinc-Oxide (a-IGZO) is most used semiconductor among AOS materials. However, for AOS materials to be applied to the above-mentioned next-generation displays, low field-effect mobility and low stability under bias stresses, which are lower than LTPS, must be overcome.

In this sense, we propose the fabrication of a-IGZO TFTs with high mobility and high stability through insertion of a carrier induced interlayer (CII). CII is a layer introduced between the channel layer and the gate insulator layer, which is thinly deposited to absorb oxygen in the effective channel of a-IGZO through oxidation. Consequently, mobility of a-IGZO TFTs can be improved by oxidation of CII increasing carrier concentration of the a-IGZO front channel.

In this study, thin aluminum layer was deposited for CII by RF sputtering process at 80 W with various deposition time 60, 90, and 120 s. Then, a-IGZO layer was deposited on the CII for channel layer while changing the oxygen partial pressure from 1.7 to 8.3%. After the activation process through thermal annealing at 300°C for 1 hour, Al was deposited by RF sputtering and used as source and drain electrodes. When the a-IGZO channel was deposited with oxygen partial pressures of 1.7, 3.3, and 5% without CII, the saturation mobility was 7.36, 5.45, and 2.83 cm²/Vs, respectively. If it exceeds 5%, it is insulated. The above phenomenon caused by the oxygen vacancy concentration in the a-IGZO thin film decreases with increasing oxygen partial pressure. If the partial pressure of oxygen is less than 5%, Al for CII cannot be completely oxidized, resulting normally conductive property. On the other hand, if the partial pressure of oxygen is more than 5%, the characteristics of the TFTs deteriorate. As a result, 5% condition achieves the best characteristics and determined as the optimize condition.

In the transfer characteristics of the TFTs with various CII thickness, the saturation mobility of the TFTs with CII of 60 s and 90 s deposition were calculated as 11.30 and 13.96 cm²/Vs respectively. As the thickness of CII increases, the saturation mobility also increases. However, switching characteristics of the TFTs with CII are gradually degraded due to insufficient oxidation of CII with metal Al over 120 s of the CII deposition time. The CII with insufficient oxidation acts as current path at the interface between the gate insulator and the channel layer, resulting in a drastically increased conductivity. Consequently, the optimize condition was determined to be CII deposition time of 90 s.

Lastly, bias stress tests were performed to determine the stability of the TFTs. Negative bias temperature illumination stress (NBTIS) test under -20 V, 50°C and 1000 lux for 3600 s was conducted on the TFT fabricated with oxygen partial pressure of 5% with CII deposition time of 90 s. When the result was compared with the a-IGZO TFT without CII (pristine), the stability characteristic was improved as the threshold voltage shifts of the pristine showed -12.05V and the device with oxygen partial pressure of 5% and with CII showed -6.73V.

S.E.L01.06.26
Determining the Surface Chemistry of Lithiated Nickel-Manganese-Cobalt Oxide from Density Functional Theory and First-Principles Thermodynamics Josiah Roberts1, Chad Risko1 and Aashi R. Gurijala2; 1University of Kentucky, United States; 2Arizona State University, United States

Surfaces of materials such as lithiated nickel-manganese-cobalt oxide (NMC) can be characterized through experimental techniques such as photoelectron spectroscopy. These techniques take advantage of high-vacuum environments, though the vacuums are never perfect, and the materials are often exposed to ambient conditions prior to characterization or application, all of which could impact the surface composition. Hence, questions arise as to the data derived from periodic density functional theory (DFT) calculations that assume chemically clean surfaces in perfect vacuum and are used to describe these materials. To reconcile these differences, we investigate the surface chemistry of NMC through a combination of DFT and first-principles thermodynamics calculations. By examining the bulk structure, bare surfaces, and the adsorption of various atmospheric molecular and ionic species, we develop phase diagrams that reveal the expected surface chemistries as a function of various partial pressures, predicting the NMC surface chemistry as a function of the environment. Such predictions can be used to modify future computational studies of the material both in vacuum and in solution, providing additional tools for characterization.

S.E.L01.06.33
Effects of Very High Workfunction Metals or Metal Alloys (NiCr) on High Switching Speed, HV Schottky Diodes for Mixed-Signal or RF ASIC James Pan; Northrop Grumman Corporation, United States

For high switching speed HV Schottky diodes, with very high work function metal and extremely lightly doped epi, the built-in potential may be too high for thermionic emission to occur, when the applied external voltage is quite low (near the forward voltage: VF = 0.07V). If the epi is lightly doped p type, the built-in potential (V_{Built-in}) potential difference between the metal and silicon Fermi levels) is 1.0V (measured with CV). If the external bias is 0.1V, near the measured VF, it is not enough to overcome the built-in potential for thermionic emission as illustrated in the Figures. It is likely that in addition to
thermionic emission, tunneling and diffusion currents also contribute to the total HV Schottky diode forward current. TCAD simulation of HV Schottky diodes with N’ guard bands suggests the potential barrier and electric fields at the Schottky junction are relatively high for thermionic emission to occur, when external bias \( V \gg V_F \).

In the Advanced Technology Laboratory (ATL) at Northrop Grumman Corporation, high performance RF ASICs and power devices in silicon, GaAs, GaN and 4H SiC are simulated, designed, fabricated, and packaged. Extensive DC and RF tests are conducted. The performance of HV Schottky diode is superior to conventional p-n junction diode due to higher BV, lower reverse leakage, lower \( V_F \) and higher output current. We have fabricated HV Schottky Diodes. \( BV > 150V \), \( V_F = 0.07V \). High breakdown voltage, low forward voltage drop, and low reverse leakage are achieved with very high work function metal alloys and low doping epi films.

Lightly doped p (100) or n (100) type silicon films are deposited with epitaxy. Metal or metal alloys are deposited with sputtering. Figure 1 shows the measured I-V’s for the Schottky Diodes. Avalanche breakdown voltage > 150V is recorded with low reverse leakage current. The voltage required to turn the diode on is defined as \( V_F \) – when the current reaches 0.1\( \mu \)A.

Forward bias characteristics of Ti, Au, and NiCr are measured. These data indicate that in order to achieve low \( V_F \) and high current, very high work function metals are needed.

High frequency CV tests are conducted using the HV Schottky Diodes. These CV data are used to extract the doping profiles.

Metal work functions are extracted with the \( 1/C^2 \) vs. \( V \) plots. Interception with the x axis is \( D V \), which is the potential difference between metal and silicon Fermi levels, or built-in potential \( V_{\text{built-in}} \). Metal work function is extracted with \( D V \). One of the Figures shows the measured doping profiles and \( 1/C^2 \) vs. \( V \) plots. From the measured I-V and C-V data we may calculate the avalanche breakdown critical electric fields and metal work functions. A summary of HV Schottky diodes fabricated with NiCr, Ti, Au in Si n and p epi films will be presented.

Energy band diagram is analyzed for HV Schottky diodes: NiCr in p epi (external bias = 0V) \( V_{\text{built-in}} = 1.00V \).

Another energy band is analyzed for HV Schottky diodes: NiCr in n epi (external bias = +0.50V). \( V_{\text{built-in}} = 1.56V \).

In conclusion: we have fabricated HV Schottky Diodes. \( BV > 150V \), \( V_F = 0.07V \). High breakdown voltage, low forward voltage drop, and low reverse leakage are achieved with very high work function metal alloys and low doping epi films. Diffusion and tunneling currents likely contribute to the total Schottky junction current.

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**S.EL01.06.39**

**Fast and Simplified Synthesis of Spiky-Like Copper Sulfide Nanoballs by Soft Chemistry Method for Optoelectronics Applications**

Anderson Klay R. Jaime, Diana V. Hernández, Judith Celina T. Córdova and Santos J. Castillo; Universidad de Sonora, Mexico

Fast synthesis of copper sulfide nanoparticles through two different methods is described in the present investigation. The first reaction was carried out by applying of heating in constant temperature water bath while in the second case the mixture was sonicated. As copper and sulfur sources, copper nitrate and thiourea solutions were used respectively. Main physicochemical properties of the synthesized samples were studied using several characterization techniques. Formation of copper sulfide with hexagonal crystalline structure was corroborated, coinciding with previously reported values for covellite. The most important results corresponded to the un-sonicated sample, which exhibited spiky-like nanoballs morphology and better size distribution. Optical tests revealed band gaps of 1.69 and 2.05 eV, while photoluminescence emissions at 421 and 430 nm, showing promising possibilities for applications in solar cells, catalysis and optoelectronic devices.

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**S.EL01.06.41**

**An Improved Model of Ge Bi-Layers Incorporated CZTSe Devices with MoSe2 Interlayer**

Sanghyun Lee¹, Kent Price² and Edgardo Saucedo³; ¹Indiana State University, United States; ²Morehead State University, United States; ³Institut de Recerca en Energia de Catalunya, Spain

An improved model of Ge bi-layers incorporated CZTSe devices with MoSe2 interlayer.
As environmentally benign and highly-efficient thin-film solar cells, low-cost Cu$_2$ZnSn(S,Se)$_4$ (or kesterite) solar cells, herein CZT(S,Se) have been steadily emerging as an alternative for the 2nd generation Cu(In,Ga)Se$_2$ (CIGS) and CdTe solar cells in the past several years. CZT(S,Se) solar cells have several advantages such as high absorptions coefficient (>10$^4$ cm$^{-1}$), tunable direct band gap energy (1 to 1.4 eV), and usage of abundant elements in earth's crust, becoming an ideal platform to harvest solar energy. However, the efficiency improvement and understanding of emerging CZT(S,Se) is still in an early stage compared to the 2nd generation counterparts. In recent progress, our team reported that Germanium (Ge) incorporation into CZTSe solar cells has improved device performance, which contributed to deepening understanding of Ge-alloyed CZT(S,Se) solar cells, in particular, on the Schottky-type back-contact barrier. We present the complete set of models about the Schottky barrier with the MoSe$_2$ interlayer between the absorber and Molybdenum (Mo) back-contact. Developed analytical models with in-house MATLAB simulators agree well with TCAD numerical simulation and experimental results. A new concept of an effective back-contact barrier is introduced, which provides the mechanism of the improved device performance with lower back-contact barrier for CZTSe Ge bi-layers devices. By incorporating nanoscale Ge bi-layers below and above the CZTSe absorber, the back-contact barrier is improved by 33 %, and power conversion efficiency is improved by 1.1 % than Ge single-layer devices. Based on the back-contact model, defect concentration of Ge reference devices is estimated to be 5.4 x 10$^{16}$ cm$^{-3}$, whereas Ge bi-layers devices show an estimated <9.8 x 10$^{15}$ cm$^{-3}$ at the back-contact interface. To compare models with experimental results, we fabricated three different types of CZTSe: nanoscale Ge devices. The property of the back-contact barrier is assessed by characterizing a temperature-dependent behavior of CZTSe alloyed devices. Collectively, the reduced defect concentration by Ge incorporation in the MoSe$_2$ interlayer improves the barrier height of back-contact. As the defect concentration of the MoSe$_2$ interlayer increases, the benefit from the back-contact barrier lowering by the valence bands offset is reduced and essentially eliminated. Moreover, the increased effective back-contact barrier degrades the series resistance and the overall device performance. However, the barrier at the interface between MoSe$_2$ and Mo metal contact remains the same, even with MoSe$_2$ defect concentration increase. Incorporating thin Ge nanolayer at the interface between the absorber and MoSe$_2$ could positively influence and possibly reduce the defect states, which lowers the effective back-contact barrier from modeling and simulation results. Hence, the Ge layer at the back-contact interface successfully improves the conversion efficiency up to 8.3 % with the improved back-contact.

**S.EL01.06.28**

**Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces** Saima A. Sumaiya, Mohammad R. Vazirisereshk, Ashlie Martini and Mehmet Z. Baykara; University of California, United States

Electrical contact resistance (ECR) directly influences the performance of micro-scale devices, where contact between components occurs through nanometer-scale patches. Consequently, developing the ability to accurately measure ECR as a function of true contact size at the nanometer scale is of crucial importance. To achieve this goal, we present an approach based on conductive atomic force microscopy, which is applied on a material system comprising atomically flat interfaces formed between gold nano islands and a graphite substrate [1]. Proof-of-principle experiments are complemented by atomistic simulations, which are used to predict the maximum island sizes below which the ECR at the island-graphite junction can be reliably extracted from the measurements. This approach has the potential to contribute to fundamental studies of electron conduction, e.g. through an investigation of the transition between the diffusive and ballistic transport regimes.


**S.EL01.06.53**

**Design and Demonstration of Novel Spectrally Selective Thermal-Radiation Material** Takashi Ando$^1$, Maki Ito$^1$, Naoki Maruyama$^2$, Takanobu Kobayashi$^2$ and Yoshitaka Takezawa$^2$; $^1$Hitachi Ltd, Japan; $^2$Hitachi Chemical Co., Ltd., Japan

Electronic devices, such as electronic control unit, power module, mobile equipment, etc., are required downsizing and higher power density. To achieve the downsizing and higher power density, electronic parts are closely mounted together in a small external package, which causes an increase of heat density. Thermal-radiation is one of the heat dissipation methods. However, conventional thermal-radiation is not useful in the electronic devices, since most of the radiated heat is absorbed by an external package such as resin. The purpose of this study is to newly develop a thermal-radiation material, which generated heat is converted into infrared light with spectrum transmitting through the resin. The material is so-called spectrally selective thermal-radiation material (SSTRM). The studied SSTRM is composed of metallic spheres arrayed on the surface of a heating element, and resin film covering the metallic sphere array. The film is formed by applying a coating solution including metallic spheres. The optimum diameter and arrangement of the metallic sphere are founded numerically and experimentally.
The thermal-radiation spectrum was calculated by using an optical simulation tool based on Rigorous Coupled Wave Analysis. The calculation results clearly showed the localized plasmon resonance excited in the metallic spheres array. The localized plasmon resonance enhanced the emission at the resonance wavelength. The resonance wavelength was controlled by changing the diameter and arrangement of the metallic spheres. It was revealed that infrared light with spectrum transmitting through the resin film is emitted, when the spheres with a diameter of 1.5 µm are densely arrayed. The effectiveness of the SSTRM was experimentally demonstrated by evaluating thermal-radiation characteristics under the stationary atmosphere with a temperature of 298 K. Input power to a heating element was fixed at a constant value, so that the surface temperature of the heating element was 381.1 K. Three types of coating materials were prepared as follows; A. only resin film, B. metallic spheres dispersed in resin film, and C. optimized metallic sphere array covered with resin film (SSTRM). The surface temperatures of the heating elements coated with the films A, B, and C were evaluated to be 358.3K, 355.8K, and 348.1K, respectively. The film C achieved drastical temperature reduction of 33K compared with the heating element without the coating materials. The temperature of the film C was lower than that of B, due to the effect of the metallic sphere array formation. Consequently, the optimized metallic spheres array acted as the spectrally selective emitter that radiates infrared light transmitting through the resin. The SSTRM will be powerful material for heat dissipation from electronic devices packed in resin case or mold.

**S.EL01.06.29**  
**Directed Patterning of Quantum Dots Using Chemically Modified Surface for Light Emitting Diodes** Su Hong Min, Ho-Jong Kang and Dong Hyun Lee; Dankook University, Korea (the Republic of)

Colloidal quantum dots (QDs) have been widely used for light-emitting diodes (LEDs) because of their outstanding characteristics including high color purity, narrow emission peak, high luminescence efficiency, low operating voltage and adjustable emission wavelength that are tunable as a function of their size and composition. For the fabrication of QD-based LEDs, they have been applied to several processes such as spin-casting, inkjet printing and micro contact printing. However, these processes suffer from practical limitations such as high-resolution patterning, high cost, multiple-layer structures, and long processing time. In order to overcome the issues currently suggested, micro-contact printing method using the relief patterns on a master has been introduced and utilized extensively for QD-LEDs. In this way, the regular patterns of QDs layer is transferred on the hole transport layer (HTL) by simply physical contact between the master and the HTL surface. In spite of its efficiency, however, the cyclic process of the micro-contact printing inevitably gives rise to sever damages to the master patterns. Here, we demonstrate a unique method for directed patterning of colloidal quantum dots for the light emitting diodes from chemically modified surface. The chemically modified line-type patterns are initially fabricated on the substrate by using a conventional photolithography technique and selective chemical reaction of surface-modifying molecules such as the octadecytrichlorosilane (OTS) sequentially. The width of line-type patterns produced is varying from 40 µm to a few µm. The quantum dots of CdSe(core)-ZnS(shell) that are covered with oleic acid as capping molecules are then spin-coated on the chemically patterned surface. To transfer the QDs layer to a hole transport layer, the polymethylmethacrylate (PMMA) is first spin-coated on the QDs layer followed by placing commercial adhesive tapes on the PMMA layer. Then the QDs/PMMA layer is detached from the original substrate by peeling the adhesive tapes and transferred to the target substrate. The target substrate consists of ITO(Anode), PEDOT: PSS(HIL), and TFB(HTL), respectively. It is noted that the only designed QD patterns are selectively transferred from the chemically modified surface due to surface energy difference during the transfer process. As the PMMA/tape layers are removed by rinsing with acetone, which is a selective solvent, the only QD patterns remain on the HTL layer of the target substrate. For the fabrication of QD-LEDs, ZnO(ETL) and Ag(Cathode) layers are deposited on the QDs layer sequentially. Consequently, the QD-LEDs fabricated in this study are characterized by measuring their electrical properties like luminance, current density and external quantum efficiency.

**S.EL01.06.56**  
**Pulsed Laser Deposited Polycrystalline Thin Films of MoO3 for Sensing of High-Energy Moieties** Dhanashree Sable, Swapnali Rabade and Sangeeta N. Kale; Defence Institute of Advanced Technology, India

Among various nanostructured metal oxides, molybdenum oxide (MoO3), a wide band-gap n-type semiconductor, has attracted much interest as a promising gas sensor because of its excellent sensitivity, good reproducibility, low cost, high compatibility with microelectronic processing, low electron recombination rate, and high stability. The MoO3 thin films have promising electrical properties for gas sensing applications. To synthesize two-dimensional materials under ultra-high vacuum is a key advantage for enhancing the properties of nanostructured materials. In this presentation, we demonstrate the synthesis, characterization, and gas sensing properties of MoO3 films, which were grown using Krypton-Fluoride (248 nm) excimer laser. Deposition was done under 200 mTorr Oxygen pressure at the substrate temperature of 600°C. The targets used for deposition were synthesised using hydrothermal
method. The deposition was done with the optimized parameters, to ensure good polycrystalline films on the Si (001) substrate. The optical, morphological and compositional properties of MoO3 films were studied by using UV-Visible spectroscopy, Scanning Electron Microscopy and Raman Spectroscopy. The formation of MoO3 was also confirmed using X-Ray Diffraction technique. The MoO3 films showed excellent response to NOx and NO2 gas moieties, at even low gas concentrations from 100 ppm onwards. The sensor not only exhibits high sensitivity but also good selectivity towards NO2 gas.

S.E.L01.06.30
The Chemistry of Interface Defects in SiC/SiO2 Probed by Hard X-Ray Photoelectron Spectroscopy Anna Regoutz; University College London, United Kingdom

Interfaces govern the behaviour of all electronic devices. Herbert Kroemer coined the famous phrase “the interface is the device” in his 2000 Nobel Prize lecture, and we are still applying tremendous effort to understand interfaces in new material generations, with wide-bandgap materials being no exception. If anything, wide bandgap materials are more vulnerable to defect states purely due to their larger bandgap. Understanding gained for the bulk behaviour of semiconductors can often not be extended to the behaviour of materials in structured film stacks were interfaces play a vital role. SiC/SiO2 is a prototypical wide-bandgap semiconductor/dielectric interface, which represents the challenges faced by many such material systems. A multitude of different defects leads to unacceptably large defect densities exceeding $10^{13}$ cm$^{-2}$ eV$^{-1}$ in the vicinity of the conduction band of 4H-SiC. The management of interfacial defects remains a topic of lively discussion and current interest.

Here, we present a systematic study of the 4H-SiC/SiO2 interface in industrially manufactured samples with a particular focus on the effects of nitridation in N$_2$, NO, NH$_3$ and NO+NH$_3$ atmospheres. High temperature nitridation has been shown to compensate interface defects leading to an increase in device performance, however, information on the local chemistry at the interface after such processes is scarce, which limits the understanding of the interface and consequently the targeted improvement of device characteristics. Clear differences are found in both spectroscopy and electrical behaviour after high temperature treatments. The present work uses energy-dependent hard X-ray photoelectron spectroscopy (HAXPES) to systematically study the elemental distributions and chemical environments across the 4H-SiC/SiO2 interface. We combine both laboratory- and synchrotron-based HAXPES results to obtain a complete picture of this important technological interface and to benchmark the capabilities of this spectroscopic technique for the exploration of buried interfaces in device heterostructures in general.

S.E.L01.06.51
Surface Chemical Composition Evolution During In-situ Annealing of Low-Strain Ge$_{1-x}$Sn$_x$ Layers on Core/Shell Nanowires Michael Braun1, Ishaq Bishnoi1, Andrew C. Meng2, John Z. Lentz1 and Paul McIntyre1; 1Stanford University, United States; 2University of Pennsylvania, United States

Metastable germanium-tin has attracted significant interest as a potential group IV direct bandgap material for CMOS compatible electronics and photonics. With sufficient tin incorporation, there is experimental evidence of a direct bandgap germanium-tin material. Although this is a promising step for germanium-tin devices, there are further considerations for incorporating germanium-tin into a full device. Namely, the evolution of the germanium-tin surface during subsequent annealing and growth of additional device components. Previous annealing results on strained germanium-tin thin films have shown surface tin segregation and island formation. In this study, we report results from in-situ X-ray photoelectron spectroscopy during annealing of vertical core/shell Ge/Ge$_{1-x}$Sn$_x$ nanowires grown via chemical vapor deposition. We have previously shown the capability of the core/shell structure to produce a largely strain-free Ge$_{1-x}$Sn$_x$ shell material on a highly tensile-strained Ge core. This structure is utilized here to investigate the annealing characteristics of the germanium-tin surface and native oxide for tin contents in the range of 2 at% - 12 at% in air-exposed nanowires. Our results show the presence of a thin oxide rich oxide with a composition dependent decomposition temperature. After in-situ decomposition of the native oxide, the tin content of the germanium-tin surface is observed to remain constant throughout annealing at temperatures exceeding 500 °C and for anneal durations greater than one hour. Additionally, we have measured the photoluminescence at room temperature, characterized strain by X-ray diffraction, and imaged the nanowire sidewall morphology before and after annealing to examine its effects on material performance, bulk tin distribution, and local surface structure.

Chemistry Behind Dodecanethiol Treatment of Colloidal CsPbBr3 Nanocrystals with Photoluminescence Quantum Yields Reaching ~100% Md Aslam Uddin, Justin K. Mobley, Abdullah A. Masud, Tuo Liu, Rosemary L. Calabro, Doo Y. Kim, Christopher I. Richards and Kenneth R. Graham; University of Kentucky, United States

Metal halide perovskite nanocrystals (NCs) are attractive materials for optoelectronics because of their optical and electronic properties, such as tunable direct band gaps, high absorption coefficients, low exciton binding energies, relatively high electron and hole mobilities, narrow emission line-widths, and high photoluminescence quantum yields ($\Phi_{PL}$). However, further improvements in stability and reproducibility in $\Phi_{PL}$ of NCs are essential for enabling future optoelectronic applications. Inadequate surface passivation due to labile parent ligands, such as oleate and oleylammonium ions is a major cause of instability and less than unity $\Phi_{PL}$. Herein, we probe the influence of multiple molecular and ionic ligand binding groups including thiols, thioethers, phosphine, phosphine oxide, sulfobetaine, thiocyanate, and sulfate salts on the colloidal stability and $\Phi_{PL}$ of CsPbBr$_3$ NCs. Among all the binding ligands, post-synthetic treatment with dodecanethiol reproducibly yields highly stable NCs with near unity $\Phi_{PL}$ for a range of synthetic conditions and initial $\Phi_{PL}$ of the as-synthesized NCs. A few of the other ligands can also increase the $\Phi_{PL}$, but in ambient atmosphere they are unable to maintain stability more than 5 days. A mechanistic investigation shows that thiol addition to the as-synthesized NC dispersion leads to the thiol-ene reaction with octadecene, oleic acid, & oleylamine and formation of thiolate ions and thioethers. Both thiolates and thioethers are suspected to bind to undercoordinated Pb atoms and consequently eliminate metallic Pb particles commonly observed with transmission electron microscopy on the NC surfaces. The process of enhancing PL intensity and stability can be rapidly accelerated through exposure to blue or UV light.

16.5% ZMO/CdTe Solar Cells with Copper Thiocyanate as Back Contact Dengbing Li, Sandip S. Bista, Fadhil K. Alfadhiili, Niraj Shrestha, Rasha A. Awni, Zhaoning Song and Yanfa Yan; University of Toledo, United States

The replacement of traditional CdS buffer layer with magnesium doped zinc oxide (ZMO) has been demonstrated helpful to boost higher CdTe solar cell performance exceeding 18% due to the reduced interface recombination and parasitic light absorption by buffer layer. However, due to the atmosphere sensitivity of ZMO film, the post-treatments of ZMO/CdTe stacks, including CdCl$_2$ treatment, back contact deposition et. al, which are critical for high performance CdTe solar cells, became crucial challenge. In order to maximize the expected benefit of ZMO cooperation, plenty of investigation need to be accomplished in the future. Here, copper thiocyanate (CuSCN) is demonstrated to be a powerful back-contact material with multi-advantages without degrading ZMO layer in CdTe solar cells, even with ammonium hydroxide as the solvent. The thickness of CuSCN film as well as the subsequent annealing temperature are systematically investigated and the highest efficiency 16.5% has been achieved with open-circuited voltage 850 mV, short-circuited current 26.2 mA/cm$^2$ and fill factor 74.0%.


Halogenated Si(100) Surface Chemistries for Atomically-Precise Fabrication Kevin J. Dwyer$^{1,2}$, Karen Gaskell$^1$ and Robert Butera$^2$; $^1$University of Maryland, United States; $^2$Laboratory for Physical Sciences, United States

The use of halogen chemistries on silicon surfaces offers a promising path towards atomic-scale manufacturing of acceptor-based devices. Atomically-precise fabrication of electronic devices in silicon has been widely demonstrated using a scanning tunneling microscope (STM) and hydrogen-based surface chemistries to precisely place phosphorous donor atoms on the surface. A lithographically patterned hydrogen resist is used to selectively incorporate PH$_3$ to produce metallic wires, quantum dots defined by electrostatic gates, and single donor atom qubits for quantum information (QI) research. However, interest in acceptor dopants and hole-based devices necessitates the development of alternate precursors and/or resist chemistries for device fabrication. To incorporate acceptors into silicon with atomic placement, halogen chemistry is potentially more favorable than hydrogen. To that end, we explore halogen-based resists including chlorine, bromine, and
Photothermoelectric Detection of Crystal Defects and Grain Boundaries in Gold

Lucia Gan, Charlotte Evans, Rui Yang, Mahdiyeh Abbasi, Xifan Wang, Rachel Traylor, William Nix, Douglas Natelson and Jonathan Fan
1Stanford University, United States; 2Rice University, United States

As devices continue to trend towards the micro- and nanoscale, the influence of individual crystal defects on their optical, electronic, and thermal properties becomes significant. As an example, the thermoelectric properties of these nanodevices are closely related to the presence of crystal defects, grain boundaries, and strain. While the effects of interfaces and grain boundaries on thermoelectric performance have been widely studied in semiconductor materials, there remains an incomplete understanding of the role that crystal defects play in metals. A major challenge in pinpointing the origins of thermoelectric variation in metallic nanodevices is the difficulty in preparing high quality crystalline thin-film metal microstructures on thermally and electrically insulating amorphous substrates.

Controlling the micro- and nanostructure of metals offers the opportunity to investigate and engineer the properties of metal nanotechnologies. Here, we report a high-throughput method for preparing patterned crystalline gold microstructures grown directly on amorphous insulating oxide via rapid melt growth. In this growth process, thin-film gold-platinum metal-seed microstructures are encapsulated in an insulating crucible and annealed at temperatures above gold’s melting point. During cooling, liquid epitaxial growth directs single crystal solidification [1]. We can extend this platform to controllably prepare single grain boundaries [2], enabling the systematic study of the role of defects in governing local thermoelectric behavior. A scanning photothermoelectric (PTE) setup to allows us to probe the microscopic variations in photovoltage across the gold single crystal and bicrystal wires. Surprisingly, we observe a photovoltage distribution where local changes in Seebeck coefficient are highly influenced by long-range strain fields and concentrated dislocations and uncorrelated with plane grain boundary defects. Our results showcase the link between the presence of elastic strain and dislocations to the PTE effect using a model material system.


Improved Efficiency of Photo-Induced Electron Detection under UV Light Source by ZnO Nanowire Array on Aligned PVDF-TrFE Nanofiber Film

Dong Hee Kang, Na Kyong Kim and Hyun Wook Kang; Chonnam National University, Korea (the Republic of)

Zinc oxide (ZnO) is a versatile semiconductor material used for a wide range of applications in electronics, photonics, and optics. Bulk ZnO is a wide band gap (3.37 eV) semiconductor that generates electrons under an electromagnetic wavelength shorter than the ultraviolet (UV) range. ZnO nanowires (ZnO NWs) exhibit enhanced electrical properties over ZnO thin film via a nano size effect based on the electrical resistivity of chemical under UV irradiation. The NW structure induces movement of electrons along an axial direction due to the electron confinement effect by structural features. In order to utilize the advantages of nanostructured film in commercial sensors, mass production should be achieved with simple manufacturing processes. Electrospinning with a continuous process is possible in mass production with a roll-to-roll system. The use of a high porous electrospun nanofiber (ES NF) film is advantageous in terms of fabricating dense ZnO NWs. Additionally, a highly aligned state of ES NF films is possible to fabricate via controlling the electrospinning condition without entailing additional processes. The aligned nanofiber film aids in electron movement along the direction of the fiber, thereby revealing possibilities for its application to high responsibility in UV detector. Under the UV irradiation condition, ZnO NWs on ES NF film generate electrons under light energy absorption conditions that exceed the energy required to excite electrons based on Planck’s equation. Under continuous UV irradiation on the ZnO NWs surface, electrons in the valence band are excited to the conduction band when the electrons gain sufficient energy. The excited electrons on the ZnO NWs surface along the ES NF support have a strong directionality that tends to flow into the low current density region. The electrical conductivity on ZnO NWs increases by using aligned ES NF when compared to that of random ES NF by large gradient of current density. Linearity error of the ZnO NWs on aligned and random ES NF films are less than ±0.58% and
Tin sulfide (SnS) is a desirable absorber layer for thin film solar cells. Its optical bandgap of 1.1 eV, absorption coefficient of $10^7$ cm$^{-1}$ in the visible region, inherent p-type electrical conductivity, non-toxicity, earth abundance of the constituent elements, and stability in humid and oxygen ambient are all attractive toward developing alternative solar cell technology. Nevertheless, solar cells of SnS have reached a photovoltaic conversion efficiency of only 4.8%. The presence of secondary phases (SnS$_2$, Sn$_2$S$_3$) and small grains is among the efficiency limiting factors. Here, we present methods to enhance the quality of chemically deposited SnS films through using thin layers of Sn and SnCl$_2$ as flux materials produced by thermal evaporation and/or sulfur vapor to play a key role in grain growth during heating at 450 °C, while conserving its p-type electrical conductivity.

We prepared SnS thin films of 300 nm in thickness in an autoclave at 2.5 atmospheres and 55 °C with duration of deposition of 6 h. The deposition solution contained tin chloride and sodium thiosulfate. The as-deposited SnS thin films were of orthorhombic crystal structure, with an optical bandgap of 1.33 eV (indirect) and electrical conductivity of $1 \times 10^{-4}$ Ω$^{-1}$ cm$^{-1}$ in the dark and $1 \times 10^{-3}$ Ω$^{-1}$ cm$^{-1}$ under illumination. The films presented compact surface and dense cross-sectional morphology. We heated this film for 30 min, in a tubular oven in nitrogen atmosphere at 450 °C. Different flux materials were added during the heating to promote grain growth: sulfur, evaporated thin films of Sn metal, or SnCl$_2$. The film heated with sulfur powder was p-type, with electrical conductivity, $10^{-4}$ Ω$^{-1}$ cm$^{-1}$. SnS films heated under the same conditions using Sn as well as SnCl$_2$ as flux materials retained the single phase of SnS with the formation of well-defined columnar grains of size equivalent to film thickness. They have a bandgap of 1.1 eV (indirect) and p-type electrical conductivity, $10^{-3}$ Ω$^{-1}$ cm$^{-1}$ in the dark, which increases to 1.5 times, under illumination. Thus, heating SnS absorber films deposited at a low temperature using chemical methods, with Sn or SnCl$_2$ as flux materials is a promising methodology to achieve grain growth. We shall illustrate the effect of this in solar cells using SnS as absorbers.
RF sputtering at room temperature. ZTO/r-IZO heterostructure is suitable for the formation of 2DEG due to the large difference in work function, so it could produce high field-effect mobility even when fabricated at room temperature. Also, the large on-current could be achieved by precisely controlling the formation of 2DEG through Na$_2$S$_2$O$_4$ reducing agent treatment on the IZO front channel. To confirm the formation of 2DEG at the interface between the ZTO film and the r-IZO film, we performed a UV-vis spectrophotometer and ultraviolet photoelectron spectroscopy (UPS) measurements. The 2DEG was successfully formed by showing the difference of 170 meV work function at the heterointerface. However, conventional 2DEG-based oxide TFTs have high off-current because 2DEG free electrons remained at the heterointerface regions even when the TFT is in the off-state. To solve this problem, the ZTO back channel was applied to different oxygen partial pressures to the lower ZTO layer (20%) and the upper ZTO layer (30%) when deposited via sputtering. As a result, the high off-current could be adjusted to near the $10^{-12}$ A range and ZTO/r-IZO TFTs exhibit field-effect mobility of 29.55 cm$^2$/Vs, a subthreshold swing of 0.48 V/decade, and an on/off current ratio of $5.02 \times 10^8$.

The results show that room temperature fabricated ZTO/r-IZO heterostructure TFTs can be used as a general route for high field-effect mobility TFTs and controllable oxide semiconductor devices for offering compatibility of the flexible and high-end display technology.

S.EL01.06.66

Plasma-Based Modification of Superconducting/dielectric Interfaces Evgeniya H. Lock$^1$, Sandra Rodriguez Villanueva$^2$, Peng Xu$^3$, Yaniv Rosen$^1$, Michael Katz$^2$ and Kevin Osborn$^3$; 1US Naval Research Laboratory, United States; 2University of Puerto Rico at Rio Piedras, United States; 3University of Maryland, United States; Lawrence Livermore National Laboratory, United States; National Research Council, United States; Laboratory of Physical Sciences, United States

Superconducting resonators and qubits are essential for the development of quantum-computing architectures. These systems depend on high quality superconducting materials and interfaces, in which the two-level systems loss is minimal. Our previous work focused on understanding of the effects of plasma modification of vacuum/silicon and vacuum/superconductor interfaces on the performance of TiN/Si superconducting microwave resonators. In this paper, we discuss plasma-based modification of TiN/Si interface. We provide a systematic study of every step in the preparation of the TiN/Si heterostructures, namely the chemical treatment with hydrofluoric acid of SiO$_2$/Si surface, the plasma treatment of H-terminated Si and the TiN film deposition processes. We find that both the gas environment and the plasma processing conditions affect the modification of Si, which in turn affects the composition of the TiN/Si interface. The impact of this work lay in providing new approaches to TiN/Si interface preparation which may enable reduction of metal/dielectric interface losses thus improving the superconducting microwave resonators performance. This work was partially supported by the office of Naval Research through Naval Research Laboratory Base Program.

S.EL01.06.62

The Effects of Etching Parameters on Surface Morphologies by Anisotropic Etching with Resist-Mask Pin Y. Chen, Yu-De Li and Kun-Dar Li; National University of Tainan, Taiwan

For a long time, the etching technique played an important role in the electronics industry, and had a critical influence on the development of modern manufacturing technologies. Regarding to the operation of electronics devices, surfaces and interfaces significantly affect the functionality and performance of the devices. To investigate the formation mechanisms for characteristic surface morphologies during chemical etching, in this study an anisotropic chemical etching model was established and the formation and evolution of surface structures with resist-masks were simulated numerically. In this theoretical model, two major crystallographic orientations in a cubic system, such as $<100>$ and $<111>$ directions, were taken into consideration and included in the reactions of surface diffusion and anisotropic etching. By adjusting the numerical parameters corresponded to the different experimental conditions, various surface profiles could be created and the influence of the experimental parameters on the surface morphologies would be revealed. From the calculations of anisotropic etching along $<100>$ preferred-directions, a V-shape profile with faceted surface morphologies appeared. A larger loss of linewidth or a higher etch bias was displayed with the increase of the etching rate. While an anisotropic etching along $<111>$ preferred-direction was examined, etch pits were firstly produced in the early stage of etching process. A different surface evolution during a chemical etching was distinctly demonstrated due to the crystallographic structure. In addition, since the resist-mask was included in the numerical model, the phenomenon of undercutting in an anisotropic chemical etching could be also discussed in this study. These numerical simulations could provide a fundamental information to understand the formation mechanism of etched surface, and broaden the applications of chemical etching in the advanced manufacturing technologies.

S.EL01.06.63

High Efficiency X-Band AlGaN/GaN HEMT with Improved TiN/Ti/Al/Ni/Au Ke Wei, Yichuan Zhang, Shen Zhang, Guoguo Liu, Xiaojuan Chen, Yingkui Zheng, Sen Huang, Xinghua Wang and Xinyu Liu; Chinese Academy of
GaAs based high electron mobility transistors (HEMTs) are considered of great potential to be the building blocks in the next-generation microwave power devices due to their excellent power handling capabilities. Ohmic contact and passivation technologies are the main factors of device power and efficiency. Improving device efficiency is the premise of improving application system efficiency. Nowadays, more and more efforts are made to improve the efficiency of GaN HEMTs. In this paper, we report the AlGaN/GaN HEMT with improved ohmic contact and double layer passivation. The device shows an excellent power characteristics.

The epitaxial layers consists of a 1.5nm GaN cap layer, 22nm Al0.25GaN, 2nm AlN and GaN buffer layer. The process for GaN HEMT devices is as followed the steps: a) metal, b) ohmic contact etching ion; c) isolation; d) gate; e) double passivation by Au/AlN/SiN; f) via and metal. The source-drain and gate length are 2.40μm and 0.25μm. The TEM result shows the details of the interface of ohmic contact. Conventional structures of MOCVD HEMT is also fabricated simultaneously.

Measurements are performed in continuous wave (CW) mode, load-pull power measurements of this 4×50μm device at 10 GHz is carried out. The device is biased at a voltage of 35V, the output power reached 31.50dBm (7.0W/mm) with 70% power-added efficiency (PAE) and 14dB gain. Such a good RF power performance comes from the improved ohmic contact and new double passivation layer.

The interface of ohmic contact is analyzed by means of TEM. It is found that tin thin layer combined with recessed process is more conducive to the formation of low contact resistance.

**S.EL01.06.68**

**Monitoring the Adsorption of Thiol and Isocyanide Molecules on Silver Surface by In Situ Surface-Enhanced Raman Scattering**

Shi Shi, Jaewan Ahn and Dong Qin; Georgia Institute of Technology, United States

In this talk, we report the use of surface-enhanced Raman scattering (SERS) to investigate the adsorption of thiol and isocyanide molecules on colloidal Ag nanocubes in situ. In a typical process, we mixed Ag nanocubes with ligand molecule solutions at different concentrations and then collected SERS spectra at different time points. We demonstrate that 4-nitrothiophenol (4-NTP) binds to the Ag surface rapidly because of the strong Ag—S chemical bonding. By decreasing the concentration of 4-NTP, we observe red shifts of the νNO2 band, which suggests the change to the orientation of ligands on the surface. Different from thiols, the 1,4-phenylene diisocyanide (1,4-PDI) binds to the Ag surface through σ-donation with weaker binding strength. By increasing the concentration of 1,4-PDI, our results indicate that the molecules tend to adopt an orientation that tilts away from the surface. More interestingly, we investigate the competitive binding behavior of these two ligands by introducing Ag nanocubes into a solution containing both 4-NTP and 1,4-PDI. Our results show that thiol is more preferential to bind onto the surface when the concentrations of the two ligands are comparable in the solution.

**S.EL01.06.89**

**Bandgap Engineered III-V InAs –GaSb TYPE-II Superlattice (T2SL) Infrared Detectors for Multispectral Range**

Chhaya Ravi Kant; Indira Gandhi Delhi Technical University, India

Infrared detector technology has shown remarkable progress towards the selection of detector materials and device architectures. Infrared detectors are an integral part of various surveillance devices, remote sensing system, night vision, all weather surveillance, missile tracking, thermography, enhanced vision systems for aeroplanes, automobiles and gas sensing. Current InSb and HgCdTe based IR technologies have shown high performance because of excellent material properties, covering near infrared (NIR 0.75-1.1mm), short-wavelength infrared (SWIR 1-3mm), mid-wavelength IR (MWIR 3-5mm), long-wavelength IR (LWIR 8-14mm) and very long-wavelength IR (VLWIR 14-30 mm) range. However, these need to be cooled to cryogenic temperatures making them bulky and power hungry. Thus future infrared photodetector systems must possess reduced cooling requirements, consume less power, exhibit longer lifetimes, and have improved manufacturability. These targets have been partly addressed by the development of nBn detector architecture raising the operation temperature, reliability, higher sensitivity and low SWaP (Small Weight and Power).

Type2Superlattice (T2SL) detectors combine key advantages of InSb and Mercury-CadmiumTelluride (MCT)-based technologies namely scalability of focal plane arrays (FPAs), high sensitivity, lower tunneling currents and suppressed Auger recombination rates nad also facilitates a higher operating temperature. A super lattice is made up of a repeated series of very thin epilayers of different materials that leads to creation of sub-bands. The corresponding bandgap energies of these subbands determine the cut-off wavelength of the sensor. The III-V InAs –GaSb materials, based on nBn unipolar photodetector architecture, with an n-type absorption layer, a barrier layer, and an n-type contact layer have been fabricated and engineered for bandgap tunability. The barrier layer is constrained to have both a negligible valence band energy offset with the absorption layer, that suppresses the Shockley-Read-Hall (SRH) generation current thereby decreasing the primary
noise. In addition, detector is passivated to minimise the surface leakage current. The nBn photodetector, through the near elimination of SRH and surface leakage currents, requires less cooling to operate optimally than the p-n junction photodiodes. Bandgap engineering and optimization of the material composition to achieve maximum quantum efficiency, low dark current, maximum absorption strength and higher operating temperature.

Appropriate tools suitable for the design of T2SL material systems are not yet fully developed due to the intricacies of T2SL material system and paucity of experimental data for input and for the validation of mathematical formulations. A holistic approach has been followed involving design of graded energy-gap T2SL structure, growth of material system, characterization of material, fabrication and characterization. Our design is aimed to grow T2SL epilayers with optimized thickness, material composition, energy gap grading and varied doping concentrations by Molecular Beam Epitaxy and detector fabrication with a combination of wet and dry etching. A favorable impact ionization coefficient leads to higher bandwidth range with low excess noise to achieve maximum quantum efficiency, low dark current, high avalanche gain, low excess noise, maximum absorption strength and higher operating temperature. Design optimization has resulted in high quantum efficiency of 75% validated with FTIR measurements and low NETD of 18mK at an elevated operation temperature of 140K. Current-Voltage measurements, quantum efficiency, noise equivalent temperature difference (NETD) and issues related with growth of graded energy-gap T2SL material system will form part of the full paper.

S.EL01.06.70
Vertically Aligned Metal Nanowire Composites for Flexible and Conductive Thermal Interface Materials
Max Kuciej1,2, Jesse Tice2, Dwight Streit1 and Michael T. Barako2; 1University of California, Los Angeles, United States; 2Northrop Grumman Corporation, United States

Conventional thermal management solutions in microelectronics packaging suffer from an inability to effectively couple thermal conduction and mechanical compliance into a single material, routinely necessitating a sacrifice in thermal, and therefore device, performance in favor of mechanical reliability. For the past few decades, compliant thermal interface materials (TIMs) have been limited to polymers loaded with dispersions of unaligned or randomly distributed conductive elements which can only achieve thermal conductivities up to ~5 W m⁻¹K⁻¹. Here, we present the processing and characterization of a compliant, vertically-aligned metal nanowire composite ideal for achieving thin, flexible interfaces with low thermal resistance. The aligned nanowire composite is fabricated by electroplating copper into a 25-45% porous, sacrificial ceramic template, liberating the nanowires by chemically dissolving the template, and infusing the resulting nanowire array with a thermally stable polymer by capillary-driven wicking. An integrated bonding layer is added by subfilling the template with copper and sequentially electroplating metallic solder to form localized solder tips on the nanowires. The entire fabrication process can be completed at wafer-scale with a lateral area up to 12.5 inches². The thermal performance of the composite TIM was evaluated with a modified thermal resistance measurement designed to mimic typical operating conditions. The double-sided construction of the composite and integrated bonding layers facilitate integration between any two arbitrarily-chosen surfaces by enabling the absorption of interfacial strain, mismatch, and roughness while achieving thermal conductivities up to 200 W m⁻¹K⁻¹, significantly advancing the state-of-the-art in TIMs.

S.EL01.06.94
Co-Electrodeposited MnO₂ and Co₃O₄ on Well-Aligned Electrospun Carbon Nanofibers for Sensitive Glucose Detection
Ziyu Yin, Xinping Zeng and Jianjun Wei; The University of North Carolina of Greensboro, United States

Binary manganese oxide/cobalt oxide (MnO₂/Co₃O₄) composites on the well-aligned electrospun carbon nanofibers (MnO₂/Co₃O₄@ECNFs) were synthesized via a simple and economical one-step template-free electrodeposition technique with a constant low-current (60μA) for 3h, and their electrocatalytic activity towards non-enzymatic glucose sensors was evaluated in detail. The MnO₂/Co₃O₄ nanostructures were uniformly deposited on the well-aligned ECNFs with high porosity, effective interconnectivity and large amounts of extended number of conducting channels. The electrocatalytic performances of as-prepared MnO₂/Co₃O₄@ECNFs towards the oxidation of glucose were carried out by cyclic voltammetry (CV) and chronoamperometry (CA), and the experimental results show that the MnO₂/Co₃O₄@ECNFs exhibited a superior sensing performance towards glucose including a rapid glucose response within 5 seconds, a wide range (5 μM to 10.89 mM), excellent sensitivity of 973.91 μA mM⁻¹ cm⁻² and a low detection limit of 0.02 μM (S/N=3) with satisfactory selectivity, great reproducibility and stability. These excellent electrochemical performances were attributed to the synergistic effect of binary metal oxides and the unique porous architecture of the electrode. These features indicate that as-synthesized MnO₂/Co₃O₄ binary nanostructure decorated well-aligned ECNFs hold great potential in the development of a commercialized glucose sensor.

S.EL01.06.79
Optical Filter Free Color Imaging with Perovskite Alloys
Md Wayesh Quarony1,2, Mohammad I. Hossain1, Haris Ahmed

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Color image sensing by a smartphone or digital camera is usually performed by an array of sensor elements covered by color filters. The optical color filters cause color errors like the color aliasing or Color Moiré effect. Furthermore, the quantum efficiency of typical conventional optical color sensor consisted of side-by-side arranged color filters is limited to 1/N, where N is the number of color channels per pixels. Hence, the efficiency of the color detection process is limited to max. 33% by the side-by-side arrangement of sensor channels. In this study, color sensors consist of vertically stacked diodes using perovskite alloys is described with maximum quantum efficiency approaching 100%. The described sensor structure is color aliasing or Color Moiré error free, while conventional sensors using optical filters are limited by this error. The optical constants of the required perovskite alloys were determined by applying the energy shift model to experimentally determined optical constants of pure perovskites. The spectral sensitivities of the color sensors were determined by electromagnetically modelling. The spectral sensitivities of the sensors were colorimetrically characterized and compared to sensors in literature including conventional sensors using optical filters. Up to our knowledge for the first time it could be shown that a vertically stacked three color sensor exhibits a color error equal to, or smaller than errors of conventional sensors using optical filters as well as silicon based Foveon stacked color sensor. Details on the used materials, the device design, and the colorimetric analysis are provided.

S.E.L01.06.90

Effect of Yarn Structure and Processing Conditions of Screen Printing on Electrical/Antenna Performance for E-Textile Applications Jung Hun Lee and Ju-Hee So; Korea Institute of Industrial Technology, Korea (the Republic of)

Wearable wireless communication systems based on Electronic textile (E-textile) have become significant interests owing to their potential applications in sportwear, military, firefighting, health care, and tracking systems. Among the fabrication methods of conductive textile, screen printing which prints metal nanoparticle based conductive inks on a fabric substrate has been known to be a promising approach in the field of wearable electronic applications. However, the morphological characteristics of textile materials such as high surface roughness, high porosity, and capillary force in the woven fabric structures and the lack of manufacturing technology to overcome the issues are obstacles to commercialization of electronic textiles (E-textile). Herein, we compare the flat and round yarn based polyethylene terephthalate (PET) fabrics as the substrates for screen printing. We also investigate the effect of the parameters of the screen printing process such as the screen mesh size (70, 120 pixel/inch) and the printing counts. The uniformity of the screen-printed layers and their electrical properties are directly related with the shape of the yarn, the roughness of fabric substrates, and the printing processing conditions. A minimum average sheet resistance of 16 ± 3 mΩ/sq. was achieved on the flat yarn PET fabrics, and there was little change in electrical performance after the bending test (r=3mm) was carried out 1,000 times. To demonstrate, we show textile antennas operating at 2.4GHz which is most widely used for public wireless LAN service, Bluetooth, radio frequency identification (RFID). We analyzed the effects of the uniformity and the conductivity of the printed layers on the antenna performance. The field tests of the textile antennas in open areas showed better performance than commercial antennas. This study aims to advance E-textile devices with excellent electrical properties and mechanical durability for wearable wireless communication applications.

S.E.L01.06.75

Exciton-Trapping by Stacking Fault Defects in GaAs Peter V. Sushko1, Steven R. Spurgeon1, Bethany Matthews1, Xiayu Linpeng2, Mikhail Durnev2, Mikhail Glazov3, Maria Viitaniemi2, Andreas Wieck4, Arne Ludwig4 and Kai-Mei Fu2; 1Pacific Northwest National Laboratory, United States; 2University of Washington, United States; 3Ioffe Institute, Russian Federation; 4Lehrstuhl für Angewandte Festkörperphysik, Germany

The need to increase coherence times in quantum devices simulates the search for materials systems that can exhibit electronic states not affected by structural and chemical inhomogeneities. Owing to the advances in synthesis of III-V semiconductors, concentrations of point defects and impurities in these materials can be well controlled, while stacking faults (SFs) provide asymmetric quasi-2-dimensional potential wells that behave as internal interfaces capable of trapping excitons [1]. Here we use *ab initio* simulations to examine how the stability and electronic properties of SFs change as a function of the distance between them and how the details of their configuration affect spatial distribution of the electron and hole components of excitons and their effective masses. Our simulations suggest that a potential drop of the order of 10 meV is associated with an isolated SF, which is sufficient for the hole to localize predominantly at the SF and to induce an asymmetric distribution of the excited electron density in the vicinity of the SF. For interacting SFs, we find that the electron distribution is sensitive to both the type of the SFs and the distance between them. This coupling provides a pathway to the
design of materials with spatially resolved excitonic properties and photo-emission energies by controlling the density and relative arrangements of the stacking faults.


S.E.L01.06.76
Observation of Hyperfine Interactions of Silicon Vacancies in 4H-SiC Metal-Oxide-Semiconductor Field-Effect Transistors Utilizing Ultra-Low Field Frequency Swept Electrically Detected Magnetic Resonance James Ashton1, Patrick Lenahan1, Brian R. Manning1 and Aivars J. Lelis2; 1The Pennsylvania State University, United States; 2U.S. Army Research Laboratory, United States

4H-SiC metal-oxide-semiconductor field-effect transistors (MOSFETs) have great potential in high power and high temperature applications. However, near-interface defects degrade the effective channel mobility and thus limit the performance of 4H-SiC MOSFETs. In this work, we utilize electrically detected magnetic resonance (EDMR) to study hyperfine interactions with spin-dependent recombination (SDR) of silicon vacancy defects at the 4H-SiC interface in 4H-SiC MOSFETs. The physical foundation of EDMR is electron paramagnetic resonance (EPR). In EPR and EDMR, a sample is subjected to a large, slowly varying magnetic field and an RF or microwave oscillating field at a frequency $\nu$. In the simplest case, EPR is achieved when $h\nu=ge\beta H$. Here, $h$ is Planck’s constant, $\nu$ is the electromagnetic radiation frequency, $g_e$ is the free electron $g$ factor ($g_e \approx 2.0023$), $\beta$ is the Bohr magneton, and $H$ is a large externally applied magnetic field. At resonance, the electron transitions from its $+1/2$ to $-1/2$ spin state (or vice versa). The analytical power of EPR and EDMR comes from deviations from this simple case caused by the paramagnetic site environment. These perturbations are, for the most part, caused by hyperfine interactions, interactions of the electron with magnetic nuclei, and spin-orbit coupling. EPR detected via SDR allows for measurements of small numbers of defects via spin-dependent changes in device current. The sensitivity of SDR/EDMR is very nearly independent of the field or frequency at which the measurement is made. Prior continuous wave EDMR (cwEDMR) studies have linked interface and near-interface defects to carbon dangling bond defects and silicon vacancy defects. The identification of silicon vacancy defects in 4H-SiC MOSFETs was based on measuring nearest neighbor carbon 13 hyperfine interactions. $^{29}$Si next-nearest neighbor (NNN) hyperfine interactions are too small to resolve in an EDMR measurement due to the width of the center part of the resonance signal. The interactions of NNN $^{29}$Si are isotropic with a value 2.96 G determined from conventional EPR. Broadening in EDMR obscures these $^{29}$Si NNN hyperfine interactions. We have overcome the EDMR broadening problem using the Breit-Rabi effect, a shift in the hyperfine side peaks towards lower fields and frequencies. This effect is sufficiently large so that it may be detected in ultra-low field and frequency measurements. We utilize frequency swept EDMR (fsEDMR). With fsEDMR, tuning the resonance condition is performed by varying a low static field. In fsEDMR, the magnetic field $H$ is held constant as frequency is swept. Our experiments were carried out at fields less than 10 G and frequencies less than 30 MHz. We observe a centerline with a sharp peak on the low field side only at these low fields and frequencies. We attribute the peak to otherwise unresolved hyperfine interactions made observable by shifting due to Breit-Rabi effects. The peak has fairly large amplitude. EasySpin$^6$ was utilized to simulate the results accounting for the presence of one $^{29}$Si NNN. The results of the simulation are in good agreement with our experimental observation.


S.E.L01.06.80
Optical Management of Flexible Thin Crystalline Silicon Solar Cells Using Textured PDMS Optical Sticker Inchan Hwang and Kwanyong Seo; UNIST, Korea (the Republic of)

Thin crystalline silicon (less than 50 μm thickness) with outstanding flexibility has been considered as a means for developing flexible crystalline silicon (c-Si) solar cells. However, the optical management of the thin c-Si is required for developing the highly efficient c-Si flexible solar cells due to the high surface reflection (more than 30%) and absorption loss over 900 nm wavelength region. Here, we introduce novel high efficiency c-Si flexible solar cells which include random inverted pyramidal polydimethylsiloxane (RIP-PDMS) optical sticker on the 20-μm-thick thin c-Si solar cells. Due to the enhanced light absorption at the entire wavelength region, the thin c-Si with RIP-PDMS optical stickers showed the improved integrated photon flux absorption up to 85.4% (75.0% to 85.4%). The RIP-PDMS sticker enhances the light absorption...
capability of the thin c-Si by increasing the optical path length in the thin c-Si up to 10%. Further, we analyzed the optical enhancement of the thin c-Si with the RIP-PDMS optical sticker through the finite-difference time-domain (FDTD) simulation. From the optical simulation, we confirmed that the optical path length in the thin c-Si increased because the angles of incident light at the front and rear surface of the thin c-Si tilted up to 10° and 15°, respectively, by attaching the RIP-PDMS optical stickers. Notably, the thin c-Si solar cells with the RIP-PDMS optical stickers showed 18.4% power conversion efficiency while maintaining superior flexibility (bending radius of 10 mm). In addition, our flexible thin c-Si solar cells with the RIP-PDMS optical stickers showed high bending stability without any change in efficiency, even with 1000 bending cycles with a bending radius of 10 mm. Thus, we believe that the thin c-Si solar cells with RIP-PDMS optical stickers can be a promising candidate for the highly efficient flexible solar cells.

**SESSION S.LP01.01: Live Poster Session I: Electronics and Photonics (S.EL01)**
Session Chairs: Silvia Armini and Hong Zhao
Sunday Afternoon, November 29, 2020
5:00 PM - 7:00 PM
S.EL01

**S.EL01.06.03 Photovoltaic and Photoconductive Action Due to PbS Quantum Dots on Graphene/SiC Schottky Diodes from NIR to UV**
Mathew Kelley, Joshua Letton, Grigory Simin, Fiaz Ahmed, Cole Love-Baker, Andrew B. Greytak and MVS Chandrashekhar; University of South Carolina, United States

We demonstrate photovoltaic and photoconductive responses to near-infrared light in a new class of devices formed by depositing a film of gel permeation chromatography purified PbS quantum dots (QDs) on top of n-SiC epitaxial layers with natively grown, 10-15 monolayer thick epitaxial graphene (EG) Schottky contacts. The QD-film was removable by selective chemical etching, resetting the EG/SiC Schottky diode to its pristine state for multiple PbS-QD depositions. EG in these devices simultaneously forms Schottky contacts to SiC and ohmic contacts to PbS-QD, enabling electrical screening and isolation of these interfaces from each other. After PbS-QD deposition, the diodes exhibit photovoltaic and photoconductive response at photon energies far below the SiC bandgap, extending to the NIR gap of the QD film. Scanning photocurrent microscopy illustrates that this is due to charge transfer from the QD-film to the n-type 4H-SiC through a trap-limited, rectifying PbS-QD/SiC heterojunction with ideality n=2 in parallel with the EG/SiC Schottky diode. The photoconductive gain at this QD/SiC interface could be useful for IR detection in wide bandgap platforms. Response times as fast as 40 ms are suitable for imaging applications, although careful contact design is required to optimize work-function matching and spreading resistance.

**S.EL01.06.07 Comparative Study of Surface Energy Engineering for Low Temperature (< 453 K) Nanobonding™ of LiTaO3 and LiNbO3 to Si and α-Quartz SiO2**
Mohammed Sahal, Brian Baker, Nicole Herbots, Nikhil C Suresh, Shaurya Khanna, Amber A Chow, Saaketh R. Narayan, Aashi R. Gurijala, Robert J. Culbertson, Lauren Puglisi and Thilina N. Balasooriya; Arizona State University, United States

Opto-electronic integration yields high density and high complexity electronic devices by improving speed and reducing interconnection bottle-necks. Heteroepitaxy and wafer bonding are the main technologies to achieve monolithic integration of heterogeneous materials. However, heteroepitaxy is limited by the mismatches between dissimilar lattice constants and between different coefficients of thermal expansion (CTE). Direct Wafer Bonding (DWB) is the fusion of two mirror-polished, flat wafers, which overcomes the limitations of heteroepitaxy. DWB can be applied to many materials including bonding III–V, II-IV semiconductors and piezoelectrics to Si.

In this work, low-temperature DWB via NanoBonding™ is investigated to bond LiTaO3 and LiNbO3 to Si(100) and α-quartz SiO2(100). Low-temperature NanoBonding™ of piezoelectrics such as LiTaO3 and LiNbO3 on Si-based materials can avoid issues arising from their CTE mismatch, since conventional DWB requires anneal temperature > 673 K.

The highly anisotropic CTE of LiTaO3 ranges from ~ 4 x 10^-6 /K along the c-axis to up to ~ 16 x 10^-6/K along the a-axis.
Thus, the CTE for LiTaO3 is 2-10 times larger than the CTE for Si, 2.6 - 2.77 x 10^{-6} /K, and 10-30 times larger than the CTE for fused SiO2 and α-quartz SiO2, which ranges 0.54 - 0.76 x 10^{-6} /K. Thus even a low T anneal at 473 K is found to shatter a 6" LiTaO3/Si bonded pair. Nano-Bonding™ at T < 473 K uses Surface Energy Engineering (SEE) instead of high temperature anneal to bond surfaces. In addition, processing temperatures for LiTaO3 are found to be limited by thermal decomposition LiTaO3 into Ta2O5 at T ≥ 453 K due to Li out-diffusion, as much as by LiTaO3 fractures due to CTE mismatch.

SEE is guided by surface energy and hydro-affinity measurements, using Three Liquid Contact Angle Analysis (3LCAA) and the Van-Oss-Chaudhury-Good theory. 3LCAA is conducted with high statistics, by mapping wafers for three surface interactions, namely van der Waals interactions, electron donors, electron acceptors interactions. Multiple metered 10-µl drops of three liquids, water, glycerin, and α-bromo-naphthalene are used. The contact angles are extracted from a large set of drops and their reflection via an automated, fast, accurate algorithm, DROPTM. The “as received” surfaces are characterized at equilibrium, to yield insights for SEE into modifying the initial surface energy and hydro-affinity to a far-from-equilibrium state.

As received 6" Si(100) wafers are initially hydrophilic with a uniform average water contact angle of 37.7 ± 0.6°, and an average surface energy γT of 57.6 ± 0.5 mJ/m². As-received α-quartz SiO2(100) wafers surface were hydrophobic with an average water contact angle of 66.7 ±1.7° and an average γT of 33.2 ± 0.8 mJ/m². 6" wafers of LiTaO3 are initially mostly hydrophobic with an average water contact angle of 64.4 ± 2.7°, while water contact angle average 54.2 ± 8.1° LiTaO3 and LiNbO3 surface energies γT are low and very close: 38.8 ± 4 mJ/m² and 39 ± 2.5 mJ/m² respectively.

SEE via aqueous HF creates far-from-equilibrium Si surfaces by decreasing the initial γT of Si(100) from 57.6 ± 0.5 mJ/m² to 35 ± 0.03 mJ/m² and increasing the γT of α-quartz SiO2(100) was increased from 33.2 ± 0.8 mJ/m² to 48.7 ± 1.5 mJ/m². Likewise, LiTaO3 and LiNbO3 were made hydrophilic via SC1(H2O:NH4OH:H2O2) solution (4:1:1) followed by aqueous HF etching.

Nano-contacting of LiNbO3, LiTaO3 on Si(100) and α-quartz SiO2(100) and subsequent anneal at T < 453 K was performed to create a bonded interfacial phase. However, nano-contacting was only observed for hydrophobic LiTaO3 and LiNbO3 with hydrophilic Si-based surfaces. Results show that bonding hydrophobic LiTaO3 and LiNbO3 to hydrophilic Si or SiO2 without anneal is much more effective than trying to bond hydrophilic LiTaO3 to hydrophobic Si or SiO2. This can be attributed to the modification of surface polarity and will be discussed based on the surface crystallography of LiTaO3 and LiNbO3.

S.EL01.06.11
Low Temperature c-Si/4H-SiC Heterojunction Growth Using Metal Induced Crystallization Fabian Triendl, Georg Pfusterschmied, Christopher Zellner, Sabine Schwarz, Werner Arter and Ulrich Schmid; Technische Universität Wien, Austria

Metal induced crystallization is a well-known technique to reduce the crystallization temperature of amorphous semiconductors like a-Si using a catalytic metal. Crystallization temperatures even below 200 °C have been realized making it compatible with organic materials or other applications where only a limited temperature budget is acceptable. A combination of the wide band gap semiconductor 4H-SiC and such a low temperature process is barely investigated, although the Si/4H-SiC heterojunction offers huge potential in the field of e.g. heterojunction diodes, bipolar junction transistors and optical detectors. Conventional growth methods like chemical vapor deposition (CVD) need temperatures well above 800 °C to achieve epitaxial growth of Si on SiC. A low temperature method could make this heterojunction more practical, also in combination with other materials and temperature sensitive processes.

We present the first results to achieve partially epitaxial c-Si/4H-SiC interfaces using Al as catalytic metal. Sputter deposited amorphous silicon has been successfully crystallized on 4H-SiC at temperatures ranging from 350 to 700 °C. Annealing led to an almost complete layer exchange of Al and Si as well as to a heteroepitaxial interface of crystallized Si islands and the SiC surface. Si <111> was found to be the dominating crystallographic orientation of the re-crystallized Si. X-ray diffraction measurements show the change in Si crystallinity and the crystallographic impact of the underlying SiC substrate in this temperature range. TEM and SEM imaging was performed to investigate the film microstructure and the interface quality, thus revealing a clean and abrupt interface of large Si grains and the SiC substrate.

S.EL01.06.13
A Review on Controlling Nano-Scale Chemically Modified Thin Films for CMP Processes Development G. Bahar Basim; University of Florida, United States
As the microelectronics manufacturing faces the challenges related to the Beyond Moore’s Scale adaptation, Chemical Mechanical Planarization (CMP) process control becomes much more critical yet difficult simultaneously. The need for planarizing larger scale wafers at an atomic scale precision with superior removal rate selectivity and zero-defect focus demands a nano-scale control on the process performance. This study reviews the atomic-scale chemical and mechanical interactions on CMP as it applies to traditional as well as the next generation materials in microelectronics manufacturing. Once the behavior of the wafer surface is understood at an atomic level, the process control metrics can be tuned accordingly.

In an attempt to come up with the design criteria for the slurry chemistry, chemically modified layer formation is evaluated on conducting, semiconducting and insulating materials as a function of evaluating the nano-scale surface topography and change in surface energy. Metallic films are studied in terms of their corrosion and passivation behavior through macro-scale electrochemical evaluations as well as surface-sensitive characterization techniques such as XRR, XRD and FTIR [1, 2]. In addition, a modeling approach is introduced through Cahn Hilliard Equation (CHE) approximation to the surface energy minimization on the metal-oxide formation by nucleation [3]. Furthermore, removal rate selectivity properties of the semiconductor materials are discussed on conventional and III-V semiconductors and insulators as a function of chemically modified film alteration [4-5]. Some high-end applications such as (i) tungsten T-gate transistors, (ii) new liner/barrier materials [6], (iii) germanium based high-speed, shallow trench isolation transistors and (iv) high-power transistors and LED applications where III/V semiconductors are deliberated. As a new challenge, 3-D implementations of the CMP process, where the chemically modified nano-films impact the performance of the materials are also introduced.


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Direct Write Waveguides Using Multiphoton Lithography Michael Gallegos, Daryl Dagel, Amber Dagel, Andrew Pomerene, Allen Vawter, Erik Skogen and Bryan Kaehr; Sandia National Laboratories, United States

Abilities to capture, guide, and direct light into pixelated detectors (CCDs, CMOS sensors, FPAs, etc.) using free-form trajectories would be transformative for a range of technologies that currently use traditional optics (lenses, mirrors, prisms, etc.) for light coupling. However, few manufacturing techniques provide the appropriate scale and surface quality to address this task. In this work, we consider “free-form waveguides” using the high-resolution 3D printing technique of multiphoton lithography (MPL; also known as direct laser writing, DLW). First, we printed hollow and solid core vertical waveguide arrays spanning millimeters with single (5 micron) and multimode (30 micron) compatible cross-sections. Unsupported 5-micron diameter pillars generally succumbed to capillary forces during development and drying and thus sheathed waveguides were designed by anchoring fibers to a support scaffold. In addition, we examined direct printing onto active devices (coupling a source to a sensor) using an air-clad multimode design. Efficient light coupling was observed with scattering losses primarily from fabrication artifacts such as stitch lines. To address these issues, we considered stitch-free cores using a clad-only design resulting in encapsulated photoresist in the interior that is subsequently cured (UV, thermal) following development. These initial results, combined with the limitless design space afforded the MPL technique, provide a promising path forward to develop ultra-wide-field and highly compact imaging devices.

Role of Carbon and Oxygen Coverage in the Modification of Surface Energy and Hydro-Affinity of GaAs and Si for
Native oxides increase electrical resistance and inhibit epitaxy on semiconductors. Their removal is key in opto-electronic integration for devices such as tandem solar cells. Besides heteroepitaxy, Direct Wafer Bonding (DWB) is a viable integration technology for GaAs and Si. NanoBonding™ is DWB conducted at low T (~200°C) by modifying surface energy and hydro-affinity to reach far-from-equilibrium states and activate cross-bonding and electron exchange between the surfaces.

Hence, the surface energy has to be increased (if it is initially low), or decreased (if it is high). One of the surfaces in the pair has to be made hydrophilic if it is initially hydrophobic, and the other one hydrophilic if it is initially hydrophobic. Moreover, the surfaces have to be modified in a complementary way to so that electrons are transferred from electron donors on one surface to electron acceptors on the other.

To conduct Surface Energy Engineering (SEE) of GaAs and Si into a bonding pair, the initial surface energy, hydro-affinity, surface composition, and oxidation levels of as-received GaAs(100) and Si(100) are initially characterized. Next, the initial surface energies and hydro-affinities are modified not only by oxygen removal via chemical etching, but also to maximize cross-bonding. The characterization methods are Three Liquid Contact Angle Analysis (3LCAA) for surface energy and hydro-affinity, High Resolution Ion Beam Analysis (HR-IBA) for O coverage, and X-Ray Photoelectron Spectroscopy (XPS) for oxidation and C contamination.

In 3LCAA, the total surface energy, \( \gamma_T \), is determined by the van Oss-Chaudhury-Good theory using 3 components: Lifshitz- Van der Waals, electron donors, and acceptors. GaAs(100) native oxides are hydrophobic with a low surface energy (\( \gamma_T = 33.4 \pm 1.1 \text{ mJ/m}^2 \)) while Si(100) native oxides are hydrophilic with a high surface energy (59.7 ±1.7 mJ/m² ). GaAs surfaces are then etched with NH₄OH:H₂O (1:10) to be highly hydrophilic, while their \( \gamma_T \) can be reproducibly increased by a factor of 2 to 65.5 ±1.4 mJ/m². HF:CH₃OH (1:20) etching makes Si(100) hydrophobic and decreases its \( \gamma_T \) by 20% to 48.2 ± 1 mJ/m². Nano-bonding™ of GaAs to Si does not occur between these surfaces. However, Si(100) etched by aqueous HF becomes even more hydrophilic with a 25% decrease in \( \gamma_T \) to 44.4 ±2.3 mJ/m². With this SEE of Si, GaAs nano-bonds to Si reproducibly.

O etching is measured by HR-IBA, while oxidation states and C-contamination are measured by XPS to correlate to nano-bonding. HR-IBA combines <111> channeling with O nuclear resonance to measure O coverage within ±0.2 Monolayers (ML) and analyzed via SIMNRA simulations. O coverage on GaAs is found to decrease by a factor 2 from 7.2±0.5 ML to 3.6±0.2 ML after etching.

The ratio of Ga and As is found to be unaffected by C-contamination, and remains ~54:46 within 1 atomic % by HR-IBA or ~1.18 within 10% by XPS. XPS shows that the relative ratio of Ga bound to GaAs versus Ga bound to Ga2O3 is initially 64:36 to within 1% with a slight increase in Ga bound to O. The relative ratio of As bound to GaAs versus As bound to O is much lower than Ga, 80:20 to within 1% and does not change with etching.

XPS analysis also shows that when C-contamination ranges between 12%-35% atomic %, the measured ratios of Ga and As bound to GaAs versus Ga and As bound to O vary less than 2%. After etching, Ga bound to Ga2O3 decreases with increasing carbon with a weak correlation factor of 0.4. C-contamination does not appear to significantly affect Ga oxidation. For As oxides, As2O5 shows a relative increase compared to As2O3 as C contamination increases with a strong correlation factor of 0.86 in native oxides before etching. After etching, the correlation factor is 0.55.

In summary, aqueous HF produces more hydrophobic Si(100) surfaces that can nano-bond to highly hydrophilic GaAs etched via dilute NH4OH while C contamination does not appear to modify GaAs surface composition nor oxidation.

**S.E.L01.06.24 Unraveling Vertical Inhomogeneity Effects in Vapor Phase Polymerized PEDOT:Tos Films** Shangzhi Chen and Magnus P. Jonsson; Linköping University, Sweden

Electrically conductive polymers are widely utilized in emerging electronic devices due to their excellent optoelectronic properties as a potential alternative to conventional conductors. Among them, Poly(3,4-ethylenedioxythiophene):Tosylate (PEDOT:Tos) thin films deposited by Vapor Phase Polymerization (VPP) exhibit electrical conductivity exceeding 3400 S/cm which is almost comparable to commercial ITO electrodes. [1] Systematic investigation on such films indicates a strong anisotropy in electrical and optical properties and this anisotropy is believed to be mostly caused by the preferential alignment of para-crystallines in the films. [2]

Here, I will present our recent study on the VPP PEDOT:Tos thin film system and reveal that vertical gradient could also be an important factor contributing to the electrical anisotropy. By examining the results from grazing-incidence wide-angle X-ray scattering and X-ray photo-electron spectroscopy, we observed significant differences of the top and bottom surfaces, including para-crystalline alignment preference and oxidation level (doping level). These show that the VPP PEDOT:Tos
layer is not vertically homogeneous in terms of both “crystallization” fraction and charge carriers (doping level). To explain the origin of this inhomogeneity, we propose a growth mechanism for VPP based on diffusion-limiting transport of polymerization precursors. Conductive polymer thin films with certain gradient profile may find applications in functionally graded thermoelectrics, gradient-index optics, and optoelectronic devices with gradient doping.

References

S.EL01.06.25
Interface Diffusion of AgGaTe2 Layers Prepared on Mo Electrode Layers Masakazu Kobayashi; Waseda University, Japan

Chalcopyrite materials based on CuInGaSe2 is practically used for the commercially available high efficiency solar cells. The room temperature bandgap of AgGaTe2 is about 1.3eV, hence the application of this material to the active layer of novel solar cells also attracted the attention. Among various film preparation methods, the closed space sublimation (CSS) method is suitable for the fabrication of mass production solar cells since it has various advantages toward the production cost reduction. The growth of crystallized AgGaTe2 thin films utilizing this method on Si and Al2O3 substrates have performed in past, and it was discovered that the introduction of the two-step sequence was the key to realize high quality thin films. The Ag2Te layer was deposited as the first step to avoid the melt-back etching related problems of Ga against substrate materials. Then, AgGaTe2 thin films were formed using the mixed powder source of Ag2Te and Ga2Te3. The AgGaTe2 thin films could be also prepared using the powder source of Ga2Te3. The first Ag2Te layer was disappeared during the high temperature growth process of the second sequence, and a single phase AgGaTe2 of the uniform layer has formed once the growth parameter was optimized.

It was clarified from the X-ray diffraction (XRD) measurement that the inclusion of AgGa5Te8 compounds occurred when the fraction of Ga2Te3 in the deposits was greater than that of Ag2Te. On the other hand, mixed crystal of AgGaTe2 and Ag2Te were formed when the fraction of Ga2Te3 was less than that of Ag2Te. These results corresponded to the phase diagram of the Ag2Te–Ga2Te3 system. A pn-heterojunction solar cell structure was prepared using the AgGaTe2 layer on the n-Si substrate, and the photovoltaic properties were confirmed. The AgGaTe2 layer was also prepared on the Mo/quartz substrate using the same growth sequence.

In case of the CuInGaSe2 layer growth on the Mo electrode layer, Se diffusion was observed in the Mo electrode layer. The advantage and disadvantage were still discussed for this structure. In this study, the interfacial diffusion of elements at AgGaTe2/Mo was studied to understand how the diffusion of Ga could be suppressed. High resolution cross sectional TEM images of the interfacial region was analyzed using the Z-contrast images of the high angle annular dark field (HAADF) mode and EDX-mapping mode. When AgGaTe2 layer was directly grown on the Si substrate, Si surface was etched and became very rough, and it was considered that Ga has damaged the Si substrate surface. By introducing the two step procedure, the interface quality was substantially improved and the roughening was vanished.

When the layer was grown on the Mo electrode layer, Se diffusion was observed in the Mo electrode layer. The advantage and disadvantage were still discussed for this structure. In this study, the interfacial diffusion of elements at AgGaTe2/Mo was studied to understand how the diffusion of Ga could be suppressed. High resolution cross sectional TEM images of the interfacial region was analyzed using the Z-contrast images of the high angle annular dark field (HAADF) mode and EDX-mapping mode. When AgGaTe2 layer was directly grown on the Si substrate, Si surface was etched and became very rough, and it was considered that Ga has damaged the Si substrate surface. By introducing the two step procedure, the interface quality was substantially improved and the roughening was vanished.

Further investigation is ongoing to identify the diffusion characteristics at the AgGaTe2/Mo layers. It is reconfirmed that the two step growth procedure is a very useful approach to achieve the high quality layer, but processing temperatures including the growth temperature and post growth annealing temperature are very critical parameters to achieve the high quality interface with the abrupt profile.

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S.EL01.06.26
Determining the Surface Chemistry of Lithiated Nickel-Manganese-Cobalt Oxide from Density Functional Theory and First-Principles Thermodynamics Josiah Roberts1, Chad Risko1 and Aashi R. Gurijala2; 1University of Kentucky,
Surfaces of materials such as lithiated nickel-manganese-cobalt oxide (NMC) can be characterized through experimental techniques such as photoelectron spectroscopy. These techniques take advantage of high-vacuum environments, though the vacuums are never perfect, and the materials are often exposed to ambient conditions prior to characterization or application, all of which could impact the surface composition. Hence, questions arise as to the data derived from periodic density functional theory (DFT) calculations that assume chemically clean surfaces in perfect vacuum and are used to describe these materials. To reconcile these differences, we investigate the surface chemistry of NMC through a combination of DFT and first-principles thermodynamics calculations. By examining the bulk structure, bare surfaces, and the adsorption of various atmospheric molecular and ionic species, we develop phase diagrams that reveal the expected surface chemistries as a function of various partial pressures, predicting the NMC surface chemistry as a function of the environment. Such predictions can be used to modify future computational studies of the material both in vacuum and in solution, providing additional tools for characterization.

Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces

Saima A. Sumaiya, Mohammad R. Vazirisereshk, Ashlie Martini and Mehmet Z. Baykara; University of California, United States

Electrical contact resistance (ECR) directly influences the performance of micro-scale devices, where contact between components occurs through nanometer-scale patches. Consequently, developing the ability to accurately measure ECR as a function of true contact size at the nanometer scale is of crucial importance. To achieve this goal, we present an approach based on conductive atomic force microscopy, which is applied on a material system comprising atomically flat interfaces formed between gold nano islands and a graphite substrate [1]. Proof-of-principle experiments are complemented by atomistic simulations, which are used to predict the maximum island sizes below which the ECR at the island-graphite junction can be reliably extracted from the measurements. This approach has the potential to contribute to fundamental studies of electron conduction, e.g. through an investigation of the transition between the diffusive and ballistic transport regimes.


Directed Patterning of Quantum Dots Using Chemically Modified Surface for Light Emitting Diodes

Su Hong Min, Ho-Jong Kang and Dong Hyun Lee; Dankook University, Korea (the Republic of)

Colloidal quantum dots (QDs) have been widely used for light-emitting diodes (LEDs) because of their outstanding characteristics including high color purity, narrow emission peak, high luminescent efficiency, low operating voltage and adjustable emission wavelength that are tunable as a function of their size and composition. For the fabrication of QD-based LEDs, they have been applied to several processes such as spin-casting, inkjet printing and micro contact printing. However, these processes suffer from practical limitations such as high-resolution patterning, high cost, multiple-layer structures, and long processing time. In order to overcome the issues currently suggested, micro-contact printing method using the relief patterns on a master has been introduced and utilized extensively for QD-LEDs. In this way, the regular patterns of QDs layer is transferred on the hole transport layer (HTL) by simply physical contact between the master and the HTL surface. In spite of its efficiency, however, the cyclic process of the micro-contact printing inevitably gives rise to sever damages to the master patterns. Here, we demonstrate a unique method for directed patterning of colloidal quantum dots for the light emitting diodes from chemically modified surface. The chemically modified line-type patterns are initially fabricated on the substrate by using a conventional photolithography technique and selective chemical reaction of surface-modifying molecules such as the octadecyltrichlorosilane (OTS) sequentially. The width of line-type patterns produced is varying from 40 µm to a few µm. The quantum dots of CdSe(core)-ZnS(shell) that are covered with oleic acid as capping molecules are then spin-coated on the chemically patterned surface. To transfer the QDs layer to a hole transport layer, the polymethylmethacrylate (PMMA) is first spin-coated on the QDs layer followed by placing commercial adhesive tapes on the PMMA layer. Then the QDs/PMMA layer is detached from the original substrate by peeling the adhesive tapes and transferred to the target substrate. The target substrate consists of ITO(Anode), PEDOT: PSS(HIL), and TFB(HTL), respectively. It is noted that the only designed QD patterns are selectively transferred from the chemically modified surface due to surface energy difference during the transfer process. As the PMMA/tape layers are removed by rinsing with acetone, which is a selective solvent, the only QD patterns remain on the HTL layer of the target substrate. For the fabrication of QD-LEDs, ZnO(ETL) and Ag(Cathode) layers are deposited on the QDs layer sequentially. Consequently, the QD-LEDs fabricated in this study are characterized by measuring their electrical properties like luminance, current density and external
quantum efficiency.

S.EL01.06.30
The Chemistry of Interface Defects in SiC/SiO₂ Probed by Hard X-Ray Photoelectron Spectroscopy
Anna Regoutz; University College London, United Kingdom

Interfaces govern the behaviour of all electronic devices. Herbert Kroemer coined the famous phrase “the interface is the device” in his 2000 Nobel Prize lecture, and we are still applying tremendous effort to understand interfaces in new material generations, with wide-bandgap materials being no exception. If anything, wide bandgap materials are more vulnerable to defect states purely due to their larger bandgap. Understanding gained for the bulk behaviour of semiconductors can often not be extended to the behaviour of materials in structured film stacks were interfaces play a vital role. SiC/SiO₂ is a prototypical wide-bandgap semiconductor/dielectric interface, which represents the challenges faced by many such material systems. A multitude of different defects leads to unacceptably large defect densities exceeding $10^{13}$ cm$^{-2}$ eV$^{-1}$ in the vicinity of the conduction band of 4H-SiC. The management of interfacial defects remains a topic of lively discussion and current interest.

Here, we present a systematic study of the 4H-SiC/SiO₂ interface in industrially manufactured samples with a particular focus on the effects of nitridation in N₂, NO, NH₃ and NO+NH₃ atmospheres. High temperature nitridation has been shown to compensate interface defects leading to an increase in device performance, however, information on the local chemistry at the interface after such processes is scarce, which limits the understanding of the interface and consequently the targeted improvement of device characteristics. Clear differences are found in both spectroscopy and electrical behaviour after high temperature treatments. The present work uses energy-dependent hard X-ray photoelectron spectroscopy (HAXPES) to systematically study the elemental distributions and chemical environments across the 4H-SiC/SiO₂ interface. We combine both laboratory- and synchrotron-based HAXPES results to obtain a complete picture of this important technological interface and to benchmark the capabilities of this spectroscopic technique for the exploration of buried interfaces in device heterostructures in general.

S.EL01.06.31
Experimental Study of Fundamental Material Properties of Alkali-Antimonide Photocathodes
Pallavi Saha¹, Oksana Chubenko¹, Howard A. Padmore² and Siddharth Karkare¹; ¹Arizona State University, United States; ²Lawrence Berkeley National Laboratory, United States

Alkali antimonides (such as Cs₅Sb, K₂CsSb and Na₃Ksb ) constitute a rather interesting class of materials, exhibiting high quantum efficiency (>10%) and high brightness in visible light making them interesting materials for use in photon detectors and as photoemission based electron sources for large linear particle accelerators (used for X-ray Free Electron Lasers, Electron Colliders and Hadron Beam Coolers) and time resolved electron microscopes. Despite ongoing work on these extremely vacuum sensitive materials for the last several decades, there has been no conclusive understanding and little/ no consensus on its opto-electronic properties like band gap, electron affinity, optical constants etc. Lack of knowledge of these vital properties has stood in the way of understanding the process of photoemission in these materials near the photoemission threshold. The objective of our work is to grow high quality alkali-antimonide films with smooth surfaces and perform different spectroscopic characterizations like photoluminescence, photoconductivity and ellipsometry on them, in order to explore their opto- electronic properties in ultra high vacuum. It is believed that this detailed experimental study will elucidate the exact process responsible for efficient photoemission from these materials and allow us to develop state-of-the-art electron sources with maximized brightness.

S.EL01.06.32
Enhancing Nucleation of Metal ALD by Pre-Dosing Small Organometallic Molecules
Camila de Paula, Nathaniel Richey, Li Zeng and Stacey F. Bent; Stanford University, United States

The process of thermal atomic layer deposition (ALD) of metals on non-metal surfaces is sought for many applications, but often suffers from nucleation delays that result in poor-quality films. These growth delays can result from a lack of suitable chemisorption sites on the non-metal surface. Various strategies have been explored to improve nucleation in these systems. Vapor phase pre-treatments have proven to be an especially promising nucleation enhancement strategy due to the minimal substrate-modification induced, its robustness, and its uniformity.

In this work, we demonstrate that pre-functionalizing the surface with a sub-monolayer of small organometallic molecules such as ZnEt₂, AlMe₃ and AlMe₂Cl, from the vapor phase can lead to a significant increase in the surface coverage of the metal deposited by ALD at low cycle numbers. This process is demonstrated using Pt ALD as a model process, using (methylcyclopentadienyl)trimethylplatinum (MeCpPtMe₃) and O₂ as reactants. Pt coverage was enhanced by ~ 3-fold after...
100 ALD cycles and even larger enhancements were observed at lower cycle numbers following the pre-treatment. We hypothesize that the high coverage of the small organometallic molecules provides an alternative chemisorption mechanism for the platinum precursor leading to increased MeCpPtMe3 chemisorption during the first ALD cycle. This alternative chemisorption mechanism was investigated through in-situ X-ray photoelectron spectroscopy and mass spectrometry. Nanoparticle growth was monitored using grazing incidence small angle X-ray scattering and scanning electron microscopy. We determined that chemisorption of MeCpPtMe3 on the treated substrate originates from a Brønsted acid-base reaction (i.e., proton transfer reaction), where the MeCpPtMe3 acts as the Brønsted acid and the pre-treatment molecules serves as the Brønsted base. Growth analysis indicates that the pre-treatment leads to growth of highly dense, ordered Pt nanoparticles with improved wettability at low cycle numbers, leading to continuous and pinhole free Pt films.

S.E.L01.06.38
Towards Scalable Fabrication of Atomic Wires in Silicon by Nano-Patterning Self-Assembled Molecular Monolayers Chufan Zhang and Yaping Dan; Shanghai Jiao Tong University, China

Developing a scalable method to fabricate atomic wires is an important step for building solid-state semiconductor quantum computers. In recent years, self-assembled molecular monolayer doping (MLD) has attracted intensive research interests due to its capability of facilitating mass production and forming ultra-shallow junctions with atomic precision\[1\]. MLD is believed to have a great potential in controllable dopant manipulation at sub-10 nm scale\[2\]. However, there is still no general method for effectively patterning dopant-containing monolayer at nanoscale. In this work, a novel selective doping strategy is proposed by patterning self-assembled monolayer to a few nanometers using standard nanofabrication processes, which significantly improves the lateral doping resolution of monolayer doping from microscale to nanoscale. We first found an effective way to remove the self-assembled monolayer via oxygen plasma followed by HF etching, which is confirmed by X-Ray photoelectron spectroscopy and Van der Pauw measurements. Electron beam resist HSQ (XR1541-002, Dow Corning) was used to create patterns that protect part of the self-assembled DVP monolayers from being oxidized by oxygen plasma, since HSQ will turn into amorphous SiO2 after electron beam exposure. To increase the resistance of the HSQ SiO2 against HF etching, a second time of high dosage exposure was performed on the HSQ structure. The high dosage electron beam exposure might induce a thin amorphous carbon layer covering the HSQ structures and dramatically improved the resistance of HSQ against HF etching. Using this method, we further explore the possibility to fabricate phosphorus atomic wires in silicon by patterning self-assembled diethyl vinylphosphonate monolayers into lines with a width ranging from 500 nm to 10 nm. The phosphorus dopants are driven into silicon by rapid thermal annealing, forming dopant wires. Four-probe and Hall effect measurements are employed to characterize the dopant wires. The results show that the conductance is linear with the width for the wires, showing the success of the monolayer patterning process to nanoscale. To fabricate atomic wires made of one or a few lines of phosphorus atoms, we need to shorten the thermal diffusion length and increase the dopant incorporation rate at the same time. Pulsed laser annealing may be a promising solution. The present work provides a promising pathway for mass fabrication of atomic wires in silicon that may find important applications in quantum computing.

References

S.E.L01.06.48
Optimizing n-Type Dopant Incorporation in GaAsBi for Multijunction Photovoltaics Margaret A. Stevens, Kevin Grossklas, Samuel Lenney, John H. McElearney and Thomas E. Vandervelde; Tufts University, United States

Multijunction photovoltaics employed in solar concentrator architectures can have theoretical efficiencies as high as 65% for a 4-junction cell [1]. For these devices, sub-cell band gaps of 0.96-1.18 eV are required. Epitaxially grown GaAsBi is of interest for this application due to (1) less lattice mismatch to GaAs than InGaAs for comparable band gaps [2] and (2) a proposed temperature-insensitive band gap and reduction in Auger recombination [3]. However, these materials are challenging to grow due to the surfactant-like nature and low solubility of bismuth (Bi) in this system. The low growth temperatures necessary for good bismuth incorporation is often at odds with good material quality. The need for depleted arsenic overpressure can often lead to challenging dopant incorporation [4], a critical requirement if these devices are to be employed in PN junctions.
In this work, we explore methods to improve dopant incorporation and carrier mobility in GaAsBi$_{0.02}$ and GaAsBi$_{0.06}$ for future photovoltaic devices. Samples were grown on a Veeco GENxplor MBE using a valved As$_4$ source and a solid source effusion cell for group-III elements and Bi. Bismuth fraction and strain state were determined by high-resolution x-ray diffraction and absorption edge was measured by transmission spectroscopy. Select samples are grown lattice matched to InGaAs virtual substrates to decrease compressive strain which delays both Ga-Bi droplet formation and defect formation from strain relaxation [5]. Samples grown on GaAs and InGaAs substrates are doped with silicon or tellurium for n-type and beryllium for p-type doping. The benefits and challenges of using a group-IV n-type dopant versus using a group-VI n-type dopant in this materials system will be discussed. Mobility of GaAsBi as a function of dopant concentration was measured using Hall effect measurements and compared for the different choice of dopants. Temperature-dependent Hall measurements are utilized to explore scattering mechanisms. Additionally, the effects of ex situ thermal annealing at 500 °C on optical and electrical parameters will be discussed. Finally, mobility data will be fed into device simulations using Silvaco to evaluate best device architectures to use bulk GaAsBi films in photovoltaics.


S.E.L01.06.51
Surface Chemical Composition Evolution During In-situ Annealing of Low-Strain Ge$_{1-x}$Sn$_x$ Layers on Core/Shell Nanowires Michael Braun$^1$, Ishaa Bishnoi$^1$, Andrew C. Meng$^2$, John Z. Lentz$^1$ and Paul McIntyre$^1$; $^1$Stanford University, United States; $^2$University of Pennsylvania, United States

Metastable germanium-tin has attracted significant interest as a potential group IV direct bandgap material for CMOS compatible electronics and photonics. With sufficient tin incorporation, there is experimental evidence of a direct bandgap germanium-tin material. Although this is a promising step for germanium-tin devices, there are further considerations for incorporating germanium-tin into a full device. Namely, the evolution of the germanium-tin surface during subsequent annealing and growth of additional device components. Previous annealing results on strained germanium-tin thin films have shown surface tin segregation and island formation. In this study, we report results from in-situ X-ray photoelectron spectroscopy during annealing of vertical core/shell Ge/Ge$_{1-x}$Sn$_x$ nanowires grown via chemical vapor deposition. We have previously shown the capability of the core/shell structure to produce a largely strain-free Ge$_{1-x}$Sn$_x$ shell material on a highly tensile-strained Ge core. This structure is utilized here to investigate the annealing characteristics of the germanium-tin surface and native oxide for tin contents in the range of 2 at% - 12 at% in air-exposed nanowires. Our results show the presence of a tin rich oxide with a composition dependent decomposition temperature. After in-situ decomposition of the native oxide, the tin content of the germanium-tin surface is observed to remain constant throughout annealing at temperatures exceeding 500 °C and for anneal durations greater than one hour. Additionally, we have measured the photoluminescence at room temperature, characterized strain by X-ray diffraction, and imaged the nanowire sidewall morphology before and after annealing to examine its effects on material performance, bulk tin distribution, and local surface structure.


S.E.L01.06.52
Enhancement of Electrical Characteristics of Amorphous Indium-Gallium-Zinc-Oxide Thin-Film Transistors by Inserting Carrier Induced Interlayer Changsic Yoon, Hyung Tae Kim, Min Seong Kim, Hyukjoon Yoo, Jeong Woo Park, Dong Hyun Choi, Dongwoo Kim and Hyun Jae Kim; Yonsei university, Korea (the Republic of)
Since the development of display technology, a new type of industry, such as augmented reality (AR), virtual reality (VR), and wide screen displays, has arrived. Requirements of performance standards on new type of displays have become more severe. Therefore, improving the mobility and stability of thin-film transistors (TFTs) for using in such devices have been actively conducted. To date, low temperature polycrystalline silicon (LTPS) with high field-effect mobility of about 100 cm²/Vs has been widely used as channel material for TFTs, but some problems remain, such as poor uniformity for large area, high leakage current, and high fabrication costs. To resolve the issues mentioned above, amorphous oxide semiconductor (AOS) has been attracted attention due to low off current, large area uniformity, and relatively low fabrication cost. Especially, amorphous Indium-Gallium-Zinc-Oxide (a-IGZO) is most used semiconductor among AOS materials. However, for AOS materials to be applied to the above-mentioned next-generation displays, low field-effect mobility and low stability under bias stresses, which are lower than LTPS, must be overcome.

In this sense, we propose the fabrication of a-IGZO TFTs with high mobility and high stability through insertion of a carrier induced interlayer (CII). CII is a layer introduced between the channel layer and the gate insulator layer, which is thinly deposited to absorb oxygen in the effective channel of a-IGZO through oxidation. Consequently, mobility of a-IGZO TFTs can be improved by oxidation of CII increasing carrier concentration of the a-IGZO front channel. In this study, thin aluminum layer was deposited for CII by RF sputtering process at 80 W with various deposition time 60, 90, and 120 s. Then, a-IGZO was deposited on the CII for channel layer while changing the oxygen partial pressure from 1.7 to 8.3%. After the activation process through thermal annealing at 300°C for 1 hour, Al was deposited by RF sputtering and used as source and drain electrodes. When the a-IGZO channel was deposited with oxygen partial pressures of 1.7, 3.3, and 5% without CII, the saturation mobility was 7.36, 5.45, and 2.83 cm²/Vs, respectively. If it exceeds 5%, it is insulated. The above phenomenon caused by the oxygen vacancy concentration in the a-IGZO thin film decreases with increasing oxygen partial pressure. If the partial pressure of oxygen is less than 5%, Al for CII cannot be completely oxidized, resulting normally conductive property. On the other hand, if the partial pressure of oxygen is more than 5%, the characteristics of the TFTs deteriorate. As a result, 5% condition achieves the best characteristics and determined as the optimize condition. In the transfer characteristics of the TFTs with various CII thickness, the saturation mobility of the TFTs with CII of 60 s and 90 s deposition were calculated as 11.30 and 13.96 cm²/Vs respectively. As the thickness of CII increases, the saturation mobility also increases. However, switching characteristics of the TFTs with CII are gradually degraded due to insufficient oxidation of CII with metal Al over 120 s of the CII deposition time. The CII with insufficient oxidation acts as current path at the interface between the gate insulator and the channel layer, resulting in a drastically increased conductivity. Consequently, the optimize condition was determined to be CII deposition time of 90 s. Lastly, bias stress tests were performed to determine the stability of the TFTs. Negative bias temperature illumination stress (NBTIS) test under -20 V, 50°C and 1000 lux for 3600 s was conducted on the TFT fabricated with oxygen partial pressure of 5% with CII deposition time of 90 s. When the result was compared with the a-IGZO TFT without CII (pristine), the stability characteristic was improved as the threshold voltage shifts of the pristine showed -12.05V and the device with oxygen partial pressure of 5% and with CII showed -6.73V.

S.E.L01.06.53
Design and Demonstration of Novel Spectrally Selective Thermal-Radiation Material Takashi Ando1, Maki Ito1, Naoki Maruyama2, Takanobu Kobayashi2 and Yoshitaka Takezawa2; 1Hitachi Ltd, Japan; 2Hitachi Chemical Co., Ltd., Japan

Electronic devices, such as electronic control unit, power module, mobile equipment, etc., are required downsizing and higher power density. To achieve the downsizing and higher power density, electronic parts are closely mounted together in a small external package, which causes an increase of heat density. Thermal-radiation is one of the heat dissipations methods. However, conventional thermal-radiation is not useful in the electronic devices, since most of the radiated heat is absorbed by an external package such as resin.

The purpose of this study is to newly develop a thermal-radiation material, which generated heat is converted into infrared light with spectrum transmitting through the resin. The material is so-called spectrally selective thermal-radiation material (SSTRM). The studied SSTRM is composed of metallic spheres arrayed on the surface of a heating element, and resin film covering the metallic sphere array. The film is formed by applying a coating solution including metallic spheres. The optimum diameter and arrangement of the metallic sphere are founded numerically and experimentally. The thermal-radiation spectrum was calculated by using an optical simulation tool based on Rigorous Coupled Wave Analysis. The calculation results clearly showed the localized plasmon resonance excited in the metallic spheres array. The localized plasmon resonance enhanced the emission at the resonance wavelength. The resonance wavelength was controlled by changing the diameter and arrangement of the metallic spheres. It was revealed that infrared light with spectrum transmitting through the resin film is emitted, when the spheres with a diameter of 1.5 um are densely arrayed. The effectiveness of the SSTRM was experimentally demonstrated by evaluating thermal-radiation characteristics under the stationary atmosphere with a temperature of 298 K. Input power to a heating element was fixed at a constant value, so that
the surface temperature of the heating element was 381.1 K. Three types of coating materials were prepared as follows; A. only resin film, B. metallic spheres dispersed in resin film, and C. optimized metallic sphere array covered with resin film (SSTRM). The surface temperatures of the heating elements coated with the films A, B, and C were evaluated to be 358.3K, 355.8K, and 348.1K, respectively. The film C achieved drastic temperature reduction of 33K compared with the heating element without the coating materials. The temperature of the film C was lower than that of B, due to the effect of the metallic sphere array formation. Consequently, the optimized metallic spheres array acted as the spectrally selective emitter that radiates infrared light transmitting through the resin. The SSTRM will be powerful material for heat dissipation from electronic devices packed in resin case or mold.

S.EL01.06.54
Improved Efficiency of Photo-Induced Electron Detection under UV Light Source by ZnO Nanowire Array on Aligned PVDF-TrFE Nanofiber Film Dong Hee Kang, Na Kyong Kim and Hyun Wook Kang; Chonnam National University, Korea (the Republic of)

Zinc oxide (ZnO) is a versatile semiconductor material used for a wide range of applications in electronics, photonics, and optics. Bulk ZnO is a wide band gap (3.37 eV) semiconductor that generates electrons under an electromagnetic wavelength shorter than the ultraviolet (UV) range. ZnO nanowires (ZnO NWs) exhibit enhanced electrical properties over ZnO thin film via a nano size effect based on the electrical resistivity of chemical under UV irradiation. The NW structure induces movement of electrons along an axial direction due to the electron confinement effect by structural features. In order to utilize the advantages of nanostructured film in commercial sensors, mass production should be achieved with simple manufacturing processes. Electrospinning with a continuous process is possible in mass production with a roll-to-roll system. The use of a high porous electrospun nanofiber (ES NF) film is advantageous in terms of fabricating dense ZnO NWs. Additionally, a highly aligned state of ES NF films is possible to fabricate via controlling the electrospinning condition without entailing additional processes. The aligned nanofiber film aids in electron movement along the direction of the fiber, thereby revealing possibilities for its application to high responsibility in UV detector. Under the UV irradiation condition, ZnO NWs on ES NF film generate electrons under light energy absorption conditions that exceed the energy required to excite electrons based on Planck’s equation. Under continuous UV irradiation on the ZnO NWs surface, electrons in the valence band are excited to the conduction band when the electrons gain sufficient energy. The excited electrons on the ZnO NWs surface along the ES NF support have a strong directionality that tends to flow into the low current density region. The electrical conductivity on ZnO NWs increases by using aligned ES NF when compared to that of random ES NF by large gradient of current density. Linearity error of the ZnO NWs on aligned and random ES NF films are less than ±0.58% and ±1.60%, respectively. Under UV irradiation conditions, the sheet resistance of ZnO NWs on the aligned ES NF film (0.17MΩ/) is 9.88 times lower than that for ZnO NWs on random ES NF film (1.68MΩ/). The results for ZnO NWs on ES NF films under the UV irradiation and dark conditions indicate sheet resistance ratios (Rsq,off/Rsq,on) of 551.0 and 47.8 for ZnO NWs on the aligned ES NF film and ZnO NWs on the random ES NF film, respectively. The sheet resistance ratio of ZnO NWs on the aligned ES NF film is 11.5 times than that of ZnO NWs on the random ES NF film. The electric current on aligned ES NF surface shows higher flow rate than electric current on random ES NF surface. Even though under the identical hydrothermal conditions to fabricate ZnO NWs, a geometry of ES NF film substrate is an important factor for improving the photo detecting performance of ZnO NWs on ES NF films.

S.EL01.06.90
Effect of Yarn Structure and Processing Conditions of Screen Printing on Electrical/Antenna Performance for E-Textile Applications Jung Hun Lee and Ju-Hee So; Korea Institute of Industrial Technology, Korea (the Republic of)

Wearable wireless communication systems based on Electronic textile (E-textile) have become significant interests owing to their potential applications in sportswear, military, firefighting, health care, and tracking systems. Among the fabrication methods of conductive textile, screen printing which prints metal nanoparticle based conductive inks on a fabric substrate has been known to be a promising approach in the field of wearable electronic applications. However, the morphological characteristics of textile materials such as high surface roughness, high porosity, and capillary force in the woven fabric structures and the lack of manufacturing technology to overcome the issues are obstacles to commercialization of electronic textiles (E-textile). Herein, we compare the flat and round yarn based polyethylene terephthalate (PET) fabrics as the substrates for screen printing. We also investigate the effect of the parameters of the screen printing process such as the screen mesh size (70, 120 pixel/inch) and the printing counts. The uniformity of the screen-printed layers and their electrical properties are directly related with the shape of the yarn, the roughness of fabric substrates, and the printing processing conditions. A minimum average sheet resistance of 16 ± 3 mΩ/sq. was achieved on the flat yarn PET fabrics, and there was little change in electrical performance after the bending test (r=3mm) was carried out 1,000 times. To demonstrate, we show textile antennas operating at 2.4GHz which is most widely used for public wireless LAN service, Bluetooth, radio frequency
identification (RFID). We analyzed the effects of the uniformity and the conductivity of the printed layers on the antenna performance. The field tests of the textile antennas in open areas showed better performance than commercial antennas. This study aims to advance E-textile devices with excellent electrical properties and mechanical durability for wearable wireless communication applications.

SESSION S.LP01.02: Live Poster Session II: Electronics and Photonics (S.EL01)
Session Chairs: Santanu Bag and Mandakini Kanungo
Sunday Afternoon, November 29, 2020
7:15 PM - 9:15 PM
S.EL01

S.EL01.06.04
Investigation of Buried Junctions in CdSe$_{1-x}$Te$_{1-x}$ / CdTe Devices Sean Jones$^{1,2}$, John Moseley$^2$, Harvey Guthrey$^2$ and Brian Gorman$^1$; $^1$Colorado School of Mines, United States; $^2$National Renewable Energy Laboratory, United States

CdSe$_{1-x}$Te$_{1-x}$ alloys now used in state-of-the-art CdTe solar cell technology can be further characterized and optimized. Se alloying can significantly reduce the bandgap of the CdTe absorber due to the strong bandgap bowing between CdTe and CdSe. This has been demonstrated to the enhance quantum efficiency in the infrared and boost the device short-circuit current ($J_{SC}$). Interestingly, despite having a lower bandgap, devices using Se have achieved open-circuit voltages ($V_{OC}$) on par with (unalloyed) CdTe-based devices. Recent time-resolved photoluminescence and cathodoluminescence data suggest that the CdSe$_{1-x}$Te$_{1-x}$ materials have lower recombination rates and improved grain-boundary passivation relative to CdTe, and this appears to be making up for bandgap-related $V_{OC}$ losses[1]. Further characterization studies should reveal additional relationships between absorber processing and the CdSe$_{1-x}$Te$_{1-x}$ composition, current collection, recombination, etc., that can be used to optimize device performance.

There are two methods of CdSe$_{1-x}$Te$_{1-x}$ growth. The first method creates a CdSe window layer for a CdTe device then allows diffusion to create a dopant gradient. The second processing method deposits a CdSe$_{1-x}$Te$_{1-x}$ alloy layer and then a CdTe layer. Previous characterization studies have focused on the CdSe/CdTe device structure and the effects of changing window layer thickness and composition. A study by Poplawsky, et al. [2], indicated that, as CdSe window thickness increased, device performance increased then quickly decreased. Quantum efficiencies and correlative SEM/TEM analysis indicated that if the Se concentration was above 40 at%, grains could change phases from zinc-blende to wurtzite and stop contributing to the device photocurrent. In the CdSe$_{1-x}$Te$_{1-x}$/CdTe structure, the Se concentration can be kept below 40 at% to prevent the formation of the wurtzite phase.

To better understand the impact of Selenium concentration on device photo-collection, an Electron Beam Induced Current (EBIC) study is presented which studies the impact of Selenium on device collection for the CdSe$_{1-x}$Te$_{1-x}$/CdTe device structure. EBIC is an SEM-based characterization technique which uses an electron beam to locally excite carriers, which are subsequently collected and analyzed to understand microstructural effects on recombination. A current collection map can thus be created with sub-micron resolution. EBIC has been previously used to identify local variation in collection current at microstructural features such as heterojunction interfaces and grain boundaries[2]. In this study, selenium concentration was varied in the alloy layer from 0 to 40 atomic percent while maintaining constant deposited layer thickness. EBIC analyses of these alloy junctions indicate that the highest carrier collection was near the CdSe$_{1-x}$Te$_{1-x}$/CdTe interfaces with a second collection peak near the TCO/CdSe$_{1-x}$Te$_{1-x}$ interface. This finding is indicative of a buried junction in the CdSe$_{1-x}$Te$_{1-x}$/CdTe device. Previous studies on the CdSe/CdTe structure have shown highest collection near the TCO contact with no buried junctions. The position and strength of this buried junction could decrease the effect of interface recombination at the TCO interface, but it could also decrease drift velocity, negatively impacting performance. These competing effects need to be better understood for the optimization of CdSe$_{1-x}$Te$_{1-x}$/CdTe device performance.

The presence of a buried junction in the CdSe$_{1-x}$Te$_{1-x}$/CdTe device implies a complex change in carrier concentrations and band structure within these devices. In order to better understand the implications of this observation, these results are correlated with a finite element device model. Using this model, it is possible to calculate the equilibrium band structure of the device and estimate the built-in potential between at each junction.


S.EL01.06.33
Effects of Very High Workfunction Metals or Metal Alloys (NiCr) on High Switching Speed, HV Schottky Diodes for Mixed-Signal or RF ASIC

James Pan; Northrop Grumman Corporation, United States

For high switching speed HV Schottky diodes, with very high work function metal and extremely lightly doped epi, the built-in potential may be too high for thermionic emission to occur, when the applied external voltage is quite low (near the forward voltage: $V_F = 0.07\text{V}$). If the epi is lightly doped p type, the built-in potential ($V_{\text{Built-in}}$: potential difference between the metal and silicon Fermi levels) is 1.0V (measured with CV). If the external bias is 0.1V, near the measured $V_F$, it is not enough to overcome the built-in potential for thermionic emission as illustrated in the Figures. It is likely that in addition to thermionic emission, tunneling and diffusion currents also contribute to the total HV Schottky diode forward current. TCAD simulation of HV Schottky diodes with N+ guard bands suggests the potential barrier and electric fields at the Schottky junction are relatively high for thermionic emission to occur, when external bias $V \gg V_F$.

In the Advanced Technology Laboratory (ATL) at Northrop Grumman Corporation, high performance RF ASICs and power devices in silicon, GaAs, GaN and 4H SiC are simulated, designed, fabricated, and packaged. Extensive DC and RF tests are conducted. The performance of HV Schottky diode is superior to conventional p-n junction diode due to higher BV, lower reverse leakage, lower $V_F$ and higher output current. We have fabricated HV Schottky Diodes. $BV > 150\text{V}$. $V_F = 0.07\text{V}$. High breakdown voltage, low forward voltage drop, and low reverse leakage are achieved with very high work function metal alloys and low doping epi films.

Lightly doped p (100) or n (100) type silicon films are deposited with epitaxy. Metal or metal alloys are deposited with sputtering. Figure 1 shows the measured I-V’s for the Schottky Diodes. Avalanche breakdown voltage > 150V is recorded with low reverse leakage current. The voltage required to turn the diode on is defined as $V_F$ -- when the current reaches 0.1uA.

Forward bias characteristics of Ti, Au, and NiCr are measured. These data indicate that in order to achieve low $V_F$ and high current, very high work function metals are needed.

High frequency CV tests are conducted using the HV Schottky Diodes. These CV data are used to extract the doping profiles.

Metal work functions are extracted with the $1/C^2$ vs. $V$ plots. Interception with the x axis is $DV$, which is the potential difference between metal and silicon Fermi levels, or built-in potential $V_{\text{Built-in}}$. Metal work function is extracted with $DV$. One of the Figures shows the measured doping profiles and $1/C^2$ vs. $V$ plots. From the measured I-V and C-V data we may calculate the avalanche breakdown critical electric fields and metal work functions. A summary of HV Schottky diodes fabricated with NiCr, Ti, Au in Si n and p epi films will be presented.

Energy band diagram is analyzed for HV Schottky diodes: NiCr in p epi (external bias = 0V) $V_{\text{Built-in}} = 1.00\text{V}$.

Another energy band is analyzed for HV Schottky diodes: NiCr in n epi (external bias = $+0.50\text{V}$). $V_{\text{Built-in}} = 1.56\text{V}$.

In conclusion: we have fabricated HV Schottky Diodes. $BV > 150\text{V}$. $V_F = 0.07\text{V}$. High breakdown voltage, low forward voltage drop, and low reverse leakage are achieved with very high work function metal alloys and low doping epi films. Diffusion and tunneling currents likely contribute to the total Schottky junction current.

S.EL01.06.36
Chemistry Behind Dodecanethiol Treatment of Colloidal CsPbBr3 Nanocrystals with Photoluminescence Quantum Yields Reaching ~100% Md Aslam Uddin, Justin K. Mobley, Abdullah A. Masud, Tuo Liu, Rosemary L. Calabro, Doo Y. Kim, Christopher I. Richards and Kenneth R. Graham; University of Kentucky, United States

Metal halide perovskite nanocrystals (NCs) are attractive materials for optoelectronics because of their optical and electronic properties, such as tunable direct band gaps, high absorption coefficients, low exciton binding energies, relatively high electron and hole mobilities, narrow emission line-widths, and high photoluminescence quantum yields ($\Phi_{\text{PL}}$). However, further improvements in stability and reproducibility in $\Phi_{\text{PL}}$ of NCs are essential for enabling future optoelectronic applications. Inadequate surface passivation due to labile parent ligands, such as oleate and oleyl ammonium ions is a major cause of instability and less than unity $\Phi_{\text{PL}}$. Herein, we probe the influence of multiple molecular and ionic ligand binding
groups including thiols, thioethers, phosphine, phosphine oxide, sulfobetaine, thiocyanate, and sulfate salts on the colloidal stability and ΦPL of CsPbBr₃ NCs. Among all the binding ligands, post-synthetic treatment with dodecanethiol reproducibly yields highly stable NCs with near unity ΦPL for a range of synthetic conditions and initial ΦPL of the as-synthesized NCs. A few of the other ligands can also increase the ΦPL, but in ambient atmosphere they are unable to maintain stability more than 5 days. A mechanistic investigation shows that thiol addition to the as-synthesized NC dispersion leads to the thiol-ene reaction with octadecene, oleic acid, & oleylamine and formation of thiolate ions and thioethers. Both thiolates and thioethers are suspected to bind to undercoordinated Pb atoms and consequently eliminate metallic Pb particles commonly observed with transmission electron microscopy on the NC surfaces. The process of enhancing PL intensity and stability can be rapidly accelerated through exposure to blue or UV light.

S.EL01.06.39
Fast and Simplified Synthesis of Spiky-Like Copper Sulfide Nanoballs by Soft Chemistry Method for Optoelectronics Applications
Anderson Klay R. Jaime, Diana V. Hernández, Judith Celina T. Córdova and Santos J. Castillo; Universidad de Sonora, Mexico

Fast synthesis of copper sulfide nanoparticles through two different methods is described in the present investigation. The first reaction was carried out by applying of heating in constant temperature water bath while in the second case the mixture was sonicated. As copper and sulfur sources, copper nitrate and thiourea solutions were used respectively. Main physicochemical properties of the synthesized samples were studied using several characterization techniques. Formation of copper sulfide with hexagonal crystalline structure was corroborated, coinciding with previously reported values for covellite. The most important results corresponded to the un-sonicated sample, which exhibited spiky-like nanoballs morphology and better size distribution. Optical tests revealed band gaps of 1.69 and 2.05 eV, while photoluminescence emissions at 421 and 430 nm, showing promising possibilities for applications in solar cells, catalysis and optoelectronic devices.

S.EL01.06.40
Effect of Si Nanoparticles on Reflectance Spectra for Ge and Ge/Si Substrates
Sabina Abdul Hadi¹, Ayman Z. Rezk² and Ammar Nayfeh³; ¹University of Dubai, United Arab Emirates; ²Khalifa University, United Arab Emirates

The continuous innovation in nano materials has allowed the development of new antireflective coats (ARCs) for optical lenses, solar cells, data storage, displays and others that require a reduced reflectance to increase efficiency. Multi-layered ARCs particularly have attracted attention lately for demonstrating low and tunable spectral reflectance.

This paper presents a simple approach for forming anti-reflective coating stacks on bulk Ge and PECVD Ge grown on Si employing colloidal dispersions of Si nanoparticles (NPs).

The Si NPs have a diameter of 2.85 nm and are prepared by chemical etching of crystalline Si wafers in HF and H₂O₂ using electrical or hexachloroplatinic acid catalyst. The nanoparticles are recovered by sonicating the wafers in isopropyl alcohol, forming a stable colloid with concentration of 10 µM [1].

Each antireflective coat is applied by the drop casting of monodispersed Si NPs on a 3 by 3 cm pieces of both Ge bulk and PECVD Ge grown on Si. A total of 5 drops are applied with each drop consisting of 100 µL. After each drop, the samples are left to dry for an hour and a half.

For bulk Ge, (110) Sb doped (n-type) Ge with a resistivity of 0.1–0.5 Ωcm were used, while for the PECVD Ge growth, (100) P doped (n-type) Si with a resistivity of 0.01–0.02 Ωcm are used as starting substrates. An Oxford Instrument System 100 PECVD activated by 13.56 MHz radio frequency signal is used to grow Ge layers on Si substrates. High purity germane (GeH₄), H₂ and Ar gases are used as precursors for Ge growth. The undoped Ge film was grown using the two-step approach, which has been described in detail in our previous work [2].

The impact of multiple drop casting of Si NPs on the antireflective properties of the Ge surfaces were investigated by the analysis of their reflection spectra. The reflectance of the coating was measured at four locations on each sample by a UV–VIS spectrophotometer (Lambda 850, PerkinElmer). The samples were qualified by controlling the reflectance at the four points within an error of 1.2%. The corresponding reflection spectra were captured as a function of the incident wavelength, ranging from 250 nm to 1500 nm.

For PECVD Ge grown on Si substrates, the average reduction in reflectance has shown to increase as the incident wavelength decreases, with a decrease of ~2% after each 100 µL coating. After 5 drops (100 µL ×5), the overall reflectance across the whole spectra is on average 9.35% lower compared to the uncoated samples. The minimum decrease in reflectance was of
2.49% at 1290 nm and the maximum of 34% at 250 nm.

For Bulk Ge, the average reduction in reflectance has shown to increase as the incident wavelength decreases from 1500 nm to 320 nm. At 500 μL, the reduction in reflectance had an average of 6.16% (Min.: 2.73% at 1500 nm, Max.: 13.75% at 320 nm and Median: 5.1%). At lower wavelengths range from 250 nm to 320 nm), the amount of reflectance reduction is less compared to wavelengths above 320 nm.

After 5 drops (100 μL × 5) on PECVD Ge samples, the incident wavelength where the minimum reflectance occurred (λ_{min}), shifted from 1050 nm where reflectance is lowered by 34.5%, to 410 nm with 25.2% reduction in reflectance. While for bulk Ge sample, λ_{min} shift occurs from ~1480 nm to ~420 nm with a decrease in reflectance of 37.9% and 28%, respectively.

Results demonstrate that it is feasible to deposit a coating of Si NPs with tunable reflectivity over a wide range by drop casting multiple layers of the nanoparticles.


S.ELO1.06.41
An Improved Model of Ge Bi-Layers Incorporated CZTSe Devices with MoSe2 Interlayer

Sanghyun Lee1, Kent Price2 and Edgardo Saucedo3; 1Indiana State University, United States; 2Morehead State University, United States; 3Institut de Recerca en Energia de Catalunya, Spain

As environmentally benign and highly-efficient thin-film solar cells, low-cost Cu2ZnSn(S,Se)4 (or kesterite) solar cells, herein CZT(S,Se) have been steadily emerging as an alternative for the 2nd generation Cu(In,Ga)Se2 (CIGS) and CdTe solar cells in the past several years. CZT(S,Se) solar cells have several advantages such as high absorptions coefficient (>10^4 cm⁻¹), tunable direct band gap energy (1 to 1.4 eV), and usage of abundant elements in earth's crust, becoming an ideal platform to harvest solar energy. However, the efficiency improvement and understanding of emerging CZT(S,Se) is still in an early stage compared to the 2nd generation counterparts. In recent progress, our team reported that Germanium (Ge) incorporation into CZTSe solar cells has improved device performance, which contributed to deepening understanding of Ge-alloyed CZT(S,Se) solar cells, in particular, on the Schottky-type back-contact barrier.

We present the complete set of models about the Schottky barrier with the MoSe2 interlayer between the absorber and Molybdenum (Mo) back-contact. Developed analytical models with in-house MATLAB simulators agree well with TCAD numerical simulation and experimental results. A new concept of an effective back-contact barrier is introduced, which provides the mechanism of the improved device performance with lower back-contact barrier for CZTSe Ge bi-layers devices. By incorporating nanoscale Ge bi-layers below and above the CZTSe absorber, the back-contact barrier is improved by 33 %, and power conversion efficiency is improved by 1.1 % than Ge single-layer devices. Based on the back-contact model, defect concentration of Ge reference devices is estimated to be 5.4 x 10^16 cm⁻³, whereas Ge bi-layers devices show an estimated 9.8 x 10^15 cm⁻³ at the back-contact interface. To compare models with experimental results, we fabricated three different types of CZTSe: nanoscale Ge devices. The property of the back-contact barrier is assessed by characterizing a temperature-dependent behavior of CZTSe alloyed devices.

Collectively, the reduced defect concentration by Ge incorporation in the MoSe2 interlayer improves the barrier height of back-contact. As the defect concentration of the MoSe2 interlayer increases, the benefit from the back-contact barrier lowering by the valence bands offset is reduced and essentially eliminated. Moreover, the increased effective back-contact barrier degrades the series resistance and the overall device performance. However, the barrier at the interface between MoSe2 and Mo metal contact remains the same, even with MoSe2 defect concentration increase. Incorporating thin Ge nanolayer at the interface between the absorber and MoSe2 could positively influence and possibly reduce the defect states, which lowers the effective back-contact barrier from modeling and simulation results. Hence, the Ge layer at the back-contact interface successfully improves the conversion efficiency up to 8.3 % with the improved back-contact.

S.ELO1.06.42
16.5% ZMO/CdTe Solar Cells with Copper Thiocyanate as Back Contact

Dengbing Li, Sandip S. Bista, Fadhil K. Alfadhili, Niraj Shrestha, Rasha A. Awni, Zhaoning Song and Yanfa Yan; University of Toledo, United States

The replacement of traditional CdS buffer layer with magnesium doped zinc oxide (ZMO) has been demonstrated helpful to boost higher CdTe solar cell performance exceeding 18% due to the reduced interface recombination and parasitic light absorption by buffer layer. However, due to the atmosphere sensitivity of ZMO film, The post-treatments of ZMO/CdTe
stacks, including CdCl2 treatment, back contact deposition et. al, which are critical for high performance CdTe solar cells, became crucial challenge. In order to maximize the expected benefit of ZMO cooperation, plenty of investigation need to be accomplished in the future. Here, copper thiocyanate (CuSCN) is demonstrated to be a powerful back-contact material with multi-advantages without degrading ZMO layer in CdTe solar cells, even with ammonium hydroxide as the solvent. The thickness of CuSCN film as well as the subsequent annealing temperature are systematically investigated and the highest efficiency 16.5% has been achieved with open-circuited voltage 850 mV, short-circuited current 26.2 mA/cm² and fill factor 74.0%.


S.EL01.06.46
Improving the Properties of Chemically Deposited SnS Thin Films via Metal/Metal Halide Assisted Heat Treatment Rohini Neendoor Mohan, Oscar Gomez Daza, Angelica L. Espinosa Santana, Diana E. Lara Llanderal, Padmanabhan Karunakaran Nair and M.T. Santhamma Nair; Universidad Nacional Autonoma de Mexico, Mexico

Tin sulfide (SnS) is a desirable absorber layer for thin film solar cells. Its optical bandgap of 1.1 eV, absorption coefficient of $10^5$ cm$^{-1}$ in the visible region, inherent p-type electrical conductivity, non-toxicity, earth abundance of the constituent elements, and stability in humid and oxygen ambient are all attractive toward developing alternative solar cell technology. Nevertheless, solar cells of SnS have reached a photovoltaic conversion efficiency of only 4.8%. The presence of secondary phases (SnS$_2$, SnS$_3$) and small grains is among the efficiency limiting factors. Here, we present methods to enhance the quality of chemically deposited SnS films through using thin layers of Sn and SnCl$_2$ as flux materials produced by thermal evaporation and/or sulfur vapor to play a key role in grain growth during heating at 450 °C, while conserving its p-type electrical conductivity.

We prepared SnS thin films of 300 nm in thickness in an autoclave at 2.5 atmospheres and 55 °C with duration of deposition of 6 h. The deposition solution contained tin chloride and sodium thiosulfate. The as-deposited SnS thin films were of orthorhombic crystal structure, with an optical bandgap of 1.33 eV (indirect) and electrical conductivity of $1\times10^{-4}$ Ω$^{-1}$ cm$^{-1}$ in the dark and $1\times10^{-3}$ Ω$^{-1}$ cm$^{-1}$ under illumination. The films presented compact surface and dense cross-sectional morphology. We heated this film for 30 min, in a tubular oven in nitrogen atmosphere at 450 °C. Different flux materials were added during the heating to promote grain growth: sulfur, evaporated thin films of Sn metal, or SnCl$_2$. The film heated with sulfur powder was p-type, with electrical conductivity, $10^{-4}$ Ω$^{-1}$ cm$^{-1}$. SnS films heated under the same conditions using Sn as well as SnCl$_2$ as flux materials retained the single phase of SnS with the formation of well-defined columnar grains of size equivalent to film thickness. They have a bandgap of 1.1 eV (indirect) and p-type electrical conductivity, $10^{-3}$ Ω$^{-1}$ cm$^{-1}$ in the dark, which increases to 1.5 times, under illumination. Thus, heating SnS absorber films deposited at a low temperature using chemical methods, with Sn or SnCl$_2$ as flux materials is a promising methodology to achieve grain growth. We shall illustrate the effect of this in solar cells using SnS as absorbers.

S.EL01.06.56
Pulsed Laser Deposited Polycrystalline Thin Films of MoO$_3$ for Sensing of High-Energy Moieties Dhanashree Sable, Swapnali Rabade and Sangeeta N. Kale; Defence Institute of Advanced Technology, India

Among various nanostructured metal oxides, molybdenum oxide (MoO$_3$), a wide band-gap n-type semiconductor, has attracted much interest as a promising gas sensor because of its excellent sensitivity, good reproducibility, low cost, high compatibility with microelectronic processing, low electron recombination rate, and high stability. The MoO$_3$ thin films have promising electrical properties for gas sensing applications. To synthesize two-dimensional materials under ultra-high vacuum is a key advantage for enhancing the properties of nanostructured materials. In this presentation, we demonstrate the synthesis, characterization, and gas sensing properties of MoO$_3$ films, which were grown using Krypton-Fluoride (248 nm) excimer laser. Deposition was done under 200 mTorr Oxygen pressure at the substrate temperature of 600°C. The targets used for deposition were synthesised using hydrothermal method. The deposition was done with the optimized parameters, to ensure good polycrystalline films on the Si (001) substrate. The optical, morphological and compositional properties of MoO$_3$ films were studied by using UV-Visible spectroscopy, Scanning Electron Microscopy and Raman Spectroscopy. The formation of MoO$_3$ was also confirmed using X-Ray Diffraction technique. The MoO$_3$ films showed excellent response to NO$_x$ and NO$_2$ gas moieties, at even low gas concentrations from 100 ppm onwards. The sensor not only exhibits high sensitivity but also good selectivity towards NO$_2$ gas.
As devices continue to trend towards the micro- and nanoscale, the influence of individual crystal defects on their optical, electronic, and thermal performances becomes significant. As an example, the thermoelectric properties of these nanodevices are closely related to the presence of crystal defects, grain boundaries, and strain. While the effects of interfaces and grain boundaries on thermoelectric performance have been widely studied in semiconductor materials, there remains an incomplete understanding of the role that crystal defects play in metals. A major challenge in pinpointing the origins of thermoelectric variation in metallic nanodevices is the difficulty in preparing high quality crystalline thin-film metal microstructures on thermally and electrically insulating amorphous substrates.

Controlling the micro- and nanostructure of metals offers the opportunity to investigate and engineer the properties of metal nanotechnologies. Here, we report a high-throughput method for preparing patterned crystalline gold microstructures grown directly on amorphous insulating oxide via rapid melt growth. In this growth process, thin-film gold-platinum metal-seed microstructures are encapsulated in an insulating crucible and annealed at temperatures above gold’s melting point. During cooling, liquid epitaxial growth directs single crystal solidification [1]. We can extend this platform to controllably prepare single grain boundaries [2], enabling the systematic study of the role of defects in governing local thermoelectric behavior. A scanning photothermoelectric (PTE) setup to allows us to probe the microscopic variations in photovoltage across the gold single crystal and bicrystal wires. Surprisingly, we observe a photovoltage distribution where local changes in Seebeck coefficient are highly influenced by long-range strain fields and concentrated dislocations and uncorrelated with plane grain boundary defects. Our results showcase the link between the presence of elastic strain and dislocations to the PTE effect using a model material system.


**S.EL01.06.60**

**Room Temperature Fabrication of Two-Dimensional Electron Gas (2DEG)-Based High Performance Oxide Thin-Film Transistors**

Dong Hyun Choi, Jeong Woo Park, Hyukjoon Yoo, Jusung Chung, Hyung Tae Kim, Min Seong Kim and Hyun Jae Kim; Yonsei University, Korea (the Republic of)

Amorphous oxide semiconductor (AOS) based thin-film transistors (TFTs) have been rapidly evolved from academic curiosity to the display industry because of their many advantages such as low off-current, high uniformity over large area fabrication, and high visible light transparency compared to conventional amorphous silicon (Si) TFTs. Despite these advantages, the poor electrical performances such as low field-effect mobility compared to low-temperature polycrystalline Si TFTs have been an issue for high resolution and high frame rate displays. Thus, a wide range of research has been conducted to enhance the field-effect mobility in AOS TFTs: doping a nano-conductor in the back channel, adoption of high-k gate insulators, and capping reduction layer. Among such researches, one of the most prominent methods was applying heterostructure with different oxide semiconductors to the channel layers of TFTs; due to large on-current and high field-effect mobility. The large difference in the work function of oxide semiconductor layers results in bandgap mismatches, forming potential wells. Therefore, electrons are confined in the potential well forming a 2-dimensional electron gas (2DEG). However, to apply 2DEG-based TFTs to the actual display industry, accurate 2DEG control and formation mechanisms need to be further studied.

In this paper, high performance oxide TFTs were fabricated by sodium hydrosulfite (Na$_2$S$_2$O$_4$) reducing agent treated indium-zinc-oxide (r-IZO) as the front channel of zinc-tin-oxide (ZTO)/r-IZO heterostructure. Front channel IZO film was deposited by RF sputtering at room temperature. For reducing the IZO film, the IZO film was dipped into Na$_2$S$_2$O$_4$ solution. Applying the Na$_2$S$_2$O$_4$ reducing agent treatment on the front channel allows controlling the amount of confined electron at the interface between the front and the back channels for heterostructure oxide TFTs. For the back channel, ZTO film was deposited by RF sputtering at room temperature. ZTO/r-IZO heterostructure is suitable for the formation of 2DEG due to the large difference in work function, so it could produce high field-effect mobility even when fabricated at room temperature. Also, the large on-current could be achieved by precisely controlling the formation of 2DEG through Na$_2$S$_2$O$_4$ reducing agent treatment on the IZO front channel. To confirm the formation of 2DEG at the interface between the ZTO film and the r-IZO film, we performed a UV-vis spectrophotometer and ultraviolet photoelectron spectroscopy (UPS) measurements. The 2DEG was successfully formed by showing the difference of 170 meV work function at the heterointerface. However, conventional 2DEG-based oxide TFTs have high off-current because 2DEG free electrons remained at the heterointerface regions even
when the TFT is in the off-state. To solve this problem, the ZTO back channel was applied to different oxygen partial pressures to the lower ZTO layer (20%) and the upper ZTO layer (30%) when deposited via sputtering. As a result, the high off-current could be adjusted to near the $10^{-12}$ A range and ZTO/r-IZO TFTs exhibit field-effect mobility of 29.55 cm$^2$/Vs, a subthreshold swing of 0.48 V/decade, and an on/off current ratio of $5.02 \times 10^8$.

The results show that room temperature fabricated ZTO/r-IZO heterostructure TFTs can be used as a general route for high field-effect mobility TFTs and controllable oxide semiconductor devices for offering compatibility of the flexible and high-end display technology.

S.EL01.06.62
The Effects of Etching Parameters on Surface Morphologies by Anisotropic Etching with Resist-Mask
Pin Y. Chen, Yu-De Li and Kun-Dar Li; National University of Tainan, Taiwan

For a long time, the etching technique played an important role in the electronics industry, and had a critical influence on the development of modern manufacturing technologies. Regarding to the operation of electronics devices, surfaces and interfaces significantly affect the functionality and performance of the devices. To investigate the formation mechanisms for characteristic surface morphologies during chemical etching, in this study an anisotropic chemical etching model was established and the formation and evolution of surface structures with resist-masks were simulated numerically. In this theoretical model, two major crystallographic orientations in a cubic system, such as $<100>$ and $<111>$ directions, were taken into consideration and included in the reactions of surface diffusion and anisotropic etching. By adjusting the numerical parameters corresponded to the different experimental conditions, various surface profiles could be created and the influence of the experimental parameters on the surface morphologies would be revealed. From the calculations of anisotropic etching along $<100>$ preferred-directions, a V-shape profile with faceted surface morphologies appeared. A larger loss of linewidth or a higher etch bias was displayed with the increase of the etching rate. While an anisotropic etching along $<111>$ preferred-direction was examined, etch pits were firstly produced in the early stage of etching process. A different surface evolution during a chemical etching was distinctly demonstrated due to the crystallographic structure. In addition, since the resist-mask was included in the numerical model, the phenomenon of undercutting in an anisotropic chemical etching could be also discussed in this study. These numerical simulations could provide a fundamental information to understand the formation mechanism of etched surface, and broaden the applications of chemical etching in the advanced manufacturing technologies.

S.EL01.06.63
High Efficiency X-Band AlGaN/GaN HEMT with Improved TiN/Ti/Al/Ni/Au
Ke Wei, Yichuan Zhang, Shen Zhang, Guoguo Liu, Xiaojuan Chen, Yingkui Zheng, Sen Huang, Xinghua Wang and Xinyu Liu; Chinese Academy of Sciences, China

GaN based high electron mobility transistors (HEMTs) are considered of great potential to be the building blocks in the next-generation microwave power amplifiers due to their excellent power handling capabilities. Ohmic contact and passivation technology are the main factors of device power and efficiency. Improving device efficiency is the premise of improving application system efficiency. Nowadays, more and more efforts are made to improve the efficiency of GaN HEMTs. In this paper, we report the AlGaN/GaN HEMT with improved ohmic contact and double layer passivation. The device show an excellent power characteristics.

The epitaxial layers consists of a 1.5nm GaN cap layer, 22nm Al0.25GaN, 2nm AlN and GaN buffer layer. The process for GaN HEMT devices is as followed the steps: a) make, b) ohmic contact etching ion; c) isolation; d) gate; e) double passivation by Al/SiN; f) via and metal. The source-drain and gate length are 2.40µm and 0.25µm. The TEM result shows the cross section of recessed TiN/Ti/Al/Ni/Au. For comparison. Conventional structures of MOCVD HEMT is also fabricated simultaneously.

Measurements are performed in continuous wave (CW) mode, load-pull power measurements of this 4x50µm device at 10 GHz is carried out. The device is biased at a voltage of 35V, the output power reached 31.50dBm (7.0W/mm) with 70% power-added efficiency (PAE) and 14dB gain. Such a good RF power performance comes from the improved ohmic contact and new double passivation layer.

The interface of ohmic contact is analyzed by means of TEM. It is found that tin thin layer combined with recessed process is more conducive to the formation of low contact resistance.

S.EL01.06.65
Halogenated Si(100) Surface Chemistries for Atomically-Precise Fabrication
Kevin J. Dwyer, Karen Gaskell and Robert Butera; 1University of Maryland, United States; 2Laboratory for Physical Sciences, United States

The use of halogen chemistries on silicon surfaces offers a promising path towards atomic-scale manufacturing of acceptor-
based devices. Atomically-precise fabrication of electronic devices in silicon has been widely demonstrated using a scanning tunneling microscope (STM) and hydrogen-based surface chemistries to precisely place phosphorus donor atoms on the surface. A lithographically patterned hydrogen resist is used to selectively incorporate PH₃ to produce metallic wires, quantum dots defined by electrostatic gates, and single donor atom qubits for quantum information (QI) research. However, interest in acceptor dopants and hole-based devices necessitates the development of alternate precursors and/or resist chemistries for device fabrication. To incorporate acceptors into silicon with atomic placement, halogen chemistry is potentially more favorable than hydrogen. To that end, we explore halogen-based resists including chlorine, bromine, and iodine in conjunction with metal-halide precursors to achieve area-selective deposition of acceptor dopants in silicon. Here, we present results on the complete surface passivation of Si(100) using Cl, Br, and I. We study the stability of halogen-terminated Si(100) surfaces in ambient environments using STM and x-ray photoelectron spectroscopy (XPS) to facilitate transport of samples outside of ultra-high vacuum environments. Finally, we present STM and secondary ion mass spectroscopy (SIMS) results on the adsorption and incorporation of metal-halide precursors on Si(100) as a viable path towards acceptor doping.

S.E.L01.06.66
Plasma-Based Modification of Superconducting/dielectric Interfaces Evgeniya H. Lock1, Sandra Rodriguez Villanueva2, Peng Xu3, Yaniv Rosen4, Michael Katz5 and Kevin Osborn6; 1US Naval Research Laboratory, United States; 2University of Puerto Rico at Rio Piedras, United States; 3University of Maryland, United States; 4Lawrence Livermore National Laboratory, United States; 5National Research Council, United States; 6Laboratory of Physical Sciences, United States

Superconducting resonators and qubits are essential for the development of quantum-computing architectures. These systems depend on high quality superconducting materials and interfaces, in which the two-level systems loss is minimal. Our previous work focused on understanding of the effects of plasma modification of vacuum/silicon and vacuum/superconductor interfaces on the performance of TiN/Si superconducting microwave resonators. In this paper, we discuss plasma-based modification of TiN/Si interface. We provide a systematic study of every step in the preparation of the TiN/Si heterostructures, namely the chemical treatment with hydrofluoric acid of SiO₂/Si surface, the plasma treatment of H-terminated Si and the TiN film deposition processes. We find that both the gas environment and the plasma processing conditions affect the modification of Si, which in turn affects the composition of the TiN/Si interface. The impact of this work lay in providing new approaches to TiN/Si interface preparation which may enable reduction of metal/dielectric interface losses thus improving the superconducting microwave resonators performance. This work was partially supported by the office of Naval Research through Naval Research Laboratory Base Program.

S.E.L01.06.68
Monitoring the Adsorption of Thiol and Isocyanide Molecules on Silver Surface by In Situ Surface-Enhanced Raman Scattering Shi Shi, Jaewan Ahn and Dong Qin; Georgia Institute of Technology, United States

In this talk, we report the use of surface-enhanced Raman scattering (SERS) to investigate the adsorption of thiol and isocyanide molecules on colloidal Ag nanocubes \textit{in situ}. In a typical process, we mixed Ag nanocubes with ligand molecule solutions at different concentrations and then collected SERS spectra at different time points. We demonstrate that 4-nitrothiophenol (4-NTP) binds to the Ag surface rapidly because of the strong Ag–S chemical bonding. By decreasing the concentration of 4-NTP, we observe red shifts of the νNO₂ band, which suggests the change to the orientation of ligands on the surface. Different from thiols, the 1,4-phenylene diisocyanide (1,4-PDI) binds to the Ag surface through σ–donation with weaker binding strength. By increasing the concentration of 1,4-PDI, our results indicate that the molecules tend to adopt an orientation that tilts away from the surface. More interestingly, we investigate the competitive binding behavior of these two ligands by introducing Ag nanocubes into a solution containing both 4-NTP and 1,4-PDI. Our results show that thiol is more preferential to bind onto the surface when the concentrations of the two ligands are comparable in the solution.

S.E.L01.06.70
Vertically Aligned Metal Nanowire Composites for Flexible and Conductive Thermal Interface Materials Max Kuciej1,2, Jesse Tice2, Dwight Streit1 and Michael T. Barako2; 1University of California, Los Angeles, United States; 2Northrop Grumman Corporation, United States

Conventional thermal management solutions in microelectronics packaging suffer from an inability to effectively couple thermal conduction and mechanical compliance into a single material, routinely necessitating a sacrifice in thermal, and therefore device, performance in favor of mechanical reliability. For the past few decades, compliant thermal interface materials (TIMs) have been limited to polymers loaded with dispersions of unaligned or randomly distributed conductive elements which can only achieve thermal conductivities up to \(\sim 5 \text{ W m}^{-1}\text{K}^{-1}\). Here, we present the processing and...
characterization of a compliant, vertically-aligned metal nanowire composite ideal for achieving thin, flexible interfaces with low thermal resistance. The aligned nanowire composite is fabricated by electroplating copper into a 25-45% porous, sacrificial ceramic template, liberating the nanowires by chemically dissolving the template, and infusing the resulting nanowire array with a thermally stable polymer by capillary-driven wicking. An integrated bonding layer is added by sub-filling the template with copper and sequentially electroplating metallic solder to form localized solder tips on the nanowires. The entire fabrication process can be completed at wafer-scale with a lateral area up to 12.5 inches². The thermal performance of the composite TIM was evaluated with a modified thermal resistance measurement designed to mimic typical operating conditions. The double-sided construction of the composite and integrated bonding layers facilitate integration between any two arbitrarily-chosen surfaces by enabling the absorption of interfacial strain, mismatch, and roughness while achieving thermal conductivities up to 200 W m⁻¹K⁻¹, significantly advancing the state-of-the-art in TIMs.

S.EL01.06.75
Exciton-Trapping by Stacking Fault Defects in GaAs Peter V. Sushko¹, Steven R. Spurgeon¹, Bethany Matthews¹, Xiayu Linpeng², Mikhail Durnev³, Mikhail Glazov³, Maria Viitaniemi², Andreas Wieck⁴, Arne Ludwig⁴ and Kai-Mei Fu²; ¹Pacific Northwest National Laboratory, United States; ²University of Washington, United States; ³Ioffe Institute, Russian Federation; ⁴Lehrstuhl für Angewandte Festkörperphysik, Germany

The need to increase coherence times in quantum devices simulates the search for materials systems that can exhibit electronic states not affected by structural and chemical inhomogeneities. Owing to the advances in synthesis of III-V semiconductors, concentrations of point defects and impurities in these materials can be well controlled, while stacking faults (SFs) provide asymmetric quasi-2-dimensional potential wells that behave as internal interfaces capable of trapping excitons [1]. Here we use ab initio simulations to examine how the stability and electronic properties of SFs change as a function of the distance between them and how the details of their configuration affect spatial distribution of the electron and hole components of excitons and their effective masses. Our simulations suggest that a potential drop of the order of 10 meV is associated with an isolated SF, which is sufficient for the hole to localize predominantly at the SF and to induce an asymmetric distribution of the excited electron density in the vicinity of the SF. For interacting SFs, we find that the electron distribution is sensitive to both the type of the SFs and the distance between them. This coupling provides a pathway to the design of materials with spatially resolved excitonic properties and photo-emission energies by controlling the density and relative arrangements of the stacking faults.


S.EL01.06.76
Observation of Hyperfine Interactions of Silicon Vacancies in 4H-SiC Metal-Oxide-Semiconductor Field-Effect Transistors Utilizing Ultra-Low Field Frequency Swept Electrically Detected Magnetic Resonance James Ashton¹, Patrick Lenahan², Brian R. Manning¹ and Aivars J. Lelis²; ¹The Pennsylvania State University, United States; ²U.S. Army Research Laboratory, United States

4H-SiC metal-oxide-semiconductor field-effect transistors (MOSFETs) have great potential in high power and high temperature applications. However, near-interface defects degrade the effective channel mobility and thus limit the performance of 4H-SiC MOSFETs. In this work, we utilize electrically detected magnetic resonance (EDMR) to study hyperfine interactions with spin-dependent recombination (SDR) of silicon vacancy defects at the 4H-SiC interface in 4H-SiC MOSFETs. The physical foundation of EDMR is electron paramagnetic resonance (EPR). In EPR and EDMR, a sample is subjected to a large, slowly varying magnetic field and an RF or microwave oscillating field at a frequency v. In the simplest case, EPR is achieved when hv=gβH. Here, h is Planck’s constant, v is the electromagnetic radiation frequency, g, is the free electron g factor (g ≈ 2.0023), β is the Bohr magneton, and H is a large externally applied magnetic field. At resonance, the electron transitions from its +1/2 to -1/2 spin state (or vice versa). The analytical power of EPR and EDMR comes from deviations from this simple case caused by the paramagnetic site environment. These perturbations are, for the most part, caused by hyperfine interactions, interactions of the electron with magnetic nuclei, and spin-orbit coupling. EPR detected via SDR allows for measurements of small numbers of defects via spin-dependent changes in device current. The sensitivity of SDR/EDMR is very nearly independent of the field or frequency at which the measurement is made. Prior continuous wave EDMR (cwEDMR) studies have linked interface and near-interface defects to carbon dangling bond defects and silicon vacancy defects. The identification of silicon vacancy defects in 4H-SiC MOSFETs was based on measuring nearest neighbor carbon 13 hyperfine interactions. ²⁹Si next-nearest neighbor (NNN) hyperfine interactions are too small to resolve in an EDMR measurement due to the width of the center part of the resonance signal. The interactions of NNN ²⁹Si are isotropic with a value 2.96 G determined from conventional EPR. Broadening in EDMR obscures these ²⁹Si
N NNN hyperfine interactions. We have overcome the EDMR broadening problem using the Breit-Rabi effect, a shift in the hyperfine side peaks towards lower fields and frequencies. This effect is sufficiently large so that it may be detected in ultralow field and frequency measurements. We utilize frequency swept EDMR (fsEDMR). With fsEDMR, tuning the resonance condition is performed by varying a low static field. In fsEDMR, the magnetic field H is held constant as frequency is swept. Our experiments were carried out at fields less than 10 G and frequencies less than 30 MHz. We observe a centerline with a condition is performed by varying a low static field. In fsEDMR, the magnetic field H is held constant as frequency is swept. We utilize frequency swept EDMR (fsEDMR). With fsEDMR, tuning the resonance sharp peak on the low field side only at these low fields and frequencies. We attribute the peak to otherwise unresolved hyperfine interactions made observable by shifting due to Breit-Rabi effects. The peak has fairly large amplitude. EasySpin was utilized to simulate the results accounting for the presence of one $^{29}$Si NNN. The results of the simulation are in good agreement with our experimental observation.


**S.E.L01.06.79**

**Optical Filter Free Color Imaging with Perovskite Alloys**

Md Wayesh Qarony, Mohammad I. Hossain, Haris Ahmed Khan, Masayuki Kozawa, Alberto Salleo, Jon Yngve Hardeberg, Hiroyuki Fujiwara, Yuen Hong Tsang, and Dietmar Knipp; 1The Hong Kong Polytechnic University, Hong Kong; 2University of California Davis, United States; 3NTNU-Norwegian University of Science and Technology, Norway; 4Gifu University, Japan; 5Stanford University, United States

Color image sensing by a smartphone or digital camera is usually performed by an array of sensor elements covered by color filters. The optical color filters cause color errors like the color aliasing or Color Moiré effect. Furthermore, the quantum efficiency of typical conventional optical color sensor consisted of side-by-side arranged color filters is limited to $1/N$, where N is the number of color channels per pixels. Hence, the efficiency of the color detection process is limited to max. 33% by the side-by-side arrangement of sensor channels. In this study, color sensors consist of vertically stacked diodes using perovskite alloys is described with maximum quantum efficiency approaching 100%. The described sensor structure is color aliasing or Color Moiré error free, while conventional sensors using optical filters are limited by this error. The optical constants of the required perovskite alloys were determined by applying the energy shift model to experimentally determined optical constants of pure perovskites. The spectral sensitivities of the color sensors were determined by electromagnetically modelling. The spectral sensitivities of the sensors were colorimetrically characterized and compared to sensors in literature including conventional sensors using optical filters. Up to our knowledge for the first time it could be shown that a vertically stacked three color sensor exhibits a color error equal to, or smaller than errors of conventional sensors using optical filters as well as silicon based Foveon stacked color sensor. Details on the used materials, the device design, and the colorimetric analysis are provided.

**S.E.L01.06.80**

**Optical Management of Flexible Thin Crystalline Silicon Solar Cells Using Textured PDMS Optical Sticker**

Inchan Hwang and Kwayong Seo; UNIST, Korea (the Republic of)

Thin crystalline silicon (less than 50 μm thickness) with outstanding flexibility has been considered as a means for developing flexible crystalline silicon (c-Si) solar cells. However, the optical management of the thin c-Si is required for developing the highly efficient c-Si flexible solar cells due to the high surface reflection (more than 30%) and absorption loss over 900 nm wavelength region. Here, we introduce novel high efficiency c-Si flexible solar cells which include random inverted pyramidal polydimethylsiloxane (RIP-PDMS) optical sticker on the 20-μm-thick thin c-Si solar cells. Due to the enhanced light absorption at the entire wavelength region, the thin c-Si with RIP-PDMS optical stickers showed the improved integrated photon flux absorption up to 85.4% (75.0% to 85.4%). The RIP-PDMS sticker enhances the light absorption capability of the thin c-Si by increasing the optical path length in the thin c-Si up to 10%. Further, we analyzed the optical enhancement of the thin c-Si with the RIP-PDMS optical sticker through the finite-difference time-domain (FDTD) simulation. From the optical simulation, we confirmed that the optical path length in the thin c-Si increased because the angles of incident light at the front and rear surface of the thin c-Si tilted up to 10° and 15°, respectively, by attaching the RIP-PDMS optical stickers. Notably, the thin c-Si solar cells with the RIP-PDMS optical stickers showed 18.4% power conversion efficiency while maintaining superior flexibility (bending radius of 10 mm). In addition, our flexible thin c-Si solar cells with the RIP-PDMS optical stickers showed high bending stability without any change in efficiency, even with 1000 bending cycles with a bending radius of 10 mm. Thus, we believe that the thin c-Si solar cells with RIP-PDMS optical stickers can be a promising candidate for the highly efficient flexible solar cells.
The process by which strongly-photoexcited semiconductors return to their ground state consists of a series of complex, strongly-correlated many-body interactions which overlap in space and time, resulting in an evolution of behaviors that is both difficult to study and valuable, both for fundamental insights into the quantum nature of matter and for control of device and material behaviors in electronic and optoelectronic applications. Extensive work has been done in this regard, illuminating the sequence of hot carrier excitation, carrier-carrier scattering, carrier-lattice scattering and thermalization, recombination, and lattice heat diffusion. After strong photoexcitation creates a high-energy bath of “hot” carriers, electron-phonon coupling results in the emission of optical phonons, which decay into lower-energy phonons, either optical or acoustic. The resulting nonequilibrium phonon populations can in turn influence hot carrier relaxation and transport, an inextricability which has been demonstrated through transient Raman scattering [1-3]. The inseparable nature of structural behavior from that of excited electron-hole plasmas is further demonstrated by the result that when not in equilibrium, acoustic mode phase velocities change as a function of time due to residual Coulomb interaction caused by imperfect screening by electrons [4]. Thus, a thorough understanding of ultrafast post-excitation structural dynamics is essential to a full comprehension of semiconductor behavior.

As electronic devices continue to shrink, the associated increased importance of device surfaces, interfaces, and defects add an additional layer of complexity to the structural behavior. Techniques typically employed to investigate post-excitation responses operate in reciprocal or momentum space and require spatial averaging, reducing real-space resolution. It is known that interfaces change the electronic structure in their surrounding regions, strongly influencing carrier dynamics, and it has been shown in our previous work that phonons are structure-directed, propagating specifically from interfaces and repeatedly traveling perpendicularly to the launching interface [5]. In sum, electron-phonon coupling behaviors are known to be influenced by structure, making real-space information relevant to a complete picture of post-excitation behavior. Here we use ultrafast electron microscopy (UEM) to image phonons in real space and thereby demonstrate the influence of both the meso-scale and atomic structure of GaAs on the post-excitation phonon behavior. Making use of combined picosecond-nanometer real-space resolutions, we have directly imaged excitation of GHz coherent strain waves propagating exclusively from specimen-vacuum interfaces with initial hypersonic velocities which decay over time to the speed of sound in GaAs. We also report the change in the properties of these waves upon laser annealing of the specimen, epitaxially crystallizing the focused-ion-beam-induced amorphous surface layer and resulting in measurable hardening of the specimen. This appears in the phonon behavior as an increase in the velocity of the phonons. By imaging the phonon interactions with both the specimen-vacuum interface and the amorphous-crystalline interface within the specimen, we demonstrate the importance of interfaces in fully understanding the phonon dynamics in photoexcited GaAs.


Bandgap Engineered III-V InAs–GaSb TYPE-II Superlattice (T2SL) Infrared Detectors for Multispectral Range Chhaya Ravi Kant; Indira Gandhi Delhi Technical University, India

Infrared detector technology has shown remarkable progress towards the selection of detector materials and device architectures. Infrared detectors are an integral part of various surveillance devices, remote sensing system, night vision, all weather surveillance, missile tracking, thermography, enhanced vision systems for aeroplanes, automobiles and gas sensing. Current InSb and HgCdTe based IR technologies have shown high performance because of excellent material properties covering near infrared (NIR 0.75-1.1mm), short-wavelength infrared (SWIR 1-3mm), mid-wavelength IR (MWIR 3-5mm), long-wavelength IR (LWIR 8-14mm) and very long-wavelength IR (VLWIR 14-30 mm) range. However, these need to be cooled to cryogenic temperatures making them bulky and power hungry. Thus future infrared photodetector systems must possess reduced cooling requirements, consume less power, exhibit longer lifetimes, and have improved manufacturability. These targets have been partly addressed by the development of nBn detector architecture raising the operation temperature, reliability, higher sensitivity and low SwaP (Small Weight and Power).

Type2Superlattice (T2SL) detectors combine key advantages of InSb and Mercury-CadmiumTelluride (MCT)-based technologies namely scalability of focal plane arrays (FPAs), high sensitivity, lower tunneling currents and suppressed Auger
recombination rates nad also facilitates a higher operating temperature. A super lattice is made up of a repeated series of very thin epilayers of different materials that leads to creation of sub-bands. The corresponding bandgap energies of these subbands determine the cut-off wavelength of the sensor. The III-V InAs –GaSb materials, based on nBn unipolar photodetector architecture, with an n-type absorption layer, a barrier layer, and an n-type contact layer have been fabricated and engineered for bandgap tunability. The barrier layer is constrained to have both a negligible valence band energy offset with the absorption layer, that suppresses the Shockley-Read-Hall (SRH) generation current thereby decreasing the primary noise In addition, detector is passivated to minimise the surface leakage current. The nBn photodetector, through the near elimination of SRH and surface leakage currents, requires less cooling to operate optimally than the p-n junction photodiodes. Bandgap engineering and optimization of the material composition to achieve maximum quantum efficiency, low dark current, maximum absorption strength and higher operating temperature.

Appropriate tools suitable for the design of T2SL material systems are not yet fully developed due to the intricacies of T2SL material system and paucity of experimental data for input and for the validation of mathematical formulations. A holistic approach has been followed involving design of graded energy-gap T2SL structure, growth of material system, characterization of material, fabrication and characterization. Our design is aimed to grow T2SL epilayers with optimized thickness, material composition, energy gap grading and varied doping concentrations by Molecular Beam Epitaxy and detector fabrication with a combination of wet and dry etching. A favorable impact ionization coefficient leads to higher bandwidth range with low excess noise to achieve maximum quantum efficiency, low dark current, high avalanche gain, low excess noise, maximum absorption strength and higher operating temperature. Design optimisation has resulted in high quantum efficiency of 75% validated with FTIR measurements and low NETD of 18mK at an elevated operation temperature of 140K. Current-Voltage measurements, quantum efficiency, noise equivalent temperature difference (NETD) and issues related with growth of graded energy-gap T2SL material system will form part of the full paper.

S.EL01.06.94

**Co-Electrodeposited MnO$_2$ and Co$_3$O$_4$ on Well-Aligned Electrospun Carbon Nanofibers for Sensitive Glucose Detection**
Ziyu Yin, Xinping Zeng and Jianjun Wei; The University of North Carolina of Greensboro, United States

Binary manganese oxide/cobalt oxide (MnO$_2$/Co$_3$O$_4$) composites on the well-aligned electrospun carbon nanofibers (MnO$_2$/Co$_3$O$_4$@ECNFs) were synthesized via a simple and economical one-step template-free electrodeposition technique with a constant low-current (60μA) for 3h, and their electrocatalytic activity towards non-enzymatic glucose sensors was evaluated in detail. The MnO$_2$/Co$_3$O$_4$ nanostructures were uniformly deposited on the well-aligned ECNFs with high porosity, effective interconnectivity and large amounts of extended number of conducting channels. The electrocatalytic performances of as-prepared MnO$_2$/Co$_3$O$_4$@ECNFs towards the oxidation of glucose were carried out by cyclic voltammetry (CV) and chronoamperometry (CA), and the experimental results show that the MnO$_2$/Co$_3$O$_4$@ECNFs exhibited a superior sensing performance towards glucose including a rapid glucose response within 5 seconds, a wide range (5 μM to 10.89 mM), excellent sensitivity of 973.91 μA mM$^{-1}$ cm$^{-2}$ and a low detection limit of 0.02 μM (S/N=3) with satisfactory selectivity, great reproducibility and stability. These excellent electrochemical performances were attributed to the synergistic effect of binary metal oxides and the unique porous architecture of the electrode. These features indicate that as-synthesized MnO$_2$/Co$_3$O$_4$ binary nanostructure decorated well-aligned ECNFs hold great potential in the development of a commercialized glucose sensor.
* Invited Paper

SESSION Tutorial S.EL02: Mixed Dimensional Heterostructures from Fundamentals to Device Applications  
Session Chairs: Sanghoon Bae, Jeehwan Kim, Wei Kong, Hyunseong Kum, Kyusang Lee, Rachael Myers-Ward and Suresh Sundaram  
Saturday Morning, November 28, 2020  
S.EL02

10:00 AM *  
Remote Epitaxy—Growth of 3D Materials on 2D Materials Jeehwan Kim; Massachusetts Institute of Technology, United States  
I will discuss about new epitaxy lift-off technique so called remote epitaxy that can produce freestanding semiconductor membranes. Discussion will include 1) Remote epitaxy mechanism 2) High yield peeling mechanism 3) Reusability of the substrates 4) Economic aspect of remote epitaxy 5) Heterointergration of 3D materials with 2D materials for advanced heterostructuring.

11:00 AM BREAK

11:05 AM *  
Epitaxial Growth of 2D and 3D Materials Abdallah Ougazzaden; GeorgiaTech Lorraine, France  
Instructor will provide the overview regarding the epitaxial growth of Nitride-based semiconductor materials by MOVPE including GaN and h-BN, and design device structures for opto-electronic devices. In addition, Dr. Ougazzaden will cover the fabrication of nanostructures and materials characterization. The epitaxial growth of 3D and 2D materials and characterization of them is the basis of fabrication of heterointegration system for various device applications.

12:05 PM BREAK

12:10 PM *  
Heteoepitaxy on Graphene for Transferable and Flexible Optoelectronics Kunook Chung; Ulsan National University of Science and Technology, Korea (the Republic of)  
High device performance has been expected using a single crystalline inorganic compound semiconductor because of its high radiative recombination rate and mobility, as well as its excellent thermal and mechanical characteristics. Nevertheless, the high growth temperatures of single-crystalline inorganic semiconductors make it difficult to use a conventional plastic substrate with a low melting temperature. In addition, a continuous, rigid inorganic film has little tolerance for mechanical deformation. These obstacles can be overcome using inorganic microstructures and nanostructures grown on two-dimensional layered materials, such as graphene and hexagonal boron nitride as a flexible substrate, which exhibit high temperature compatibility and good mechanical flexibility. The instructor will review the current state-of-art technology of inorganic compound semiconductors heteroeptaxy on the 2D films for the transferable and flexible inorganic optoelectronics toward next-generation wearable devices and integrated devices with electronics.

1:10 PM BREAK

1:15 PM *  
Lift-Off Technology Toward Heterogeneous Integration Kyusang Lee; University of Virginia, United States  
The layer-transfer technique has been in development for over a decade as a cost-saving strategy as well as a means of enabling heterointegration of dissimilar functional materials and flexible electronics. Instructor will review three major layer-transfer technologies, which are chemical lift-off, optical lift-off and mechanical lift-off. However, most of conventional layer-transfer methods lead to various issues such as surface roughening that limits substrate reusability. Instructor will
introduce new lift-off technology including two-dimensional layer transfer method that permits rapid mechanical release of epilayers leaving behind atomically smooth released surface without additional process to recondition the surface. Lift-off technology holds promise to unlock cost-efficient growth/transfer/stacking of high quality semiconductors and heterointegration of them without lattice matching restriction as well as substrate cost restrictions.

SESSION S.EL02.05: Live Keynote and Lightning/Flash I: Advanced Manufacturing of Mixed Dimensional Heterostructures

Session Chairs: Sanghoon Bae, Jeehwan Kim and Kyusang Lee
Sunday Afternoon, November 29, 2020
S.EL02

12:30 PM OPENING COMMENTS

12:35 PM **S.EL02.01.18**
Mixed-Dimensional Heterostructures for Electronic and Energy Applications **Mark C. Hersam**; Northwestern University, United States

Layered two-dimensional (2D) materials interact primarily via van der Waals bonding, which has created new opportunities for heterostructures that are not constrained by epitaxial growth [1]. However, it is important to acknowledge that van der Waals interactions are not limited to interplanar interactions in 2D materials. In principle, any passivated, dangling bond-free surface interacts with another via non-covalent forces. Consequently, layered 2D materials can be integrated with a diverse range of other materials, including those of different dimensionality, to form mixed-dimensional van der Waals heterostructures [2]. Furthermore, chemical functionalization provides additional opportunities for tailoring the properties of 2D materials [3] and the degree of coupling across heterointerfaces [4]. In order to efficiently explore the vast phase space for mixed-dimensional heterostructures, our laboratory employs solution-based additive assembly [5]. In particular, constituent nanomaterials (e.g., carbon nanotubes, graphene, transition metal dichalcogenides, black phosphorus, boron nitride, and indium selenide) are isolated in solution, and then deposited into thin films with scalable additive manufacturing methods (e.g., inkjet, gravure, and screen printing) [6]. By achieving high levels of nanomaterial monodispersity and printing fidelity [7], a variety of electronic and energy applications can be enhanced including photodetectors [8], optical emitters [9], and lithium-ion batteries [10-12]. Furthermore, by integrating multiple nanomaterials into heterostructures, unprecedented device function is realized including anti-ambipolar transistors [13], gate-tunable photovoltaics [14], and neuromorphic memtransistors [15]. In addition to technological implications for electronic and energy technologies, this talk will explore several fundamental issues including band alignment, doping, trap states, and charge/energy transfer across previously unexplored mixed-dimensional heterointerfaces [16].

Two-dimensional (2D) layered materials have strong in-plane covalent bonding and weak van der Walls interaction between the planes, which host a wide variety of interesting physical and chemical phenomena. Here I will present our research over 15 years on nanostructured 2D materials. First, I will show how we synthesize these 2D materials into rich morphologies including nanoplates, nanoribbons, layer-vertical aligned films as well as lateral and vertical heterostructures. Second, we developed liquid-gel gating, solid state ion gating, chemical and electrochemical intercalation to control the physical and chemical property of 2D materials. Third, we demonstrated exciting new exciting application of using 2D materials for batteries and catalysis applications.

Combined photonic and electronic systems require diverse devices to be co-integrated on a common platform. This heterogeneous integration is made possible through several separation and transfer methods where the functioning epilayers are essentially released from their growth substrate. The use of 2D layered h-BN as a mechanical release layer has been demonstrated to be a promising technique for the hybrid integration of III-nitride devices. In this talk we will give an overview regarding the epitaxial growth of Nitride-based semiconductor materials by MOVPE including GaN and h-BN, and design device structures for opto-electronic devices. In addition, results on wafer-scale growth and pick-and-place transfer of LED devices via h-BN van der Waals epitaxy, starting from sapphire growth substrates will be presented. Broader range of devices (HEMTs, solar cells, sensors, etc.) and applications (transport, environment, health, etc) will be discussed.

Recent advances in MOVPE enabled the high-quality growth of layered h-BN on sapphire substrates, and has resulted in the realization of series of 2D-3D III-nitride based device structures. This 2D layer also enables damage free mechanical lift-off which may drive future flexible and wearable industry with advanced high-efficient devices. Reliable wafer-scale 2D-2D heterostructure based devices have also been fabricated previously. Here we report, demonstration of MOVPE van der Waals epitaxial growth of GaN based nanostructures on 2D h-BN with a focus on large area van der Waals epitaxy and successful transfer to flexible platform. This approach to the growth of III-N nanostructures on h-BN avoids transfer processes and scaling issues seen with other 2D materials, since both the 1D (GaN nanorods) and 2D (h-BN) are grown at the wafer-scale and in one growth run. Further, this process is used to grow vertical core–shell p-GaN/InGaN/n-GaN nano-PIN device structures on wafer-scale 2D h-BN on sapphire and silicon substrates. Interesting results obtained on this futuristic process and mechanisms involved will be discussed.

Infrared (IR) photodetectors are nowadays in high demand in a wide range of fields such as telecommunication, thermal imaging, remote sensing, night assistance car driving etc. Recently, hybrid phototransistors made of highly efficient light absorbing 0D quantum dots and high mobility 2D materials have introduced a new technology, which dramatically increases the responsivity and gain of the photodetector. In 2012, such low dimensional IR phototransistor based on graphene/PbS QD hybrid was proposed in literature [1, 2] for the first time. Later in 2017, a high-resolution broadband image sensor based on
such hybrid materials was demonstrated \[3\], which is sensitive to ultraviolet, visible and infrared light (300–2000 nm).

We have investigated similar graphene/PbS QD hybrid phototransistors and explored the enhancement of their photo-sensing qualities compared to bare graphene phototransistor in the visible-NIR-SWIR region of optical spectra. Initially, we studied CVD-grown single layer graphene phototransistor in the visible-NIR region, which showed a responsivity of about $10^4$ A/W, associated with the low–doped Si substrate, which acts as the primary material for optical absorption. Such responsivity is $10^7$ orders of magnitude higher \[4\] than conventional graphene phototransistor \[5\]. However, the photo-sensing wavelength range of such device is limited up to 1100 nm depending on the principal absorption material Si. In order to expand the photo-sensing wavelength range up to SWIR region, we have explored the potential of graphene/PbS QD hybrid phototransistors. We synthesized the colloidal PbS QDs absorbing in the NIR as well as SWIR regions and developed a layer-by-layer dip coating with simultaneous ligand exchange procedure to deposit homogeneous PbS QD layers on graphene sheet leading to a well fabricated hybrid phototransistor. We achieved a significantly high responsivity of at 940 nm with irradiation power density of $10^4$ W/m². In the NIR range, the peak responsivity appears to be $\sim 10^7-10^8$ A/W, whereas in the SWIR range, the observed peak responsivity is $\sim 10^6$ A/W. Moreover, graphene/PbS QD hybrid exhibits high sensitivity at low irradiation power (< 0.05 nW), where bare graphene photodetector is unable to sense such low intensity light in the visible-NIR region.

The heterogeneous integration of dissimilar materials is a long pursuit of the material science community and has defined the material foundation for modern electronics and optoelectronics. The typical material integration approaches usually involve strong chemical bonds and aggressive synthetic conditions and are often limited to materials with strict structure match and processing compatibility. Alternatively, \textit{van der Waals} integration, in which freestanding building blocks are physically assembled together through weak \textit{van der Waals} interactions, offers a bond-free material integration strategy without lattice and processing limitations, as exemplified by the recent blossom of 2D \textit{van der Waals} heterostructures. Here I will discuss the fundamental forces involved in \textit{van der Waals} integration and generalize this approach for flexible integration of radically different materials to produce artificial heterostructures with minimum interfacial disorder and enable high-performing devices. Recent highlights include the formation of \textit{van der Waals} metal/semiconductor junctions free of Fermi level pinning to reach the Schottky-Mott limit; the creation of a new class of high-order \textit{van der Waals} superlattices with highly distinct constituents of atomic or molecular layers; and the development of \textit{van der Waals} thin film electronics with unprecedented flexibility and stretchability. I will conclude with a brief perspective on exploring such artificial heterostructures as a versatile material platform with electronic structure by design to unlock new physical limits and enable device concepts beyond the reach of the existing materials.

2:11 PM *S.EL02.03.20

III-Nitride \textit{van der Waals} Epitaxy on 2D BN for Lift-Off, Transfer and Integration Michael Snure, Eric Blanton, Nicholas Glavin and Kelson Chaback; Air Force Research Laboratory, United States

Van der Waals (vdW) surfaces of 2D materials such as graphene and BN are attractive for growth of GaN and other III-nitride films and device structures. The weak inter-planar vdW bonding between 2D layers allows for easy mechanical separation of III-nitride films from the growth substrate for lift-off, transfer and integration on to arbitrary substrates. This approach of vdW lift-off is suitable for transfer of delicate single devices, like T-gate high electron mobility transistors (HEMT), as well as, wafer sized films. However, to obtain high performance devices, control over nucleation and epitaxy on 2D layers is necessary for high quality films. Additionally, to enable a simple transfer process strain and adhesion between the film and 2D layer must be balanced. In this paper, we describe the growth of high quality GaN and AlGaN/GaN HEMT structures on 2D BN. The effects of nucleation, III-nitride epitaxial growth process and BN morphology will be discussed demonstrating how they effect material quality, properties, strain and adhesion. We will then discuss transfer schemes for individual AlGaN/GaN HEMTs and large area membranes transferred to both flexible polymer substrates and a variety of rigid substrates. With access to GaN and AlGaN/GaN two dimensional electron gas (2DEG) membranes on flexible substrates, we investigate the effects of strain on basic materials properties from compressive to tensile. This is particularly powerful for probing the effects of strain on the electrical properties, like sheet carrier density and mobility, in the polarization induced AlGaN/GaN 2DEG. In transferred devices, we demonstrate exceptional transport properties with mobility > 2,000 cm²/Vs and device performance with $G_{\text{M}}$ of 300 mS/mm and $f_T$ and $f_{\text{max}}$ > 34 GHz and 75 GHz under strain while bending. Lastly, we will cover vdW and adhesive bonding to high and low thermal conductivity substrates and the effects on device performance and self-heating. This paper will highlight the great potential of vdW epitaxy and lift-off for transfer and integration of GaN on to various platforms.

2:32 PM *S.EL02.03.13

Polar Quasi-2D Oxides via Epitaxy at Weakly-Coupled Interface Jian Shi; Rensselaer Polytechnic Institute, United States

When crystals approach 2D, their ferroelectric phase may be destabilized. How their temperature-dependent polarization behaves remains largely unknown. In this work, we attempt to answer this question using 2D pyroelectric oxides. We show that quasi-2D oxides down to a unit cell thickness can be epitaxially grown on perovskite substrate by the molten salt-assisted quasi-van der Waals epitaxy following a screw-dislocation driven mechanism. We experimentally demonstrate switchable in-plane photo-ferroelectricity and thickness-dependent pyroelectricity. Weakly-coupled interface allows us to reveal that electron-phonon renormalization leads to the observed dimensionality effect. Harnessing the dimensionality effect in pyroelectricity via novel epitaxy strategies could promote their applications in uncooled infrared cooling and thermal energy harvesting.

2:53 PM S.EL02.03.09

SiC Remote Epitaxy—A New Paradigm for Stackable Electronics Rachael Myers-Ward¹, Jeehwan Kim², Matthew DeJarld¹, Kuan Qiao², Yunjo Kim², S.P. Pavunny¹ and Kurt D. Gaskill¹; ¹Naval Research Laboratory, United States; ²Massachusetts Institute of Technology, United States
Ideally, electronic heterostructures from dissimilar materials leads to enhanced functionality. Yet, experimentally forming these heterostructures is challenging due to lattice or thermal coefficient of expansion mismatch leading to defect formation or thermally driven atomic diffusion resulting in cross-doping and gradual junction transitions. These challenges may be overcome with the discovery of remote epitaxy and 2D layer transfer [1]. Here, SiC epitaxy is performed on epitaxial graphene as the electrostatic fields from the substrate penetrate the graphene and guide adatom registry. The film is easily peeled away since the graphene is not bonded to either the substrate or epilayer; the epilayer is then van der Waals bonded to a different material enabling new functionality. We will present experimental results on the remote epitaxy of SiC.

There are three necessary steps to create remote epitaxy. The first is to grow epitaxial graphene on SiC, followed by transferring the graphene to a desired substrate (if different from SiC), and finally the growth of the remote epitaxial layer. If the remote epitaxy is to be SiC, which is the focus of this paper, the second step is not necessary. Epitaxial graphene (EG) was first synthesized on 4H- and 6H-SiC in a horizontal hot-wall CVD reactor between 1540 and 1580 °C in 10 slm of Ar and 100 mbar [2]. The growth temperature was dependent upon the offcut of the substrate, where substrates with higher offcuts require a lower growth temperature to ensure 1 ML of EG, which is desired to assist in SiC adatom registry during growth. SiC remote epitaxy was then performed on the EG using silane (2% in H2) and propane precursors, where the SiC polytype replicated the underlying substrate. In an effort to transfer the remote SiC epi/EG to another substrate such as SiO2/Si, a metallization step was performed. Thin Ti and/or Ni layers were initially deposited followed by a thicker high stress metal to create strain and aide in removing the remote SiC epi/EG from the SiC substrate [1]. Once transferred, the metal was removed via a metal etch.

In this work, we will discuss the important parameters needed for successful remote SiC epitaxy, such as graphene thickness, process flows, ramping conditions and remote epitaxy growth temperature. The epitaxial morphology characterized by SEM, Nomarski microscopy and Electron Detectio and graphene coverage and transfer evaluated by Raman spectroscopy will be presented.


3:00 PM BREAK

3:05 PM S.EL02.01.25
Probing Metal Center Effects in MoS2 – Metallophthalocyanine Mixed-Dimensional Heterojunctions Samuel Amsterdam1, Teodor K. Stanev1, Qunfei Zhou1,2, Vinod K. Sangwan1, Alexander J. Lou1, Hadallia Bergeron1, Pierre T. Darancet2, Mark C. Hersam1, Nathaniel P. Stern1 and Tobin J. Marks1; 1Northwestern University, United States; 2Argonne National Laboratory, United States

Mixed-dimensional heterojunctions, such as zero-dimensional organic molecules deposited on two-dimensional transition metal dichalcogenides (TMDs), exhibit unique interfacial effects that modify the properties of the individual constituent layers. To better understand the effect of changing molecular orbital energy on the heterojunction properties, we report here a systematic study of metallophthalocyanine (MPC) – MoS2 (M = Co, Ni, Cu, Zn, H2) heterojunctions using optical absorption, Raman spectroscopy, low temperature photoluminescence, variable temperature electrical measurements, and density functional theory. Notable phenomena include the emergence of heterojunction-specific optical absorption transitions, strong Raman enhancement, and quenching of defect emission that depend on phthalocyanine metal center identity. Temperature-dependent electrical noise measurements on field-effect transistors provide further insight into the properties of these mixed-dimensional heterojunctions. These results highlight the tunable nature of metal-organic-TMD van der Waals interfaces and the importance of the organic architecture and electronic structure in designing mixed-dimensional heterojunctions for optical and electronic applications.

3:13 PM *S.EL02.01.35
Print-in-Place Electronics Using Mixed-Dimensional Nanomaterials Aaron D. Franklin; Duke University, United States

For decades we’ve been hearing about the promise of printing electronics directly onto any surface. However, despite significant progress in the development of inks and printing processes, reports on fully, direct-write printed electronics continue to rely on excessive thermal treatments and/or fabrication processes that are external from the printer. In this talk, recent progress towards print-in-place electronics will be discussed; print-in-place involves loading a substrate into a printer, printing all needed layers, then removing the substrate with electronic devices immediately ready to test. A key component of
these print-in-place transistors is the use of inks from various nanomaterials, including 1D carbon nanotubes (CNTs - semiconducting), 2D hexagonal boron nitride (hBN - insulating), and quasi-1D silver nanowires (AgNWs – conducting). Using an aerosol jet printer, these mixed-dimensional inks are printed into functional 1D-2D thin-film transistors (TFTs) without ever removing the substrate from the printer and using a maximum process temperature of 80 C. To achieve this, significant advancements were made to minimize the intermixing of printed layers, drive down sintering temperature, and achieve sufficient thin-film electrical properties. Devices are demonstrated on various substrates, including paper, and evidence of the potential for printing directly onto biological surfaces will be shown. From the versatile printed electronic thin films that have been developed, a diversity of biosensors are being pursued and will be discussed. With continued refinement of the inks and print processes, this print-in-place technique can bring the field of printed electronics closer to where it has been promised to go for so many years: load substrate, press print, remove functional sensors / circuit.

3:36 PM CLOSING COMMENTS

SESSION S.EL02.07: Live Keynote and Lightning/Flash III: Advanced Manufacturing of Mixed Dimensional Heterostructures
Session Chairs: Jeehwan Kim, Wei Kong and Suresh Sundaram
Tuesday Morning, December 1, 2020
S.EL02

8:00 AM OPENING COMMENTS

8:05 AM *S.EL02.02.01
Large Area Synthesis and Doping of Two-Dimensional Semiconductors Joshua A. Robinson; The Pennsylvania State University, United States

The last decade has seen nearly exponential growth in the science and technology of two-dimensional materials. Beyond graphene, there is a huge variety of layered materials that range in properties from insulating to superconducting. Furthermore, heterogeneous stacking and doping of 2D materials also allows for additional band structure engineering. In this talk, I will discuss recent breakthroughs in two-dimensional atomic layer synthesis and properties, with an emphasis on doping 2D semiconductors. Our recent works include development of an understanding of substrate impact on growth and doping of 2D materials to tune them from n- to p-type, and to create 2D magnets. Our work and the work of our collaborators has lead to a better understanding of how substrate not only impacts 2D crystal quality, but also doping efficiency in 2D materials.

8:26 AM *S.EL02.03.15
Emerging Epitaxy for Transferrable Flexible Optoelectronics—van der Waals and Remote Epitaxies Young Joon Hong; Sejong University, Korea (the Republic of)

Technological fashion of electronics has recently changed from device miniaturization to flexible device and 3-dimensional heterogeneous integration. For the flexible devices, organic or polymeric materials have been generally used, but inorganic semiconductor is ultimately desirable in terms of high performance, long lifetime, and harsh environment tolerance. Nonetheless, the rigid, brittle characteristics of semiconductor has limited its utilization in the flexible device applications. Graphene-inserted growth is promising for transferrable device fabrication because the surface of graphene has no dangling bonds. The van der Waals interfaces of overlayer/graphene/wafer enable mechanical exfoliation of overlayer from wafer via a facile sticky scotch tape technique. Using the graphene interlayer, there are two epitaxy regimes, which are van der Waals and remote epitaxies, that can be classified by the role of graphene. In addition, the growth of wire or rod-shaped semiconductor crystallites is promising for deformable device applications because of the spatially separate geometry. This talk introduces the aforementioned epitaxies for transferrable flexible optoelectronics. We begin discussing the role of graphene or underlying wafer how they dictate the epitaxial relation with overlayer. As the first section, the van der Waals epitaxy of InAs nanowires on graphene is presented. Use of thinnest substrate of single-layer graphene, fabrication of InAs/graphene/InAs double heterostructures using suspended graphene, and position-controlled growth, all of which were achieved through the van der Waals epitaxy, are presented. Then, as the second section, the remote epitaxy is
introduced. Hydrothermal remote epitaxy of ZnO microrods and metal–organic vapor-phase remote epitaxy of GaN microrods are presented.[7–9] We also discuss the remote heteroepitaxy of ZnO on GaN and GaN on Al2O3 for lattice less- and far-mismatched remote epitaxy, respectively.[8,9] The transfer of GaN heterostructured microrods of $p$–$n$ junction with InGaN multiple quantum-wells is demonstrated for flexible microrod-light-emitting diode panel whose mechanical property is highly robust against crumpling/folding operations and repeated bending test.[9] Especially, we show the wafer recyclability for fabricating the deformable microrod-light-emitting diode panel over again on the same wafer in the remote epitaxy. We finally show how the principle of remote epitaxy, in which the limited thickness of graphene can penetrate the bonding feature of underlying wafer to the surface of graphene for epitaxial relationship, can be applied for site-selective growth.[10] The challenges and opportunities of epitaxies on/across graphene are discussed toward future flexible, transferable displays technology.

References
[10] Jeong et al. (unpublished)

8:47 AM *S.ELO2.03.07
Mechanisms of Remote Epitaxy on Two Dimensional Materials Wei Kong, Kuan Qiao, Huashan Li, Jeffrey C. Grossman and Jeehwan Kim; Massachusetts Institute of Technology, United States

The fabrication of thin-film semiconductor relies on epitaxy, during which direct bonding is made between the epitaxial layer and the substrate, to ensure highly ordered crystalline lattices in the epitaxial layer as a copy of its substrate. The strong physical bonding between epitaxial layer and substrate implies strict requirements of lattice matching as well as difficulties in heterointegration. We have previously shown that the insertion of a monolayer graphene in between the epitaxial layer and its substrate, in the so-called “remote-epitaxy” process, did not change the crystalline orientation of the epitaxial layer, and the epitaxial alignment between the epitaxial layer and its substrate was maintained as if the monolayer graphene was “transparent” [1]. In this report, we further explore the fundamental mechanisms behind such an epitaxial alignment through two-dimensional materials. And the general rule governs remote-epitaxy will be introduced [2].

Specifically, the transparency of two-dimensional materials to the epitaxial relationship is linked to the polarization of related material systems. Although the potential field from non-polar materials is screened by a monolayer of graphene, that from polar materials is strong enough to penetrate through a few layers of graphene. Such field penetration is substantially attenuated by 2D hexagonal boron nitride, which itself has polarization in its atomic bonds. Based on the control of transparency, modulated by the nature of materials as well as interlayer thickness, various types of single-crystalline materials across the periodic table can be epitaxially grown on 2D material-coated substrates. The epitaxial films can subsequently be released as free-standing membranes, which provides unique opportunities for the heterointegration of arbitrary single-crystalline thin films in functional applications.

Dislocation-Carrier Dynamic in Halide Perovskites via Remote Epitaxy

Jie Jiang and Jian Shi; Rensselaer Polytechnic Institute, United States

Crystallographic defects, such as dislocation, are well known to strongly affect material’s physical properties. Electron-hole recombination mediated via dislocations (e.g. threading dislocation) is one of the predominant loss mechanisms for the sub-optimum performance in conventional semiconductors devices. However, how dislocation impacts its carrier dynamics in the ‘defects-tolerant’ halide perovskite is largely unknown. Stimulated by the successful pioneer work of remote homoepitaxy of semiconductor GaAs\(^1,2\), researchers have also been achieved (remote heteroepitaxy) in the systems of AlN film on sapphire\(^3\), copper film on sapphire\(^4\), and ZnO film on GaN\(^5\). In our study, we synthesize epitaxial halide perovskite with controlled dislocation density via a remote heteroepitaxy approach using polar substrates (NaCl and CaF\(_2\)) coated with graphene. Density functional theory calculations have revealed the structure and magnitude of the incompletely screened electrostatic potential from the polar substrates, supporting the remote epitaxy in the present case. The regulated film-substrate interactions have further reflected themselves in controlling the wavelengths of the ferroelastic domains. Molecular-dynamics simulations reveal the kinetic process during remote epitaxy. Comparing to the ionic epitaxy with high dislocation density (both misfit and threading), the film grown via remote shows much enhanced photoluminescence intensity and increased carrier lifetime. Our successful demonstration of remote epitaxy in halide perovskite provides an approach to develop free-standing halide perovskite film with reduced dislocation density. More importantly, dislocations and their impacts on carrier dynamics and device performance in halide perovskite have to be recognized and scrutinized.


Accurate Prediction of Energy Level Alignment in Mixed-Dimensional Heterojunctions

Qunfei Zhou\(^1\), Zhenfei Liu\(^2\) and Pierre T. Darancet\(^3\); \(^1\)Northwestern University, United States; \(^2\)Wayne State University, United States; \(^3\)Argonne National Laboratory, United States

Understanding energy level alignment between molecules and two-dimensional materials is conducive to controlling charge and energy transfer in mixed-dimensional heterojunctions. The competition between distinct energy scales, such as the ones associated with electronic correlations, interface dipole, orbital hybridization, and non-local dielectric screening, can lead to significant renormalization of the intrinsic energy levels of each material at these interfaces. The variety of these energy scales also complicates the theoretical description of the level alignment for mixed-heterojunctions accurately.

Here we study the electronic structure and level alignment for mixed 0D-2D heterojunctions containing transition metal phthalocyanines on MoS\(_2\) by first-principles density functional theory (DFT) calculations. By using optimally tuned range-separated hybrid (OT-RSH) functionals, a recently developed method for finding the optimal range-separated parameters for describing short-range and long-range electron exchange effect, we obtain energy level alignment consistent with known experimental results, a significant improvement comparing to standard DFT. This method can be used for other mixed-heterojunctions for better understanding of their electronic and optical properties.

Toward Non-Si Electronics—Producing Freestanding Single Crystalline 3D Thin Films and 2D Atomic Layers for Mixed Dimensional Heterostructure

Sanghoon Bae; Massachusetts Institute of Technology, United States

2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
The current electronics has been mainly dominated by Si-based devices due to their mature processing system and exceptional cost-effectiveness. However, next generation electronics needs novel functionalities that cannot be realized by Si because of intrinsic limitation of Si. Accordingly, demand for non-Si electronics has been getting substantially high. Unfortunately, current methodology requires extremely high cost for non-Si materials, which impedes the progress in developing the non-Si based electronics. Here, I will discuss about our group’s efforts to address this issue. Our team recently conceived a new crystalline growth, termed as “remote epitaxy”, which can copy/paste crystalline information from substrates remotely through graphene, thus generating single-crystalline films on graphene. As interfacial binding energy is attenuated by inserting graphene at interface, the single-crystalline films can be easily exfoliated from the slippery graphene surface. Also, the graphene-coated substrates can be, in principle, reused infinitely to produce single-crystalline films. Thus, the remote epitaxy can produce non-Si semiconductor films with unprecedented cost efficiency while allowing additional flexible device functionality required for current ubiquitous electronics.

Next, I will discuss about a layer splitting technique which can be a potential solution to overcome the problem in obtaining large-scale and monolayer 2D materials. A 2D material-based heterostructure has been intensively studied because of its unique device functionalities and novel physics. However, it is extremely challenging to secure large-scale and monolayer 2D materials because of following issues: 1) poor scalability for laboratory fabrication processes of 2D heterostructures and 2) lack of well-defined control parameters for kinetics of 2D materials and predictable number of layers of 2D materials. To resolve this issue, we conceived a new approach called “layer-resolved splitting” which obtains multiple monolayer from multilayer 2D materials by controlling interfacial toughness contrast. As this method is versatile and universal, we can, in principle, apply to all 2D materials. We succeeded in having large-scale, monolayer 2D materials through our approach and, thereby 2D heterostructures were demonstrated for functional devices.

Lastly, I would like to discuss opportunities of mixed-dimensional heterostructure demonstrated by remote epitaxy and layer-resolved splitting. As they produce freestanding 3D bulk films and 2D atomic layers, a new type of 3D/2D heterostructures can be realized where a new physics and new device architecture are revealed. Therefore, I believe that a new opportunity will be discovered through the mixed-dimensional heterostructures.
Doping Approaches and Junction Structure for Antimony Selenide Solar Cells Jon Major; University of Liverpool, United Kingdom

Antimony selenide solar cells are rapidly approaching 10% efficiency however a number of key materials properties are still not fully understood. In particular the mechanism by which doping is controlled in the material has not been established and there is a high degree of variability in the literature on the level of doping attainable and even carrier type. This talk will discuss the identification of potential sources of doping in Sb₂Se₃, the influence this has on carrier concentration and the subsequent impact for device performance. Through the use of Sb₂Se₃ bulk crystals we will further demonstrate routes to achieve p, i and n doping and methods to transfer this to thin film devices.

5:30 AM *S.EL02.01.03
Photonic Crystal Enhanced Photon Collection for Quantum Dot-Based Luminescent Solar Concentrator Ou Chen; Brown University, United States

A luminescent solar concentrator (LSC) is a photon managing device that can harvest, direct and concentrate solar light to small areas, enabling subsequent coupling to photovoltaic devices (PVs) for enhanced solar energy conversion. However, the intrinsic photon loss through the so-called escape cone of the LSCs significantly limits their light harvesting and concentrating performance. In this talk, I will introduce a facile and low-cost approach for the fabrication of a three-dimensional (3D) macroporous photonic crystal (PC) filter as an efficient photon reflector, which can be coated onto quantum dot (QD) based LSC devices. We demonstrate that by controlling the PC reflection band to match the emission profile of the QD emitters, the light trapping efficiency of the PC coated LSC (PC-LSC) can be significantly improved from 73.3% to 95.1% as compared to the conventional PC-free LSC due to the reduced escape cone photon loss. Both experimental and simulation results show that the enhancement in LSC device performance induced by the PC reflector increases with increasing dimension. Our study sheds light on future design and fabrication of LSC devices with enhanced photon collection and concentrating efficiencies through novel and wavelength-selective photon reflectors.

6:00 AM *S.EL02.01.04
Beyond Expectation—Advanced Materials Synthesis and Processing to Enable Novel Function in Ferroelectrics Lane W. Martin1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

Ferroic materials including oxide ferroelectrics, magnets, and multiferroics are of great interest for a range of modern applications. What’s more, these materials stand poised to revolutionize next-generation applications, if we can determine ways to overcome inherent limitations in their function. Stringent device requirements are pushing researchers to exert ever more exacting control over the chemistry, defect structures, interfaces, etc. to elicit the desired function from these materials. From the ever present need to reduce leakage currents and control imprint and fatigue to renewed interest in reducing the voltage of operation of ferroelectric and piezoelectric devices to the sub 100 mV level to the realization of beyond-binary function in the form of multi-state operation that could enable neuromorphic devices, the requirements of next-generation applications are great and varied. Such requirements have thrust materials – including ferroelectrics, piezoelectric, and multiferroics – back into the mix as candidates for many applications.

But, despite considerable research on such materials in the last few decades and advances in our ability to synthesize, control, characterize, and fabricate these materials, the requirements of these applications are already pushing these materials to their limits. In this talk, we will explore a range of materials synthesis and processing approaches that enable researchers to address these requirements. In single-layer films of materials like BaTiO₃, PbTiO₃, BiFeO₃, (1-x)PbMg₁/₃Nb₂/₃O₃-(x)PbTiO₃, and others, we will explore how the use of exacting chemical control and the ex post facto introduction of certain species (be it constituent elements themselves or specific defects) can effectively “heal” or improve ferroelectric function dramatically – improving leakage and increasing breakdown voltages. Taken further, such on demand introduction of defects can even impart exotic function – such as multi-state switching – as we leverage strong defect-polarization coupling to tune the pinning energy and, in turn, coercive voltages. One can even achieve such control at the nanoscale level, opening the door for the on-demand design of functionality. At the same time, careful synthesis and production of pristine materials and interfaces can also produce thin-film ferroelectrics that begin to approach the switching achieved in single-crystal materials. This, in turn, opens the door for record-breaking small coercive voltages and ultra-low power function and operation. In multi-layered and superlatticed materials, the careful interfacing of materials can produce new combinations of properties – including combined large polarization and large dielectric constant and tunability – in, for example, PbZr₁-xTiₓO₃ superlattices controlled to have overall compositions near the morphotropic phase boundary (MPB) composition, but being built from layers far from the MPB composition. Finally, we will explore new efforts in the production, utilization, and testing of free-
standing versions of ferroelectrics. New selectively etchable layers are now enabling the production of large, free-standing epitaxial stacks. Routes to release, transfer, and measure free-standing films will be introduced and a range of properties measured therein.

6:30 AM S.EL02.01.05
Improving Functionalization of MWCNTs through Non-Covalent Interactions with Organic Molecules Pablo Quijano Velasco1, Kyriakos Porfyrikas2 and Nicole Grobert1,3, 1University of Oxford, United Kingdom; 2University of Greenwich, United Kingdom; 3Williams Advanced Engineering Limited, United Kingdom

Tailoring the surface properties of carbon nanotubes (CNTs) through covalent or non-covalent interactions with organic molecules has been highlighted for more than a decade as promising path for the fabrication of functional nanostructures that could be successful in a wide variety of application ranging from nanomedicine to reinforced structural materials1. However, the efficient functionalization of CNTs, especially multiwalled-CNTs (MWCNTs), still faces many challenges due to the lack of understanding of the interaction mechanisms between MWCNTs and organic molecules in functionalization procedures. In this study, we compare the functionalization of MWCNTs through covalent and non-covalent methods, with the objective of elucidating clear synthetic guidelines for the efficient functionalization of MWCNTs.

To understand the mechanisms of covalent functionalization of MWCNTs we attempted the functionalization of MWCNTs with polystyrene molecules via Prato and nitrene cycloaddition reactions. Through the comparison of TGA and Raman spectroscopy of the products, we showed that the nature of the reaction has no impact on the degree of functionalization of the MWCNTs. In addition, we highlight the use of control experiments using non-reactive polystyrene molecules, that allowed us to demonstrate that the degree of functionalization of MWCNTs was comparable to the products of the covalent functionalization reactions. The independence in the degree of polymer functionalization of the reaction procedure and of the use of non-reactive polystyrene was observed for MWCNTs with different diameter sizes. These experimental evidences demonstrate that covalent bonds between polymers and pristine MWCNTs are not present and that the functionalization occurs through non-covalent forces.

Non-covalent functionalization was then performed in six different solvents to explore the impact of the solvent in the polystyrene-MWCNTs interactions. We observed a characteristic degree of functionalization for each solvent and we propose for the first time a simple model based on surface energy solubility parameter theory that can be used as a synthetic guideline for the design of polymer functionalised MWCNTs2. Finally, we demonstrate that this model can be applied for the fabrication and design of nanoparticle/carbon nanotube hybrid structures. We believe that our results and the application of the surface energy based solubility parameter theory as a qualitative model for the design of functionalized MWCNTs will lead to the rational synthesis of a wide range of novel nanostructures.

References

6:45 AM S.EL02.01.08
Synthesis Strategies Involving Local Energy Transduction—The Optically Oriented Assembly of Metal-Semiconductor Building Blocks in Solution via Photonic Nanosoldering Matthew J. Crane, Elena P. Pandres, E. James Davis, Peter Pauzauskie and Vincent C. Holmberg; University of Washington, United States

Careful control over chemistry, composition, and morphology are critical in virtually every materials system, and new methods that enable precise control over the rational assembly of constituent building blocks are vital to the future of nanoscale fabrication efforts. Here, we will discuss our recent results published in Nature Communications on the light-driven, solution-based assembly of nanoscale building blocks into periodic, one-dimensional heterostructures, consisting of repeating metal-semiconductor junctions via a photonic nanosoldering process, as well as two other recent examples where local energy transduction is used as a strategy to drive chemistry and control nanoparticle crystal growth. Effects of anisotropic radiation pressure, heat transport, and solvent choice on material transformations and nanostructure assembly will be discussed. We believe that these approaches can be generalized to enable the additive manufacturing of nanoscale structures for numerous applications, and we hope that this demonstration will lead to wider use of optical manipulation techniques for the rational assembly of diverse sets of nanomaterials in a variety of different solvent systems.

7:00 AM S.EL02.01.09
Elastic and Plastic Relaxation in Highly Strained Core-Shell Semiconductor Nanowires Slawomir Kret, Serhii Kryvyi, Dorota Janaszko, Anna Kaleta, Jakub Plachta and Piotr Wojnar; Institute of Physics PAS, Poland
Due to high ratio of surface to volume ratio the monocrystalline semiconductor core-shell nanowires (NWs) are very suitable as building blocks a of solar cells, optoelectronic, electronic and environmental sensor devices. They are also perfect model structures for studying nanomechanical behavior of defects appearing during strain relaxation in nanoscale objects. For this purpose strained ternary semiconductors core-shell nanowires were grown by molecular beam epitaxy (MBE) on Si or GaAs substrate using Vapor-Liquid-Solid (VLS) mechanism. Due to high mismatch of the lattice constant of basic compounds ZnTe, CdTe, MgTe, which can reach more than 7%, the growth of nanowires is challenging and their final shape and morphology are complex. By modification of growth conditions (temperature, stoichiometry) nonstandard crystal structure for given compound can be obtained. For example it is possible to obtain hexagonal (wurtzite) structure or polytypic superlattice in CdTe, which usually crystallizes in regular cubic structure. [1]. The core-shell NWs, investigated by transmission electron microscopy (TEM) are strained or partially relaxed depending on the core diameter, lattice mismatch and local thickness of the shell.

The residual strain field and core-shell interface misfit dislocation network is studied for individual nanowires by TEM. The Dislocation Density Tensor mapping is performed using extension of the Geometric Phase Analysis [2] performed on HRTEM and HRSTEM images obtained from different zone axis axes in planar view or/and using perpendicular FIB cross-section of the nanowires. Due to the significant deformations of the NWs (bends and twists) the high-resolution images in zone axes can be obtained only for the several tens of nanometers long fragments of the NWs having few micrometers of total length. Therefore, we use Scanning Electron NanoDiffraction (SEND) to map bending and twisting of the lattice as well as chemical lattice distortions related to the changes in elemental composition. The series of electron diffraction patterns obtained in the STEM mode is analyzed to receive the individual maps of the lattice distortions components, via combination of simulated dynamic diffraction patterns and local cross-correlation with experimental patterns. As a results, it is possible to determine local thickness, projected distortions axial and radial components, local lattice twist(alpha) as well as and tilts (beta and gamma) even for bent NWs. Combination of both approaches of strain measurements allows to determine the projection of the residual strain in such complex 3D geometry as well as establish the dependence between the spatial arrangement of interfacial misfit dislocation network on the asymmetry of the shape of nanowires and shell inhomogeneity. In the case of the CdTe/ZnTe NWs crystalizing in regular crystal structure form, the core-shell interface dislocation network consisted of 60°dislocations and dissociated Lomer dislocations. We show that lateral and radial spacing between dislocations depends strongly on the core thickness as well as the core diameter. These findings are in qualitative agreement with theoretical prediction [3]. In the case of NW with stacking fault, due to section of the [111] plane core stacking fault with shell formed [11-1] stacking fault the static Cottrell-Lomer Lock dislocations was observed with cation core polarity. The difference of the morphology of network of interface misfit dislocations between NW having wurtzite and regular crystal structure are discussed. The initial model of plastic relaxation is proposed.

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7:15 AM *S.EL02.01.10
Van der Waals Heterostructures from 2D Materials and Beyond Xiangfeng Duan; University of California, Los Angeles, United States

The heterogeneous integration of dissimilar materials is a long pursuit of material science community and has defined the material foundation for modern electronics and optoelectronics. The typical material integration approaches usually involve strong chemical bonds and aggressive synthetic conditions and are often limited to materials with strict structure match and processing compatibility. Alternatively, van der Waals integration, in which freestanding building blocks are physically assembled together through weak van der Waals interactions, offers a bond-free material integration strategy without lattice and processing limitations, as exemplified by the recent blossom of 2D van der Waals heterostructures. Here I will discuss the fundamental forces involved in van der Waals integration and generalize this approach for flexible integration of radically different materials to produce artificial heterostructures with minimum interfacial disorder and enable high-performing devices. Recent highlights include the formation of van der Waals metal-semiconductor junctions free of Fermi level pinning to reach the Schottky-Mott limit; the creation of a new class of high-order van der Waals superlattices with highly distinct constituents of atomic or molecular layers; and the development of van der Waals thin film electronics with unprecedented flexibility and stretchability. I will conclude with a brief perspective on exploring such artificial heterostructures as a versatile material platform with electronic structure by design to unlock new physical limits and enable device concepts beyond the reach of the existing materials.
Vertically Stacked 0D/2D Materials Based Hybrid Infrared Phototransistor
Anindita Sahoo, Peter Reiss, Etienne Quesnel, Jacques Cluzel, Luc Andre, Eric De Borniol and Berangere Hyot; Univ. Grenoble Alpes, CEA, France

Infrared (IR) photodetectors are nowadays in high demand in a wide range of fields such as telecommunication, thermal imaging, remote sensing, night assistance car driving etc. Recently, hybrid phototransistors made of highly efficient light absorbing 0D quantum dots and high mobility 2D materials have introduced a new technology, which dramatically increases the responsivity and gain of the photodetector. In 2012, such low dimensional IR phototransistor based on graphene/PbS QD hybrid was proposed in literature \cite{1, 2} for the first time. Later in 2017, a high-resolution broadband image sensor based on such hybrid materials was demonstrated \cite{3}, which is sensitive to ultraviolet, visible and infrared light (300–2000 nm).

We have investigated similar graphene/PbS QD hybrid phototransistors and explored the enhancement of their photo-sensing qualities compared to bare graphene phototransistor in the visible-NIR-SWIR region of optical spectra. Initially, we studied CVD-grown single layer graphene phototransistor in the visible-NIR region, which showed a responsivity of about $10^4$ A/W, associated with the low–doped Si substrate, which acts as the primary material for optical absorption. Such responsivity is 10$^7$ orders of magnitude higher \cite{4} than conventional graphene phototransistor \cite{5}. However, the photo-sensing wavelength range of such device is limited up to 1100 nm depending on the principal absorption material Si. In order to expand the photo-sensing wavelength range up to SWIR region, we have explored the potential of graphene/PbS QD hybrid phototransistors. We synthesized the colloidal PbS QDs absorbing in the NIR as well as SWIR regions and developed a layer-by-layer dip coating with simultaneous ligand exchange procedure to deposit homogeneous PbS QD layers on graphene sheet leading to a well fabricated hybrid phototransistor. We achieved a significantly high responsivity of at 940 nm with irradiation power density of $10^{-4}$ W/m$^2$. In the NIR range, the peak responsivity appears to be $10^7$-10$^8$ A/W, whereas in the SWIR range, the observed peak responsivity is $10^6$ A/W. Moreover, graphene/PbS QD hybrid exhibits high sensitivity at low irradiation power (< 0.05 nW), where bare graphene photodetector is unable to sense such low intensity light in the visible-NIR region.


Accurate Prediction of Energy Level Alignment in Mixed-Dimensional Heterojunctions
Qunfei Zhou$^1$, Zhenfei Liu$^2$ and Pierre T. Darancet$^3$; $^1$Northwestern University, United States; $^2$Wayne State University, United States; $^3$Argonne National Laboratory, United States

Understanding energy level alignment between molecules and two-dimensional materials is conducive to controlling charge and energy transfer in mixed-dimensional heterojunctions. The competition between distinct energy scales, such as the ones associated with electronic correlations, interface dipole, orbital hybridization, and non-local dielectric screening, can lead to significant renormalization of the intrinsic energy levels of each material at these interfaces. The variety of these energy scales also complicates the theoretical description of the level alignment for mixed-heterojunctions accurately.

Here we study the electronic structure and level alignment for mixed 0D-2D heterojunctions containing transition metal phthalocyanines on MoS$_2$ by first-principles density functional theory (DFT) calculations. By using optimally tuned range-separated hybrid (OT-RSH) functionals, a recently developed method for finding the optimal range-separated parameters for describing short-range and long-range electron exchange effect, we obtain energy level alignment consistent with known experimental results, a significant improvement comparing to standard DFT. This method can be used for other mixed-heterojunctions for better understanding of their electronic and optical properties.

Two-Dimensional Materials for Energy
Yi Cui$^{1,2}$; $^1$Stanford University, United States; $^2$SLAC National Accelerator Laboratory, United States

Two dimensional (2D) layered materials have strong in-plane covalent bonding and weak van der Walls interaction between
the planes, which host a wide variety of interesting physical and chemical phenomena. Here I will present our research over 15 years on nanostructured 2D materials. First, I will show how we synthesize these 2D materials into rich morphologies including nanoplates, nanoribbons, layer-vertical aligned films as well as lateral and vertical heterostructures. Second, we developed liquid-gel gating, solid state ion gating, chemical and electrochemical intercalation to control the physical and chemical property of 2D materials. Third, we demonstrated exciting new exciting application of using 2D materials for batteries and catalysis applications.

8:45 AM *S.EL02.01.16  
Dimensional Engineering in Solid-State Quantum Simulators  
Na Young Kim; University of Waterloo, Canada

We engineer electronic and photonic structures to control light-matter interactions including dimension and geometries. These hybrid electronic and photonic structures, especially forming microcavity exciton-polaritons are basis to build solid-state quantum simulators. Quantum simulators are constructed with special-purpose to tackle a certain class of challenging problems for example, investigation of emerging topological quantum materials and their underlying physical mechanisms. Successful demonstration of quantum simulators relies on the controllability of engineered systems. I present our current methods to establish engineered quantum simulators based on solid-state systems with performance status and future perspectives.

9:15 AM *S.EL02.01.17  
Gate-Tunable Narrow-Band Extinction of Near-Infrared and Visible Light in Graphene/LaAlO3/SrTiO3 Nanostructures  
Jeremy Levy1,2, Erin Sheridan1,2, Lu Chen1,2, Jianan Li1,2, Qing Guo1,2, Hyungwoo Lee1, Jung-Woo Lee1, Chang-Beom Eom1 and Patrick Irvin1,2; 1University of Pittsburgh, United States; 2Pittsburgh Quantum Institute, United States; 3University of Wisconsin–Madison, United States

The absorption spectrum for pristine, undoped graphene is constant at 2.3 % across the visible to near-infrared (VIS-NIR) region of the electromagnetic spectrum. When these assumptions are relaxed, graphene can exhibit a strongly nonlinear optical response. Here, we explore the optical properties of graphene that has been integrated with LaAlO3/SrTiO3 nanostructures. Nanojunction devices formed at the LaAlO3/SrTiO3 interface enable large (~10⁸ V/m) electric fields to be applied to graphene over a scale of ~10 nm. Nanoscale gating of the graphene in this way causes it to interact strongly with light, producing significant broadband THz emission via difference frequency mixing as well as a sum-frequency generated (SFG) response. Unexpectedly sharp spectral features show >99.99% extinction of the response. Extinction features are observed in both the VIS-NIR and SFG response, and can shift in frequency depending on the nanojunction bias and/or linear polarization. These surprisingly strong optical nonlinearities help to probe the fundamental response of nanostructured graphene, and open the way for future exploitation in optical devices.

9:45 AM *S.EL02.01.18  
Mixed-Dimensional Heterostructures for Electronic and Energy Applications  
Mark C. Hersam; Northwestern University, United States

Layered two-dimensional (2D) materials interact primarily via van der Waals bonding, which has created new opportunities for heterostructures that are not constrained by epitaxial growth [1]. However, it is important to acknowledge that van der Waals interactions are not limited to interplanar interactions in 2D materials. In principle, any passivated, dangling bond-free surface interacts with another via non-covalent forces. Consequently, layered 2D materials can be integrated with a diverse range of other materials, including those of different dimensionality, to form mixed-dimensional van der Waals heterostructures [2]. Furthermore, chemical functionalization provides additional opportunities for tailoring the properties of 2D materials [3] and the degree of coupling across heterointerfaces [4]. In order to efficiently explore the vast phase space for mixed-dimensional heterostructures, our laboratory employs solution-based additive assembly [5]. In particular, constituent nanomaterials (e.g., carbon nanotubes, graphene, transition metal dichalcogenides, black phosphorus, boron nitride, and indium selenide) are isolated in solution, and then deposited into thin films with scalable additive manufacturing methods (e.g., inkjet, gravure, and screen printing) [6]. By achieving high levels of nanomaterial monodispersity and printing fidelity [7], a variety of electronic and energy applications can be enhanced including photodetectors [8], optical emitters [9], and lithium-ion batteries [10-12]. Furthermore, by integrating multiple nanomaterials into heterostructures, unprecedented device function is realized including anti-ambipolar transistors [13], gate-tunable photovoltaics [14], and neuromorphic memtransistors [15]. In addition to technological implications for electronic and energy technologies, this talk will explore several fundamental issues including band alignment, doping, trap states, and charge/energy transfer across previously
Unique Properties of Quasi-One-Dimensional and Mixed Dimensional van der Waals Heterostructures

Alexander A. Balandin; University of California, Riverside, United States

Two-dimensional (2D) materials, such as graphene and transition metal dichalcogenides (TMDs) MX2 (where M = many transition metals; X = S, Se, Te), have revealed new physics and demonstrated potential for practical applications. In recent years, interest in layered van der Waals materials has expanded to quasi-one-dimensional (1D) structures. Unlike the layered MX2 materials that yield 2D layers upon exfoliation, the transition metal trichalcogenides (TMTs) MX3 contain 1D motifs, i.e. atomic threads, that are weakly bound together by van der Waals forces [1-2]. In this invited talk, we will review synthesis methods, properties and possible device applications of this unique family of quasi-1D TMT material systems. As a consequence of their structures, the exfoliation or growth of MX3 crystals results in nanowires and nanoribbons rather than 2D layers. Some of TMTs can be considered as truly 1D materials while others, which have weaker covalent bonds in directions perpendicular to the atomic threads, can be considered as mixed dimensional structures. One can also fabricate heterostructures consisting of 1D and 2D van der Waals materials [1-2]. We have discovered that some of these quasi-1D nanomaterials reveal an exceptionally high current density. For example, quasi-1D TaSe3 nanowires capped with quasi-2D h-BN layers have a breakdown current density exceeding \( \text{JB} \approx 10 \text{ MA/cm}^2 \), which is larger than what can be sustained by the state-of-the-art Cu interconnects. In a recent contribution, we reported uncapped ZrTe3 nanoribbons with an even more impressive breakdown current density of \( \approx 100 \text{ MA/cm}^2 \), which is more than an order of magnitude larger than the value obtained in DC testing of Cu wires [3]. We have used low-frequency noise (LFN) spectroscopy to investigate carrier recombination in such materials and verify reliability of the van der Waals interconnects [4-5]. It was found that LFN in ZrTe3 reveals conventional \( 1/f \) behavior near room temperature (f is frequency). However, at low temperature it is dominated by the Lorentzian bulges of the generation–recombination noise at low temperatures, which is unusual for metals.

Unexpectedly, the corner frequency of the observed Lorentzian peaks revealed a strong sensitivity to the applied bias. This dependence on electric field was explained by the Frenkel–Poole effect in the scenario where the voltage drop happens predominantly on the defects, which block the quasi-1D conduction channels. The obtained results reveal the potential of quasi-1D/quasi-2D materials and heterostructures for applications in future ultimately downscaled interconnects and device technologies.

This work was supported, in part, by the National Science Foundation (NSF) through the DMREF: Collaborative Research (UCR – Stanford): Data Driven Synthesis Pathways and Distinguishing Electronic Phenomena of 1D van der Waals Bonded Solids, and by the Semiconductor Research Corporation (SRC) contract 2018-NM-2796: One-Dimensional Single-Crystal van-der-Waals Metals: Ultimately-Downscaled Interconnects with Exceptional Current-Carrying Capacity and Reliability.

Developing efficient bifunctional catalysts for overall water splitting that are earth-abundant, cost-effective, and durable is of considerable importance from the practical perspective to mitigate the issues associated with precious metal-based catalysts. In the present study, we introduce a heterostructure comprising perovskite oxides (La_{0.5}Sr_{0.5}CoO_{2−δ} (LSC)) and transition metal dichalcogenides (TMDs, MoSe_2) as an electrochemical catalyst for overall water electrolysis. Interestingly, formation of the heterostructure of LSC and MoSe_2 (LSC&MoSe_2) induces a local phase transition in MoSe_2, 2H to 1T phase, owing to electron transfer from Co to Mo, and the semiconducting MoSe_2 transforms to the metallic phase. In addition, LSC becomes more electrophilic, and Co-O and Co-OH bonds are favored owing to partial oxidation of the Co cation due to the electron transfer. Together with the electrochemically active nature of 1T MoSe_2 and the increased amount of Co-O and Co-OH bonds in LSC, the electrochemical activities are significantly improved for both hydrogen evolution reaction and oxygen evolution reaction. In the overall water splitting operation, LSC&MoSe_2 showed excellent stability at the high current density of 100 mA cm⁻² over 1,000 h, which is exceptionally better than the stability of the state-of-the-art Pt/C || IrO_2 couple.

11:15 AM *S.E.L02.01.22
Control of the Structure and Formation of Zero-Dimensional Nanostructures within Nanowires Yi-Chia Chou¹, Federico Panciera², Yuan-Wei Chang¹, Chia-Yi Wu³, Wen-Chien Miao¹ and Frances M. Ross³; ¹National Chiao Tung University, Taiwan; ²University of Paris-Saclay, France; ³Massachusetts Institute of Technology, United States

Developing new types of nanoscale electronic devices, such as switches or storage elements, often requires creating both a functional nanostructure with precisely controlled properties and a well-defined connection between the nanostructure and the larger-scale circuit. Achieving sufficient control of nanostructures and their contacts is a key step that generally involves integrating different types of materials as well as bridging between length scales. For example, in Si or Ge-based circuits, metal silicides and germanides are commonly used in low-resistance contacts, while functional nanostructures can involve combinations of semiconductors with insulators and metals. Here we consider nanowires, which are especially favorable geometries for connecting nano and macro length scales, and discuss the opportunities for creating complex nanostructures within individual nanowires. In particular, we focus on silicide and germanide nanocrystals embedded within Si and Ge nanowires.

We start by illustrating how silicide and germanide nanostructures can be formed in silicon nanowires grown by the vapor-solid-liquid (VLS) mechanism. These nanocrystals are initially created by adding the appropriate metal to the liquid droplets that catalyze the nanowire growth. We show that solid silicide or germanide nanocrystals form in the liquid and have freedom to move and rotate until a low-energy interface with the nanowire is found. The crystal attaches to the nanowire, nanowire growth is then continued, and the nanocrystal becomes encapsulated within the nanowire. The process can be repeated to form multiple inclusions that are useful for contact formation as well as for modifying nanowire properties in new ways. In situ environmental TEM clarifies the sequence of phases and structures present at the atomic level during this complex process.

After the nanocrystal-nanowire contact is first made, we find that certain types of silicide and germanide nanocrystals remain attached while others break away without forming a permanent contact. Only the nanocrystals that remain attached to their nanowire can be incorporated by continued growth of the nanowire. We have examined the factors that determine nanocrystal adhesion to the nanowire and suggest that the outcome depends on the symmetry of the contact interface and hence the crystal structures of both materials. This restricts the range of nanocrystal/nanowire combinations possible. To expand the range of materials that can be encapsulated, we explore the use of phase transformations within the nanocrystal. As an example, NiGe does not attach to the growth surface of a Ge nanowire so is difficult to incorporate. But after growing a NiGe nanocrystal we can add Si to transform the nanocrystal to a silicide and this structure does attach and incorporate. We suggest that the variety of nanostructures with incorporated nanocrystals that can be made using such reaction schemes potentially increases the opportunities for designing specific electronic and contact properties for nanostructured device applications.
11:45 AM S.EL02.01.25
Probing Metal Center Effects in MoS₂ – Metallophthalocyanine Mixed-Dimensional Heterojunctions

Samuel Amsterdam¹, Teodor K. Stanev¹, Qunfei Zhou¹ ², Vinod K. Sangwan¹, Alexander J. Lou¹, Hadallia Bergeron¹, Pierre T. Darancet², Mark C. Hersam¹, Nathaniel P. Stern¹ and Tobin J. Marks¹; ¹Northwestern University, United States; ²Argonne National Laboratory, United States

Mixed-dimensional heterojunctions, such as zero-dimensional organic molecules deposited on two-dimensional transition metal dichalcogenides (TMDs), exhibit unique interfacial effects that modify the properties of the individual constituent layers. To better understand the effect of changing molecular orbital energy on the heterojunction properties, we report here a systematic study of metallophthalocyanine (MPC) – MoS₂ (M = Co, Ni, Cu, Zn, H₂) heterojunctions using optical absorption, Raman spectroscopy, low temperature photoluminescence, variable temperature electrical measurements, and density functional theory. Notable phenomena include the emergence of heterojunction-specific optical absorption transitions, strong Raman enhancement, and quenching of defect emission that depend on phthalocyanine metal center identity. Temperature-dependent electrical noise measurements on field-effect transistors provide further insight into the properties of these mixed-dimensional heterojunctions. These results highlight the tunable nature of metal-organic-TMD van der Waals interfaces and the importance of the organic architecture and electronic structure in designing mixed-dimensional heterojunctions for optical and electronic applications.

12:00 PM S.EL02.01.27
Growth and Characterization of Ferromagnetic Manganese (IV) Selenide—Epitaxial Graphene Heterostructures

Ihteyaz A. Avash, Michael Pedowitz, Guy D. Cassuto and Kevin Daniels; University of Maryland, United States

In recent years, several transition metal dichalcogenides (TMDs) have been found to exhibit intrinsic ferromagnetic properties near the monolayer limit [1, 2]. However, unlike most ferromagnetic TMDs studied so far which only show weak ferromagnetic properties at extremely low temperature, the monolayer 1T polytype of manganese diselenide (MnSe₂) have been found to display long-range magnetic ordering and high magnetic moments (3μB per unit cell), as well as a high Curie temperature of 250K, tunable up to 375K via 5% biaxial strain [3]. Hence, this material has a high potential for future applications in low energy magnetic switching and non-volatile logic data storage [4]. In this study, two-dimensional heterostructures of manganese (IV) selenide are grown via chemical vapor deposition (CVD) on epitaxial graphene (EG) synthesized on 6H silicon carbide (SiC) substrates.

In our experiments, three different approaches for the CVD growth of the heterostructure have been investigated to grow MnSe₂. In our first approach, powdered manganese (IV) oxide (MnO₂) and selenium powder (Se) reactants were used. In the second method, manganese acetate (Mn(CH₃CO₂)₂) powder was used to improve manganese nucleation on EG. In our final method, δ-phase MnO₂ is electrodeposited on epitaxial graphene using a 0.1M solution of manganese acetate in a three-electrode electrochemical cell. Selenium powder is subsequently used in the selenification of δ-phase MnO₂ using the CVD method.

Characterization via Raman spectroscopy demonstrated the presence of MnSe₂ for all three approaches, which was also confirmed by SEM, AFM and EDX analysis. Although the characteristic A₅ Raman peak of MnSe₂ was visible at 269 cm⁻¹ for the first method, the very low intensity (almost 40% of the control FTA peak of the substrate at 203 cm⁻¹) of the peak indicated extremely low grain size and yield density. This conclusion was in agreement with the AFM and SEM data, which showed a sparse distribution of small growth particles (around 0.1 μm). Characterization of the second method displayed similar results, except the A₅ peak intensity displayed a relative increase of around 30%. The AFM and SEM data also showed a roughly 200% increase in grain size, which can be attributed to the relatively lower sublimation temperature of manganese acetate.

In the Raman data of the final approach, however, both characteristic E₆ and A₅ peaks of MnSe₂ are clearly visible (at 145 cm⁻¹ and 267 cm⁻¹ respectively) with extremely high peak intensity (around 400% of the mentioned substrate control peak), implying significantly higher MnSe₂ yield. The AFM and SEM data also demonstrated significantly high deposition density along graphene step edges. This remarkable improvement can be credited to the electrodeposited MnO₂ promoting manganese adhesion and selenification of the sample. This procedure shows great promise in the synthesis of single-crystal MnSe₂ heterolayer on epitaxial graphene. Samples grown using this mechanism has significant potential application in the field of spintronics on a wafer scale.
Reference:

12:15 PM S.E.L02.01.28
Defect-Free Assembly of Quasi-Three-Dimensional Plasmonic Nanoarrays with Arbitrary Substrate Materials and Structures Bongjoong Kim¹, Jiyeon Jeon², Yue Zhang³, Dae Seung Wie¹, Jehwan Hwang², Sang jun Lee², Dennis Walker⁴, Don Abeysinghe⁴, Augustine Urbas⁴, Baoxing Xu³, Zaiyun Ku³ and Chi Hwan Lee¹; ¹Purdue University, United States; ²Korea Research Institute of Standards and Science, Korea (the Republic of); ³University of Virginia, United States; ⁴Air Force Research Laboratory, United States

Interaction of incident light with periodic arrays of three dimensional (3D) metal-dielectric compositied nanoarrays provide remarkable opportunities to harness light in a way that cannot be obtained with conventional optics. Diverse types of 3D or quasi-3D plasmonic nanoarrays with tailored feature shapes, sizes and configurations have been explored for a broad range of light-driven sensors and actuators, including imagers, bio-sensors, lasers and antennas. However, their practical applications remain challenged by a lack of effective manufacturing methodology. To bridge this gap, we developed a new concept of methodology that enables physical separation of precisely engineered quasi-3D plasmonic nanoarrays from their donor fabrication wafer and then transfer to a preferred foreign substrate in a defect-free manner that allows the donor wafer can be repeatedly recycled, offering a major cost- and time-saving factor in the manufacturing scheme. Unlike any of existing approaches, the entire process of this method exclusively occurs in distilled (DI) water at room temperature without the need of further chemical, thermal or mechanical treatments, and which thereby can substantially extend the types of receiver substrate to nearly arbitrary materials and structures. This approach provides versatility and modular scalability to arrange various classes of quasi-3D plasmonic nanoarrays in lateral and vertical configurations, offering a unique route to generate heterogeneous material compositions, complex device configurations and tailored functionalities. Comprehensive experimental, computational and theoretical results reported here reveal the essential design features of this method and, taken together with implementation of automated equipment, provide a technical guidance for manufacturable controllability and scalability. Pilot deterministic assembly of specifically engineered quasi-3D plasmonic nanoarrays with an industrial-grade hybrid imager, such as a mid-wavelength infrared type-II superlattice (MWIR-T2SL)-based hybrid pixel detector (HPD) successfully yields the enhancement of the detection performances and functionalities which otherwise cannot be achieved by conventional counterpart systems. The established 3D nanassembly methodology has a great potential to extend the application of the deterministically assembled plasmonic nanoarchitectures for other types of imagers, antennas and biosensors.

12:30 PM S.E.L02.01.32
Van der Waals Epitaxy of the Bismuth Iodide/Semiconductor Heterostructure via Self-Assembly-Monolayer Modification and Its Application of Nonvolatile Resistive Random-Access Memory Yutien Wu¹, Chiashuo Li², Sheng-Wen Kuo¹, Po-Han Chang¹, I-Chih Ni³, Mei-Hsin Chen² and Chih-I Wu⁴; ¹National Taiwan University, Taiwan; ²National Taipei University of Technology, Taiwan

As the electronics scaling down, the interfacial properties such as dangling bonds or surficial reconstructions play a critical role in functionality and performance of devices and the crystallinity of the overlayer. In addition, large roughness and pin holes of the insulator layer usually lead to leakage current and degradation in resistive random-access memory due to unrecoverable electrical breakdown. In this study, to eliminate the lattice interaction from the underlying substrate, we present a facile and easy method to achieve van der Waals epitaxy of bismuth iodide (BiI₃) on the silicon wafer by using a self-assembly-monolayer of octadecyltrichlorosilane (OTS) as a buffer layer. As a result, the BiI₃ layer on the silicon wafer possesses considerably flatten surface and high crystallinity, and the resistive-switching devices based on the BiI₃/OTS/Si heterostructure demonstrated excellent resistive switching property with a very high on/off ratio of 10⁹, long term stability for data retention, high endurance to write/erase cycles and the capability of multistate information-storage. The resistive switching behaviors, the roughness, morphology, and crystallinity of the BiI₃ layer are systematically investigated by analyzing the current-voltage characteristics at different temperature, scanning electron microscope, atomic force microscope, X-ray photoemission spectroscopy (XPS) and x-ray diffraction patterns (XRD). Consequently, the resistive switching mechanisms is explained by formation and rupture of a conductive filament consist of metallic bismuth in the insulating layer as a result of the ion migration of iodine that changes the valence charge of BiI₃ under the electrical field. This paper will help the fabrication process in large scale and the integration of BiI₃ based resistive switching devices with the integrated
circuit technology.

12:45 PM S.EL02.01.33
A Novel Technique for Fabrication of Nanowhisker Interconnects with Near Bulk Resistivity
Prajwal Rigvedi
Madhusudan Rao and Gunther Richter; Max Planck Institute for Intelligent Systems, Germany

It has always been a challenge to fabricate devices at the nanoscale and analyse their properties, be it for the lack of equipment or the lack of techniques available. Defect free nanowhiskers attract a lot of attention as a potential candidate for interconnects. A concern regarding the resistivity of nanowires is their increased resistivity, which sometimes is 10 or 100 times larger than their bulk counterparts [1]. With this work, we are presenting a cleaner and a novel method which allows the formation of nanowhisker interconnects with near bulk resistivity facilitating a simple LASER lithography technique.

We adopt a bottom-up approach for device fabrication using what we call “Target Specific Lithography”. The whiskers which are grown by Molecular Beam Epitaxy are single crystals with a high aspect ratio and without any grain boundaries or defects [2]. These whiskers were transferred onto a Si substrate. A layer of resist is applied on this substrate and four contacts are designed in CAD and aligned with high precision so that it lies on top of an individual whisker. The contacts are exposed using a direct LASER writer. 100 nm Niobium is sputtered onto the lithographically patterned substrate. Upon liftoff, Niobium forms the contacts on the whiskers, allowing for the electrical transport measurement.

Electrical transport measurements performed on Au, Ag and Cu nanowhisker interconnects are demonstrated. The lengths of these whiskers are in the range of 18 μm to 40 μm, with an average diameter of 110 nm. The resistivity of gold at room temperature, for example, was found to be 2.20 ± 0.36 μΩcm, which is same as that of the bulk resistivity. Such results show that there is no size effect on the resistivity of the whiskers and that there are no impurities in the interface between the whisker and the contacts. We also have plans to conduct low-temperature measurements to understand the transport behaviour of the nanowhiskers as a function of temperature.


1:00 PM S.EL02.01.34
Atomically Dispersed Fe–N/C Catalysts of the New Benchmark Performance for Oxygen Reduction Reaction Synthesized by Selective Microwave Annealing
Woo Yeong Noh; Ulsan National Institute of Science and Technology, Korea (the Republic of)

The oxygen reduction reaction (ORR) is a key electrochemical reaction taking place at the cathode of various energy devices such as fuel cells and metal-air batteries. Heavily-loaded Pt catalysts are used to circumvent intrinsically sluggish kinetics of ORR, yet scarcity and high cost of Pt have triggered a recent drive toward alternative platinum group metal (PGM)-free catalysts, including non-precious metals, metal chalcogenides, metal-free, and single-atom catalysts. The single-iron-site catalyst surrounded by four nitrogen atoms (Fe–N₄) has emerged as one of the most promising electrocatalysts to replace Pt-based catalysts. To immobilize Fe–N₄ species on a conductive carbon support, however, high-temperature annealing for more than several hours is required, which induces severe aggregation of Fe metal ions along with its loose attachment on the carbon support resulting in low ORR activity and low stability. Significant deactivation is observed primarily caused by serious carbon corrosion or metal dissolution, which are common problems of carbon-supported catalysts in general because of intrinsically weak interaction of carbon with the active component. Thus, a high degree of graphitization of carbon supports is vital for the stability of a single atomic Fe–N₄ catalyst.

Carbon is one of the most common support materials for (electro)catalysts due to its high surface area, good conductivity, relative chemical inertness, and low cost. We also note that carbon is among the best microwave absorbers (susceptors) due to its high dielectric properties and short attenuation distance. Upon microwave irradiation, the carbon support can selectively absorb the radiation, keeping the catalyst precursor temperature low, and then heat is migrated from the carbon to the catalyst precursor. Because this selective and directional heat transfer mechanism dramatically reduces the chance of reaction between the catalyst precursors leading to agglomeration, and the entire process occurs in just a few seconds to minutes, the sintering of the catalyst particles is effectively mitigated. Instead, it causes strong attachment of the catalyst to the carbon surface. In this proposed new synthetic strategy, which we term “selective microwave annealing (SMA)”, there is no
temperature limit and the reaction atmosphere [oxygen (O₂), nitrogen (N₂), and argon (Ar) gases] can be easily regulated, as in the conventional heating method. Furthermore, it does not require any additional microwave susceptor, such as those used in hybrid microwave annealing systems. Thus, we applied this SMA technique utilizing the CNT support as a main microwave susceptor to fabricate atomic Fe–N₄ catalysts anchored strongly on CNT supports without Fe agglomeration. Structural characterizations by high-angle annular dark-field transmission electron microscopy (HAADF-STEM) combined with electron energy loss spectroscopy (EELS), X-ray absorption spectroscopy (XAS), and X-ray photoelectron spectroscopy (XPS) revealed that the single Fe atoms were uniformly dispersed in the form of Fe–N₄ and that a few-layer, graphene-like carbon structures were coated on the CNT surface in the selective microwave-annealed catalyst (MA-Fe-N/CNT), while severe agglomeration of Fe metal and amorphous carbon layers were observed for the thermally annealed catalyst (TA-Fe-N/CNT). As a result, the MA-Fe-N/CNT catalyst exhibited outstanding ORR activity with a half-wave potential of 0.92 V vs. reversible hydrogen electrode (VRHE) and excellent stability both in alkaline and acidic media. The catalytic performance and stability were superior to TA-Fe-N/CNT and even exceeded those of commercial Pt/C catalysts. We also have demonstrated that this SMA technique is generally applicable to other carbon supports, such as reduced graphene oxide and carbon black. Finally, we also have verified a Na-air battery with the as-prepared MA-Fe-N/CNT catalyst operates as effectively as the device with a Pt/C catalyst.

1:15 PM *S.EL02.01.35
Print-in-Place Electronics Using Mixed-Dimensional Nanomaterials Aaron D. Franklin; Duke University, United States

For decades we’ve been hearing about the promise of printing electronics directly onto any surface. However, despite significant progress in the development of inks and printing processes, reports on fully, direct-write printed electronics continue to rely on excessive thermal treatments and/or fabrication processes that are external from the printer. In this talk, recent progress towards print-in-place electronics will be discussed; print-in-place involves loading a substrate into a printer, printing all needed layers, then removing the substrate with electronic devices immediately ready to test. A key component of these print-in-place transistors is the use of inks from various nanomaterials, including 1D carbon nanotubes (CNTs - semiconducting), 2D hexagonal boron nitride (hBN - insulating), and quasi-1D silver nanowires (AgNWs – conducting). Using an aerosol jet printer, these mixed-dimensional inks are printed into functional 1D-2D thin-film transistors (TFTs) without ever removing the substrate from the printer and using a maximum process temperature of 80 C. To achieve this, significant advancements were made to minimize the intermixing of printed layers, drive down sintering temperature, and achieve sufficient thin-film electrical properties. Devices are demonstrated on various substrates, including paper, and evidence of the potential for printing directly onto biological surfaces will be shown. From the versatile printed electronic thin films that have been developed, a diversity of biosensors are being pursued and will be discussed. With continued refinement of the inks and print processes, this print-in-place technique can bring the field of printed electronics closer to where it has been promised to go for so many years: load substrate, press print, remove functional sensors / circuit.

1:45 PM *S.EL02.01.36
Thermoelectric and Thermionic Transport in Mixed Dimensional Structures Mona Zebarjadi and Md Golam Rosul; University of Virginia, United States

Solid state thermionic and thermoelectric modules can operate in power generation mode to convert heat to electricity, refrigeration, active cooling and thermal switching modes. They have potential application in waste heat recovery, solar thermal energy conversion and heat management and power generation of wearable electronics. Thermoelectric efficiency is an increasing function of material figure of merit, ZT. To obtain large ZT, high electronic conductance, large open circuit voltage (i.e. large Seebeck coefficient) and low thermal conductance is needed. The three parameters are interconnected and hence the optimization and improvement of ZT is a challenging task and requires careful control of electrons and phonons. Many of advanced thermoelectric materials are multi-phase compounds wherein thermal and electrical transport are determined not only by the average of the phases but also by the interfaces and the charge transfer between the phases. In this talk I will discuss several cases in which bulk samples are designed in which electronic transport is effectively 1D or 2D, while phonon transport is 3D and I will discuss the advantage of such structures and how thermoelectric figure of merit is enhanced using such strategy. Finally, I will discuss the thermal and electrical transport across 2D van der Waals heterostructures. The layers are weakly bonded resulting in extremely low thermal conductance. At the same time, layers could be mixed and matched to fine tune the electronic transport and to optimize the thermionic figure of merit.

2:15 PM S.EL02.01.40
Molybdenum Disulfide Nanoflower/Epitaxial Graphene Heterostructure Gas Sensors for Improved Sensitivity and Selectivity Sooram Kim1,1, Jaeseo Park2,4, Daniel Lewis1,1, Seunghyun Lee4, Balaaditya Uppalapati5, Digangana Khan5, Ferhat Bayram5, Sanjay Krishna5, Gautam Koley5, Sang-Woo Kang5,3 and Kevin Daniels1,1; 1University of Maryland, United States
In recent years, a van der Waals heterostructure device, stacking 2D architectures atomically with synergistic combinations of nanomaterials have attracted tremendous attention with many potential applications such as chemical sensors in environmental and safety monitoring, and medical diagnostics and biomedical health care systems [1,2]. Atomically thin 2D graphene and transition metal dichalcogenides (TMDs) have an extremely high surface-to-volume ratio which is the most critical parameter for chemical sensing applications. Here we have fabricated a heterostructure of molybdenum disulfide (MoS2) nanoflower and epitaxial graphene on 6H silicon carbide (SiC) substrate for chemical sensing. We have combined the advantages of high sensitivity and fast response time of graphene with the high surface-to-volume ratio of MoS2 nanoflower to develop an ultra-high sensitivity chemical sensor with improved selectivity.

Bilayer epitaxial graphene (EG) was synthesized by Si sublimation on 6H SiC, and MoS2 nanoflowers were grown on graphene/SiC directly using metal-organic chemical vapor deposition (MOCVD). The growth methods of graphene and MoS2 nanoflowers are discussed in detail elsewhere [3,4]. The structural and optical properties of the samples were investigated by scanning electron microscopy (SEM), atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, photoluminescence (PL), and cyclic voltammetry (CV). To fabricate the chemical sensor, e-beam lithography and reactive ion etching (RIE, CF4) were used to prepare a simple pattern. Finally, the metal electrode (XPS), Raman spectroscopy, photoluminescence (PL), and cyclic voltammetry (CV). To fabricate the chemical sensor, e-beam lithography and reactive ion etching (RIE, CF4) were used to prepare a simple pattern. Finally, the metal electrode (Ti/Au = 30/120 nm) was deposited using an e-beam evaporator. The prepared chemical sensor was tested with various gases such as 5 ppm of nitrogen dioxide (NO2) and ammonia (NH3), and ~1000 ppm of volatile organic compounds (VOCs) and showed superior chemical response and recovery at room temperature. It is evident that the prepared device is suitable for chemical sensing applications with high sensitivity and selectivity.


2:30 PM S.ELO2.01.41
Pulsed Electrochemical Deposition of δ-MnO2 on Epitaxial Graphene-Silicon Carbide Substrates for Selective Gas Sensing
Michael Pedowitz1,1, Soaram Kim1,1, Balaadithya Uppalapati2, Digangana Khan2, Ferhat Bayram2, Goutam Koley2 and Kevin Daniels1,1;
1University of Maryland, United States; 2Clemson University, United States

Layered δ-phase MnO2/graphene heterostructures, separated by van der Waals forces, have attracted significant interest due to their potential to combine the well-defined interlayer spacing of δ-MnO2 with the high inherent conductivity of graphene[1]. However, the variety of MnO2 polymorphs and MnO2 structures that can arise during growth makes the synthesis of δ-MnO2 and subsequent heterostructures challenging. Currently, δ-MnO2 is primarily grown through hydrothermal synthesis from potassium permanganate (KMnO4)[2]. This method suffers from scalability issues and an inability to deposit high uniformity films with precise layer control. In this work, we present an alternative electrochemical method for the synthesis of δ-MnO2. Utilizing a 0.1M manganese acetate (Mn(CH3CO2)2) solution, δ-MnO2 was grown on epitaxial graphene (EG) synthesized on 6H silicon carbide (SiC) substrates in a three-electrode electrochemical cell. The resulting MnO2 thin film was then characterized using Raman spectroscopy, energy-dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), and scanning electron microscopy (SEM) to determine its phase and surface morphology. Scanning electron microscopy revealed the thin film was made up of micro platelets, with the smallest being approximately 70µm x 80µm. Raman spectroscopy confirmed the formation of δ-MnO2 due to the presence of peaks at 577 cm⁻¹, 651 cm⁻¹, and 133 cm⁻¹[3]. An additional advantage of the δ-MnO2/EG/SiC heterostructure is that it is lithography compatible and does not require a transfer process. To demonstrate this, we constructed a gas sensor based on the δ-MnO2/EG/SiC heterostructure by depositing a metal electrode (Ti/Au = 30/120nm) on the δ-MnO2 by e-beam evaporation. This gas sensor was then tested with 5ppm nitrogen dioxide (NO2), 5ppm ammonia (NH3), and an ~1000ppm Isopropyl alcohol (C3H8O)/Methanol (CH3OH) mix, volatile organic compounds (VOCs), in an environmentally controlled chamber. In preliminary testing at room temperature the device displayed a significant response to NO2 and NH3 with ~400ms response time but displayed no response to VOCs. This result displays improved selectivity over sole graphene based chemical sensors [1]. This alternate synthesis method allows for a low temperature, low-cost route to the growth of lithography compatible δ-MnO2 heterostructures for gas sensing, batteries, and spintronics.

Flexible Electronics Enabled by Direct Transfer of Two-Dimensional Transition Metal Dichalcogenides with Contacts

Alwin Daus, Sam Vaziri, Victoria Chen, Ryan W. Grady, Connor Bailey, Cagil Koroglu, Kevin Brenner, Kirstin Schauble and Eric Pop; Stanford University, United States

Two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDs) have been proposed for future high-performance flexible nanoelectronics [1]. However, high-quality chemical vapor deposition (CVD) growth of TMDs requires high temperatures >500°C. Thus, the fabrication process must rely on layer transfer processes for integration with temperature-sensitive flexible substrates.

Most conventional transfer techniques add a thin sacrificial polymer layer on top of the TMD. This stack is released from the growth substrate in an etching solution and picked up by the target substrate, but this technique can lead to polymer residues and damage or wrinkling of the TMD film [2,3]. An alternative method is to spin-coat the flexible substrate on the TMD before transfer, however this has its own limitations because all subsequent patterning would have to be done on the flexible substrate [4].

Here, we demonstrate a novel, alternative approach which allows us to do critical lithography steps on the rigid TMD growth substrate (SiO₂/Si), then transfer the TMD films together with their metal contacts onto the flexible substrate for further integration. This approach results in the shortest channel (sub-100 nm) and highest-performance TMD transistors on flexible substrates to date, using monolayer CVD-grown MoS₂. The “hybrid” fabrication/transfer method can also enable other devices, it can be used with other TMDs like WSe₂ or MoSe₂, and the TMD thickness can range from mono- or bilayers to thicker multilayers.

We first grow the TMDs by CVD on SiO₂/Si substrates [5-7] and perform lithography and lift-off for metal contacts, with contact spacing down to 50 nm. Then, we spin-coat 6 µm flexible polyimide (PI) on top and we release the PI with the embedded TMD and metal contacts in deionized water without any other chemicals. This minimizes damage and contamination of the TMDs, as verified by Raman spectroscopy and photoluminescence. We then flip the PI/TMD stack and deposit Al₂O₃ by atomic layer deposition, then pattern metal gates by lift-off, thus creating staggered TMD transistors.

We have thus realized flexible transistors with CVD-grown MoS₂, WSe₂ and MoSe₂, reaching field-effect mobility >30 cm²V⁻¹s⁻¹ for monolayer MoS₂, which is the highest to date on flexible substrates. In sub-100 nm MoS₂ transistors, we also obtain record high on-currents of ~600 µA/µm. Thermal simulations reveal that the intimate metal contacts assist heat spreading during device operation, enabling such high performance despite the low thermal conductivity of the PI substrate. We demonstrate that the devices are stable under tensile bending to a radius of 4 mm, with negligible changes in device characteristics. We also show preliminary data on flexible MoS₂ circuits and flexible vertical devices based on TMDs.

In summary, our novel fabrication method provides a scalable approach for the integration of various types of TMD devices on a single flexible substrate, and the contact patterning before transfer enables nanoscale dimensions, down to sub-100 nm channel lengths. This method also enables vertical device structures, e.g., resistive memory and optoelectronic devices such as photodetectors or solar cells.

2. A. Gurarslan et al., ACS Nano 8, 11522 (2014).
7. J. Chen et al., ACS Photonics 6, 787 (2019).
Large Area Synthesis and Doping of Two-Dimensional Semiconductors
Joshua A. Robinson; The Pennsylvania State University, United States

The last decade has seen nearly exponential growth in the science and technology of two-dimensional materials. Beyond graphene, there is a huge variety of layered materials that range in properties from insulating to superconducting. Furthermore, heterogeneous stacking and doping of 2D materials also allows for additional band structure engineering. In this talk, I will discuss recent breakthroughs in two-dimensional atomic layer synthesis and properties, with an emphasis on doping 2D semiconductors. Our recent works include development of an understanding of substrate impact on growth and doping of 2D materials to tune them from n- to p-type, and to create 2D magnets. Our work and the work of our collaborators has lead to a better understanding of how substrate not only impacts 2D crystal quality, but also doping efficiency in 2D materials.

Wafer-Scale Growth and Assembly of Atomically-Thin Layered Semiconductors
Kibum Kang; KAIST, Korea (the Republic of)

High-performance semiconducting films with precisely engineered thicknesses and compositions are essential for developing next-generation electronic devices, which are becoming more integrated, complex, and multifunctional. My talk will introduce the novel processes that enable atomic-scale control of the thickness and spatial composition of semiconducting films on the wafer-scale. These processes include: (i) the wafer-scale generation of atomically-thin layered semiconductors such as metal dichalcogenides and metal oxy-dichalcogenides via metal-organic chemical vapor deposition (MOCVD), (ii) the atomic-level engineering of vertical thickness and composition through the layer-by-layer assembly of the layered semiconductors, and (iii) the interlayer engineering of the layered semiconductors for the property control. These capabilities provide a new material platform for both fundamental research and practical applications, including incorporation into existing integrated circuit technology to form hybrid materials and boost electrical and optical functionality.

Toward Non-Si Electronics—Producing Freestanding Single Crystalline 3D Thin Films and 2D Atomic Layers for Mixed Dimensional Heterostructure
Sanghoon Bae; Massachusetts Institute of Technology, United States

The current electronics has been mainly dominated by Si-based devices due to their mature processing system and exceptional cost-effectiveness. However, next generation electronics needs novel functionalities that cannot be realized by Si because of intrinsic limitation of Si. Accordingly, demand for non-Si electronics has been getting substantially high. Unfortunately, current methodology requires extremely high cost for non-Si materials, which impedes the progress in developing the non-Si based electronics. Here, I will discuss about our group’s efforts to address this issue. Our team recently conceived a new crystalline growth, termed as “remote epitaxy”, which can copy/paste crystalline information from substrates remotely through graphene, thus generating single-crystalline films on graphene. As interfacial binding energy is attenuated by inserting graphene at interface, the single-crystalline films can be easily exfoliated from the slippery graphene surface. Also, the graphene-coated substrates can be, in principle, reused infinitely to produce single-crystalline films. Thus, the remote epitaxy can produce non-Si semiconductor films with unprecedented cost efficiency while allowing additional flexible device functionality required for current ubiquitous electronics.

Next, I will discuss about a layer splitting technique which can be a potential solution to overcome the problem in obtaining large-scale and monolayer 2D materials. A 2D material-based heterostructure has been intensively studied because of its unique device functionalities and novel physics. However, it is extremely challenging to secure large-scale and monolayer 2D
Stackable Electronics Enabled by Freestanding 2D and 3D Materials Jeehwan Kim; Massachusetts Institute of Technology, United States

In this talk, I will discuss about our unique strategy to isolate wafer-scale 2D materials into monolayers and stack them into a heterostructures by using a layer-resolved splitting (LRS) technique [1,2]. This technique enables my group at MIT to explore unprecedented wafer-scale 2D heterodevices. While 2D heterostructures promise interesting futuristic devices, the performance of 2D material-based devices is substantially inferior to that of conventional 3D semiconductor materials. However, 3D materials exist as their bulk form, thus it is challenging to stack them together for heterostructures. Obviously, conformal coating of such single-crystalline bulks on 3D features is impossible. My group at MIT has recently invented a 2D materials-based layer transfer (2DLT) technique that can produce single-crystalline freestanding membranes from any compound materials including III-V, III-N, and complex oxides [3,4]. This technique is based on remote epitaxy of single-crystalline films on graphene followed by peeling from graphene. Stacking of freestanding 3D material membranes will enable unprecedented 3D heterostructures whose performance is expected to be superior to that of 2D heterostructures. I will talk about our group’s effort on 3D heterostructures as well as 2D-3D mixed heterostructured devices [5].


Mechanisms for Remote Epitaxy of GaSb on Graphene-Terminated GaSb (001) Sebastian Manzo, Vivek Saraswat, Austin J. Way, Patrick J. Strohbeen, Chenyu Zhang, Dongxue Du, Estiaque Shourov, Paul Voyles, Michael Arnold and Jason K. Kawasaki; University of Wisconsin, United States

Remote epitaxy is a method for growing single-crystalline materials on a graphene-terminated single-crystalline substrate, in which the epitaxial registry occurs between film and substrate rather than film and graphene. This method has been realized for several homoepitaxial systems, such as GaAs, GaN, LiF and ZnO. Yet, the microscopic mechanisms that allow for remote epitaxy remain mysterious. Here we demonstrate remote homoepitaxy of GaSb and comment on the role of defects on the apparent lattice transparency of graphene. In addition, we elucidate the effect of the graphene/substrate interface quality associated with different graphene transfer methods.

We have grown our films via molecular beam epitaxy and used x-ray and electron diffraction, along with transmission electron microscopy to confirm that the single-crystalline film is in-phase with the underlying GaSb (001) substrate. Graphene grown via chemical vapor deposition is cleanly transferred to GaSb, which has been corroborated via Raman spectroscopy and scanning electron microscopy. Remote epitaxy necessitates the absence of the semiconductor substrate’s native oxide, since this amorphous layer would inhibit epitaxial registry to the underlying substrate. Therefore, the question of how the native oxide desorbs when capped with graphene is of critical importance. We have studied this desorption mechanism through in-situ photoemission and reflective high energy electron diffraction. In addition, we have investigated the nucleation selectivity of GaSb on patterned and unpatterned graphene via in-situ scanning tunneling microscopy. The
GaSb overlayer can be readily exfoliated, which allows for the substrate to be recycled and for the exfoliated film to be transferred to arbitrary substrates.

6:00 AM S.EL02.03.04
Remote Epitaxial Growth of Compound Semiconductors through Graphene Kyusang Lee1 and Jeehwan Kim2; 1University of Virginia, United States; 2Massachusetts Institute of Technology, United States

Epitaxial growth has been widely used for high-quality growth of crystalline materials. However, epitaxial growth techniques usually require lattice match and similar thermal expansion coefficient between growth material and substrate, which blocks this growth technique from wide applicability. Recently, van der Waals (vdW) epitaxy has been demonstrated that allows to relax the limitation of epitaxial growth. vdW epitaxy on layered or two-dimensional (2D) materials is mediated by weak vdW interactions. In addition to these interactions, a substrate below 2D materials also plays a role to intervene in the epitaxial growth process, leaving room to realize a novel epitaxial growth process: remote epitaxy. Potential fluctuation—the difference between potential energy maxima and minima along the surface of the substrate—is influenced by this remote interaction; the fluctuation is predominant over the vdW force, due to the atomic thickness of 2D materials. The remote interactions can be controlled by modulation of polarities of 2D materials and epitaxy materials. Polar-material-based heterostructure, such as GaAs, InP, GaP and GaN with their substrate sandwiching 2D materials, enables the semiconductor film to be exfoliated from the underlying substrates through the 2D materials. This process is expected to open a novel avenue for the field of non-silicon electronics and photonics, where the ability to re-use graphene-coated substrates allows savings on the high cost of non-silicon substrates.

6:15 AM S.EL02.03.05
Remote Epitaxy of GaN Microrod Heterostructures for Fabricating Flexible Light-Emitting Panel Junseok Jeong1,2, Qingxiao Wang3,4, Janghwan Cha1,2, Sang Wook Lee1, Suklyun Hong1,2, Moon Kim1,4 and Young Joon Hong1,2; 1Sejong University, Korea (the Republic of); 2Graphene Research Institute–Texas Photonics Center International Research Center (GRI–TPC IRC), Korea (the Republic of); 3The University of Texas at Dallas, United States; 4Texas Photonics Center (TPC), United States

Demands on flexible lighting apparatus have been rapidly rising for the use in mobile display and wearable lighting device applications. For the device performance and stability, the use of semiconductors is ultimately desirable. Nonetheless, the rigid, brittle characteristics of inorganic semiconductor materials in a film form on wafer have so far precluded the use from the applications. In terms of growth template, graphene, which is flexible and allows delaminate of device overlayer from host substrate due to weakly bound van der Waals bonds to substrate, have begun to be utilized as an emerging epitaxy substrates for transferrable and flexible device applications. As for the overlayer, the spatially separate arrays of lighting components are adequate for fabricating the flexible devices, and vertical wire- or rod-based structures are thought to be ideal for the purpose. Without the epitaxial relationship, the rod structures cannot be uni-directionally (or vertically) aligned, which degrades the geometrical feature for conformal electrode formation on top of rod light emitters. Meanwhile, there have recently been an emerging epitaxy technique, the so-called remote epitaxy that the crystallographic registration of single-crystalline wafer is dictated to overlayer across graphene. Thus, single crystalline epi-layer is easily obtained for many compound semiconductors via the remote epitaxy. Likewise, once the remote epitaxy is adopted for fabricating the rod-based heterostructures, uni-directionally aligned, spatially separate lighting components can be obtained, which makes the arrays transferable and deformable after transferring on flexible target surface. Hence, the fabrication of rod heterostructures via graphene-mediated remote epitaxy enables flexibility and transferability of the overlayer rod-devices.

Herein, we demonstrate the deformable light-emitting diode (LED) panel via the remote heteroepitaxy of vertical GaN microrod (MR) radial $p$–$n$ junction arrays embedded with InGaN/GaN multiple quantum-wells on c-Al2O3 substrates with a gap of graphene interlayer. The remote epitaxy produced GaN MR arrays with uniform ordering of hexagonal sidewall facet orientation over whole graphene surface, suggesting a specific heteroepitaxial relationship between GaN MRs and c-Al2O3. Despite the presence of poly-domain graphene interlayer, the heteroepitaxial relation between GaN MR and substrate was revealed via cross-sectional transmission electron microscopy. Density-functional theoretical calculation demonstrates how/why the remote heteroepitaxy with large lattice mismatch is made possible across graphene. The use of graphene allowed exfoliation and transfer of MR LED overlayer onto flexible conducting copper plate, and the spatially separate MR arrays enabled to deform the LED device in diverse flexural forms, including folded, twisted, and even crumpled deformations. Repetitive bending test over 1,000 cycles between radii of curvatures of $\infty$ and 10 mm represented the robustness of MR LEDs. Also, the original substrate is recycled, which consistently re-yields the deformable LED panels over again. This study expands the epitaxy technique into flexible devices and substrate recycle.

Reference
Combined photonic and electronic systems require diverse devices to be co-integrated on a common platform. This heterogeneous integration is made possible through several separation and transfer methods where the functioning epilayers are essentially released from their growth substrate. The use of 2D layered h-BN as a mechanical release layer has been demonstrated to be a promising technique for the hybrid integration of III-nitride devices. In this talk we will give an overview regarding the epitaxial growth of Nitride-based semiconductor materials by MOVPE including GaN and h-BN, and design device structures for opto-electronic devices. In addition, results on wafer-scale growth and pick-and-place transfer of LED devices via h-BN van der Waals epitaxy, starting from sapphire growth substrates will be presented. Broader range of devices (HEMTs, solar cells, sensors, etc.) and applications (transport, environment, health, etc) will be discussed.

Specifically, the transparency of two-dimensional materials to the epitaxial relationship is linked to the polarization of related material systems. Although the potential field from non-polar materials is screened by a monolayer of graphene, that from polar materials is strong enough to penetrate through a few layers of graphene. Such field penetration is substantially attenuated by 2D hexagonal boron nitride, which itself has polarization in its atomic bonds. Based on the control of transparency, modulated by the nature of materials as well as interlayer thickness, various types of single-crystalline materials across the periodic table can be epitaxially grown on 2D material-coated substrates. The epitaxial films can subsequently be released as free-standing membranes, which provides unique opportunities for the heterointegration of arbitrary single-crystalline thin films in functional applications.

quantify the efficiency of monolayer graphene as a solid-state diffusion barrier in $M$/graphene/semiconductor heterostructures ($M = \text{Fe, Mn}$).

Through in-situ x-ray photoemission spectroscopy (XPS) we show suppression of the interfacial diffusion and reactivity in these systems by tracking core level shifts as a function of anneal temperature. In samples where $M = \text{Fe}$, we deposit 1nm of elemental Fe on Ge (001) substrates with and without monolayer graphene. The graphene is grown directly on the Ge (001) substrate by CVD to minimize the defects introduced by conventional layer transfer processes. For samples with no graphene barrier, we observe a complicated multi-component Fe 2p core level structure that evolves with increasing anneal temperature, indicative of significant Fe/Ge interfacial reactions. In contrast, for samples with a monolayer graphene barrier, the core level spectra do not change with temperature up to 300°C and there is no evidence for a reacted phase, suggesting that monolayer graphene is an excellent solid-state diffusion barrier. We will discuss similar experiments for $M = \text{Mn}$ and for different preparations of graphene on the semiconductor substrate, such as graphene layer transferred to Ge or GaAs.

Through these studies, we comment on the optimal synthesis and processing conditions for making graphene diffusion barriers.

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7:45 AM S.EL02.03.09
SiC Remote Epitaxy—A New Paradigm for Stackable Electronics Rachael Myers-Ward1, Jeehwan Kim2, Matthew DeJarld1, Kuan Qiao2, Yunjo Kim2, S.P. Pavunny1 and Kurt D. Gaskill1; 1Naval Research Laboratory, United States; 2Massachusetts Institute of Technology, United States

Ideally, electronic heterostructures from dissimilar materials leads to enhanced functionality. Yet, experimentally forming these heterostructures is challenging due to lattice or thermal coefficient of expansion mismatch leading to defect formation or thermally driven atomic diffusion resulting in cross-doping and gradual junction transitions. These challenges may be overcome with the discovery of remote epitaxy and 2D layer transfer [1]. Here, SiC epitaxy is performed on epitaxial graphene as the electrostatic fields from the substrate penetrate the graphene and guide adatom registry. The film is easily peeled away since the graphene is not bonded to either the substrate or epilayer; the epilayer is then van der Waals bonded to a different material enabling new functionality. We will present experimental results on the remote epitaxy of SiC.

There are three necessary steps to create remote epitaxy. The first is to grow epitaxial graphene on SiC, followed by transferring the graphene to a desired substrate (if different from SiC), and finally the growth of the remote epitaxial layer. If the remote epitaxy is to be SiC, which is the focus of this paper, the second step is not necessary. Epitaxial graphene (EG) was first synthesized on 4H- and 6H-SiC in a horizontal hot-wall CVD reactor between 1540 and 1580 °C in 10 slm of Ar and 100 mbar [2]. The growth temperature was dependent upon the offcut of the substrate, where substrates with higher offcuts require a lower growth temperature to ensure 1 ML of EG, which is desired to assist in SiC adatom registry during growth. SiC remote epitaxy was then performed on the EG using silane (2% in H2) and propane precursors, where the SiC polytype replicated the underlying substrate. In an effort to transfer the remote SiC epilayer to another substrate such as SiO2/Si, a metallization step was performed. Thin Ti and/or Ni layers were initially deposited followed by a thicker high stress metal to create strain and aide in removing the remote SiC epilayer from the SiC substrate [1]. Once transferred, the metal was removed via a metal etch.

In this work, we will discuss the important parameters needed for successful remote SiC epitaxy, such as graphene thickness, process flows, ramping conditions and remote epitaxy growth temperature. The epitaxial morphology characterized by SEM, Nomarski microscopy and Electron Detectio and graphene coverage and transfer evaluated by Raman spectroscopy will be presented.


8:00 AM *S.EL02.03.10
Hybrid-Dimensional Heterostructures for Flexible Devices Gyu-Chul Yi; Seoul National University, Korea (the Republic of)

Contemporary human life relies heavily on mobile devices such as smart-phone, lap-top, or tablet PC which process tremendous amount of information every day. In near future, rapid development of information technology would eventually integrate the devices as a wearable and flexible form that will collect and process information ubiquitously. For the
fabrication of flexible and stretchable devices with high performance and reliability, monolithic integration of inorganic materials and devices in flexible form must be developed. We introduce hybrid dimensional heterostructures, composed of inorganic nanostructures grown directly on 2-dimensional (2-D) layered materials such as graphene and hexagonal boron nitride (h-BN), as one of the most promising materials for flexible device applications. The inorganic nanostructures in the hybrid nanomaterials exhibit excellent electrical and optical characteristics, including high carrier mobility, radiative recombination rate, and long-term stability. Meanwhile, 2-D layered materials, such as graphene, h-BN, chalcogenides and their hybrids, in the hybrid nanomaterials are flexible, stretchable, and mechanically strong, along with interesting and excellent physical properties. Here I report position- and morphology-controlled growths of ZnO and GaN nanostructures on graphene and h-BN using catalyst-free metal-organic vapor phase epitaxy and describe the methods to fabricate flexible light emitting diodes, transistors and pressure sensors.

8:30 AM S.EL02.03.12
One Dimensional GaN Based Nano-Optoelectronic Device Structures on Layered h-BN Grown by MOVPE
Suresh Sundaram1,2,3, Xin Li3, Yacine Halfaya3, Taha Ayari3, Gilles Patriarche4, Christopher Bishop5, Saiful Alam3, Simon Gautier5, Paul L. Voss2,3, Jean Paul Salvestrini1,2,3 and Abdallah Ougazzaden1,2,3, 1Georgia Institute of Technology, United States; 2CNRS UMI 2958 GT-CNRS, France; 3Université Paris-Saclay, France; 4Institut Lafayette, France

Recent advances in MOVPE enabled the high-quality growth of layered h-BN on sapphire substrates, and has resulted in the realization of series of 2D-3D III-nitride based device structures. This 2D layer also enables damage free mechanical lift-off which may drive future flexible and wearable industry with advanced high-efficient devices. Reliable wafer-scale 2D-2D heterostructure based devices have also been fabricated previously. Here we report, demonstration of MOVPE van der Waals epitaxial growth of GaN based nanostructures on 2D h-BN with a focus on large area van der Waals epitaxy and successful transfer to flexible platform. This approach to the growth of III-N nanostructures on h-BN avoids transfer processes and scaling issues seen with other 2D materials, since both the 1D (GaN nanorods) and 2D (h-BN) are grown at the wafer-scale and in one growth run. Further, this process is used to grow vertical core–shell p-GaN/InGaN/n-GaN nano-PIN device structures on wafer-scale 2D h-BN on sapphire and silicon substrates. Interesting results obtained on this futuristic process and mechanisms involved will be discussed.

8:45 AM *S.EL02.03.13
Polar Quasi-2D Oxides via Epitaxy at Weakly-Coupled Interface
Jian Shi; Rensselaer Polytechnic Institute, United States

When crystals approach 2D, their ferroelectric phase may be destabilized. How their temperature-dependent polarization behaves remains largely unknown. In this work, we attempt to answer this question using 2D pyroelectric oxides. We show that quasi-2D oxides down to a unit cell thickness can be epitaxially grown on perovskite substrate by the molten salt-assisted quasi-van der Waals epitaxy following a screw-dislocation driven mechanism. We experimentally demonstrate switchable in-plane photo-ferroelectricity and thickness-dependent pyroelectricity. Weakly-coupled interface allows us to reveal that electron-phonon renormalization leads to the observed dimensionality effect. Harnessing the dimensionality effect in pyroelectricity via novel epitaxy strategies could promote their applications in uncooled infrared cooling and thermal energy harvesting.

9:15 AM *S.EL02.03.14
Artificial Complex-Oxide Membrane Heterostructures
Hyumseong Kum and Jeehwan Kim; Massachusetts Institute of Technology, United States

Complex-oxide materials exhibit a plethora of physical properties desirable for next-generation electronics, photonics, and quantum devices not present in other functional materials such as Si, III-V, and III-N. These properties may be present in bulk form or at a heterointerface, and may be created or enhanced by application of strain. However, to date, only epitaxial methods have been used to create various heterostructures with varying strain states. Unfortunately, epitaxial methods have strict limitations, requiring closely lattice mismatched and similar crystalline structure, which prevent unrestricted manipulation, integration, and utilization of these materials. Thus, the design space for heteroepitaxial systems are limited. Additionally, the range of strain that can be imparted by epitaxy is fixed by pseudomorphic conditions. Finally, epitaxial growth conditions, which typically occurs at high temperatures, preclude integration of materials that are less stable in such environments. This has been a consistent bottleneck preventing universal integration of dissimilar materials to date. To alleviate these restrictions, we present methods to produce freestanding complex-oxide membranes allowing artificial creation of complex-oxide heterostructures with vastly different crystalline structure, lattice, and orientation, such as perovskite, spinel, and garnet films. The first lift-off method, remote epitaxy, allows epitaxial seeding of the substrate.
were achieved through the van der Waals epitaxy, are presented. Then, as the second section, the remote epitaxy is introduced. Hydrothermal remote epitaxy of ZnO microrods and metal–organic vapor-phase remote epitaxy of GaN microrods are presented.\[7–9\] We also discuss the remote heteroepitaxy of ZnO on GaN and GaN on Al\(_2\)O\(_3\) for lattice less-mismatched remote epitaxy, respectively.\[8,9\] The transfer of GaN heterostructured microrods of \(p-n\) junction with InGaN multiple quantum-wells is demonstrated for flexible microrod-light-emitting diode panel whose mechanical property is highly robust against crumpling/folding operations and repeated bending test.\[9\] Especially, we show the wafer recyclability for fabricating the deformable microrod-light-emitting diode panel over again on the same wafer in the remote epitaxy. We finally show how the principle of remote epitaxy, in which the limited thickness of graphene can penetrate the bonding feature of underlying wafer to the surface of graphene for epitaxial relationship, can be applied for site-selective growth.\[10\] The challenges and opportunities of epitaxies on/across graphene are discussed toward future flexible, transferable displays technology.

### References


Crystallographic defects, such as dislocation, are well known to strongly affect material’s physical properties. Electron-hole recombination mediated via dislocations (e.g. threading dislocation) is one of the predominant loss mechanisms for the sub-optimum performance in conventional semiconductors devices. However, how dislocation impacts its carrier dynamics in the ‘defects-tolerant’ halide perovskite is largely unknown. Stimulated by the successful pioneer work of remote homoepitaxy of semiconductor GaAs1,2, researchers have also been achieved (remote heteroepitaxy) in the systems of AlN film on sapphire3, copper film on sapphire4, and ZnO film on GaN5. In our study, we synthesize epitaxial halide perovskite with controlled dislocation density via a remote heteroepitaxy approach using polar substrates (NaCl and CaF2) coated with graphene. Density functional theory calculations have revealed the structure and magnitude of the incompletely screened electrostatic potential from the polar substrates, supporting the remote epitaxy in the present case. The regulated film-substrate interactions have further reflected themselves in controlling the wavelengths of the ferroelastic domains. Molecular-dynamics simulations reveal the kinetic process during remote epitaxy. Comparing to the ionic epitaxy with high dislocation density (both misfit and threading), the film grown via remote shows much enhanced photoluminescence intensity and increased carrier lifetime. Our successful demonstration of remote epitaxy in halide perovskite provides an approach to develop free-standing halide perovskite film with reduced dislocation density. More importantly, dislocations and their impacts on carrier dynamics and device performance in halide perovskite have to be recognized and scrutinized.

Van der Waals (vdW) surfaces of 2D materials such as graphene and BN are attractive for growth of GaN and other III-nitride films and device structures. The weak inter-planar vdW bonding between 2D layers allows for easy mechanical separation of III-nitride films from the growth substrate for lift-off, transfer and integration on to arbitrary substrates. This approach of vdW lift-off is suitable for transfer of delicate single devices, like T-gate high electron mobility transistors (HEMT), as well as, wafer sized films. However, to obtain high performance devices, control over nucleation and epitaxy on 2D layers is necessary for high quality films. Additionally, to enable a simple transfer process strain and adhesion between the film and 2D layer must be balanced. In this paper, we describe the growth of high quality GaN and AlGaN/GaN HEMTs on 2D BN. The effects of nucleation, III-nitride epitaxial growth process and BN morphology will be discussed demonstrating how they effect material quality, properties, strain and adhesion. We will then discuss transfer schemes for individual AlGaN/GaN HEMTs and large area membranes transferred to both flexible polymer substrates and a variety of rigid substrates. With access to GaN and AlGaN/GaN two dimensional electron gas (2DEG) membranes on flexible substrates, we investigate the effects of strain on basic materials properties from compressive to tensile. This is particularly powerful for probing the effects of strain on the electrical properties, like sheet carrier density and mobility, in the polarization induced AlGaN/GaN 2DEG. In transferred devices, we demonstrate exceptional transport properties with mobility > 2,000 cm²/Vs and device performance with G_M of 300 mS/mm and f_T and f_MAX > 34 GHz and 75 GHz under stain while bending. Lastly, we will cover vdW and adhesive bonding to high and low thermal conductivity substrates and the effects on device performance and self-heating. This paper will highlight the great potential of vdW epitaxy and lift-off for transfer and integration of GaN on to various platforms.
Hybrid structures composed of conventional semiconductors (3D materials) and atomically thin two-dimensional (2D) materials have offered opportunities of recyclable device manufacturing, novel functionalities based on carrier transfer and exciton transport, and understanding natures of van der Waals gap. However, nucleation of 3D materials on 2D materials has not been understood straightforwardly due to absence of surface dangling bonds on 2D material though interaction the overgrown layer and 2D layer as a substrate has been explained by van der Waals interaction. Recent observation performed by the presenter’s team revealed that surface energy landscape is a key for nucleation of 3D materials on 2D materials. Increase in surface energy on 2D layer enhances nucleation probability of 2D materials significantly.

In the presentation those will be discussed several key aspects of nucleation of 3D materials on 2D materials, such as a few strategies to enhance surface energy on 2D layer, insights of the nucleation strategy on remote epitaxy, and demonstration of devices based on 3D/2D heterostructures.

12:00 PM S.EL02.03.24
Van der Waals Epitaxy of Germanium on Multi-Layer Graphene/h-BN Stacks—Limitation of Screening Out-of-Plane Dipole Moment Yeonhoo Kim1, Seth Swarnadeep2, Towfiq Ahmed3, Junseok Jeong3, Seokhoon Choi4, Young Joon Hong5, Ho Won Jang4, Woo Seok Yang5 and Jinkyoung Yoo3; 1Los Alamos National Laboratory, United States; 2University of Central Florida, United States; 3Sejong University, Korea (the Republic of); 4Seoul National University, Korea (the Republic of); 5Korea Electronics Technology Institute, Korea (the Republic of)

Growth of semiconducting materials on two-dimensional (2D) materials, such as graphene, hexagonal boron nitride (h-BN), and transition metal dichalcogenides, has opened up novel opportunities for controlled functionality, economical device production, and flexible hybrid device manufacturing. A key method of semiconductor growth on 2D materials is van der Waals (vdW) epitaxy. In vdW epitaxy, nucleation of semiconductors on 2D layers is the main bottleneck due to the absence of surface dangling bonds on 2D layers. Induced out-of-plane dipole moments on 2D layers has been introduced to solve the nucleation issue. As demonstrated in 2018, out-of-plane dipole moments can be generated at the interfaces between different 2D materials. However, the screening effects of multiple 2D layers on the out-of-plane dipole have not been thoroughly explored. An atomically thin 2D monolayer does not provide enough screening of potential fluctuation in a substrate. Moreover, stacking multi-layers of atomically thin 2D materials can be still transparent to the potential in a substrate. We studied the screening effects of graphene multi-layers on out-of-plane dipole moment for nucleation of germanium (Ge) on graphene/h-BN stack. Graphene/h-BN stacking enhances the out-of-plane dipole moment ~1,000 times compared to that of graphene or h-BN alone. The enhanced out-of-plane dipole moment induces a remarkably higher nucleation probability of Ge on graphene/h-BN stack compared to that on graphene. Furthermore, we explored the limitation of stacked layers of multi-graphene/h-BN to elucidate the screening effect of out-of-plane dipole moment on Ge nucleation. VdW epitaxy studies and calculation of out-of-plane dipole moment on the surface of the top graphene layer along with a number of graphene layers stacked on h-BN were systematically conducted. Electron microscopy and thin film field effect transistor characterizations were performed to correlate structural and electrical properties of Ge grown on multi-layer graphene/h-BN. In addition, insight of semiconductor device manufacturing with multi-layers of 2D materials will be discussed.

12:15 PM S.EL02.03.26
Liquid Phase Epitaxy of Low-Dimensional Ferroelectric Complex Oxide Jie Jiang, Lifu Zhang and Jian Shi; Rensselaer Polytechnic Institute, United States

The structural quality and homogeneity of the epitaxial film is critical for the performance of many electronic and optoelectronic devices. The epitaxial films are mainly grown by either vapor-phase epitaxy (VPE) or liquid-phase epitaxy (LPE). The VPE technique is capable to grow multilayer and quantum well structures with controlled deposition process down to atomic scale, so it is favored in industry and developed rapidly during the past decades. However, growth of oxides and nitrides via VPE suffers from defect-rich films containing secondary phases and numerous grain boundaries. LPE, a growth process where a film of crystalline material is deposited from a supersaturated solution onto a single-crystal substrate, yields much higher crystalline quality of epitaxial films than VPE. The supersaturation for LPE is extremely low thus enabling the growth near thermodynamic equilibrium. Therefore, epitaxial films via LPE exhibit many advantages like highest structural perfection, automatic controlled stoichiometry, homogeneous dopant incorporation, flat surfaces and possibility of upscaling and mass production.

In this study, we use a molten salt-assisted LPE technique to prepare a single crystalline epitaxial low-dimensional ferroelectric complex oxide, Dion-Jacobson quasi-2D layered oxide, on LaAlO3 (LAO) substrates. We present an in-plane polarization switching in this quasi-2D oxide. We find that the epitaxy growth follows a screw-dislocation driven mechanism. X-ray diffraction analysis confirms the epitaxial flakes with high crystalline quality. Our microscopy and second harmonic...
generation measurements show the presence of ferroelastic domains and lack of inversion symmetry, respectively, in the epitaxial film. Our quasi-2D oxide exhibits a switchable photovoltaic ferroelectric effect where the polarization is modified by above band gap megawatts nanosecond optical pumping. Our high quality of epitaxial quasi-2D oxide would renew attentions and provide a good insight of this traditional LPE technique. In this layered complex oxide, the coupling between the in-plane ferroelectricity and other physical properties, e.g. the switchable photo diode effect and the photon-induced domain switching, may enable versatile applications down to the atomic scale.

SESSION S.EL02.04: Poster Session: Advanced Manufacturing of Mixed Dimensional Heterostructures
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
5:00 AM - 8:00 AM
S-EL02

S.EL02.04.12
Radiofrequency-Transparent Electrode for Device Integration Taehoon Kim, Gwangmook Kim and Wooyoung Shim; Yonsei University, Korea (the Republic of)

When an electromagnetic wave impinges on a conductor, most of the incident wave is reflected, which makes metals and transparent conducting oxides (TCOs), such as tin-doped indium oxide (ITO), opaque to visible light (429–750 THz) and far-infrared (FIR) (< 20 THz). This incompatibility between optical transparency and electrical conductivity is well-defined fundamental material properties, but this is often not easy to enhance both simultaneously. Opacity due to electrical conductivity is more pronounced in the lower frequency range. This fundamental incompatibility creates a barrier for the realization of enhanced user-interface and device integration. We present a design strategy for preparing megahertz-range transparent conductor and a concept towards ‘device-to-device integration’ enabled by electromagnetic wave transmittance. The approach to the properties of conductors is verified using a conducting polymer, Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), whose microstructure is effectively controlled by solution process. The use of a transparent conducting polymer as an electrode enables the fabrication of a fully functional touch-controlled display device and magnetic resonance imaging (MRI)-compatible biomedical monitoring device, which would open up a new paradigm for transparent conductors.

S.EL02.04.13
Sodium-Sparked Reduced Graphene Oxide Composite for Low-Temperature Sodium-Beta Alumina Batteries Dana Jin¹, MinJung Kim¹, Yoon-Cheol Park², Keeyoung Jung² and Wooyoung Shim¹; ¹Yonsei University, Korea (the Republic of); ²Research Institute of Industrial Science & Technology, Korea (the Republic of)

Among all the anode materials, Li and Na have the highest capacity and great potential to increase the energy density of batteries. Unfortunately, dendrite growth in metal anodes is one of the safety concerns in current battery devices. One approach to address this issue is to use molten or liquid-metal electrodes. This concept has been applied to sodium-beta alumina batteries (NBBs), which are based on a liquid-Na anode and $\beta''$–Al$_2$O$_3$ solid electrolyte. Consequently, NBBs, such as Na-metal halide (ZEBRA) batteries, are among the most promising technologies for large-scale renewable energy storage because of their high theoretical specific energy, high energy efficiency, and good cycle life.

Interestingly, in the initial stages of sodium-beta alumina batteries (NBBs) development, it was not anticipated that the low performance would rise from the Na/$\beta''$–Al$_2$O$_3$ interface. Liquid Na metal should be an ideal reversible electrode, provided that it can be maintained in contact with the whole operating area of the $\beta''$–Al$_2$O$_3$ throughout the discharging and charging of the cell. It was expected to be the least problematic component of the cell. In reality, liquid Na does not fully wet the surface of the $\beta''$–Al$_2$O$_3$. Although early observations revealed that incomplete wetting of the $\beta''$–Al$_2$O$_3$ surface by Na and consequent interfacial impedance problems were likely in NBBs, little was reported for numerous years. Ideally, full contact with liquid Na should be achieved, which provides a large active interface area and thus leads to high NBB performance at low temperatures.

We propose a simple approach to achieve unprecedented NBB performance with a capillary-induced wetting concept that significantly improves the Na wetting on $\beta''$–Al$_2$O$_3$. In this study, we adopted sparked reduced graphene oxide (rGO) loaded on the surface of the $\beta''$–Al$_2$O$_3$ as an ideal “wetting sheet,” compared with previous metal (Li or Na)-ion batteries where
sparked rGO layers have been used for such metal reservoirs as an anode. The sparked rGO layers with nanogaps exhibited complete liquid-Na wetting, regardless of the surface energy between the liquid Na and graphene oxide, which originated from the capillary force in the gaps (see the figures). This indicated (i) that the Na nucleation and growth were sufficiently rapid to form liquid Na when the battery was charged and (ii) that the area of the Na$^+$ passway at the Na (anode)/β″–Al$_2$O$_3$ (electrolyte) interface was maximized when the battery was discharged. Thus, a high state-of-charge for potential state-of-art low-temperature NBBs was obtained. This cell-stacking architecture is simple and scalable and addresses the fundamental limitations of NBBs by allowing Na wetting at low temperatures.

S.EL02.04.14

**FeAs van der Waals Crystal**  
Jongbum Won$^1$, Hyesoo Kim$^1$, Eunsil Lee$^2$, Jongyoung Kim$^2$ and Wooyoung Shim$^1$; $^1$Yonsei University, Korea (the Republic of); $^2$Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of)

Van der Waals (vdW) materials are composed of two-dimensional planes that are held together by weak interlayer interaction. VdW crystals have attracted increasing attention in the past couple of decades because of their significantly different properties from three-dimensional materials. However, it is a small class of materials, with fewer than 100 layered compounds catalogued in the Inorganic Crystal Structure Database (ICSD), including graphite, h-BN, transition metal dichalcogenides, metal halides, metal pnictides, and metal oxides. Here, we present a topochemical redox concept to prepare a new binary vdW materials by structure control from ternary parent compounds. The vdW crystals obtained had the same chemical composition as known three-dimensional compounds, but exhibited layered crystal structures. In our vdW crystal design strategy, we synthesized LiFeAs and CaFe$_2$As$_2$ as parent compounds. We then selectively removed Li and Ca from parent materials by topochemical redox to obtain FeAs vdW crystals with various crystal structures. We confirmed crystal structure of FeAs vdW crystal by X-ray diffraction (XRD), transmission electron microscope (TEM), scanning transmission electron microscope (STEM) and X-ray photoemission spectroscopy (XPS) and measured electrical property and mechanical property to identify the difference FeAs vdW crystal with three-dimensional orthorhombic FeAs.

S.EL02.04.19

**Patterned All-Graphene Surface Enables Position-Controlled Remote Heteroepitaxy of ZnO Microrods**  
Junseok Jeong$^{1,2}$, Daekwon Jin$^{1,2}$ and Young Joon Hong$^{1,2}$; $^1$Sejong University, Korea (the Republic of); $^2$Graphene Research Institute–Texas Photonics Center International Research Center (GRI–TPC IRC), Korea (the Republic of)

Heteroepitaxy of semiconductor on two-dimensional atomic layered materials (2d-ALMs) has been promising for fabricating transferrable and flexible devices, because the use of 2d-ALMs allows to easily exfoliate overlayer device from host substrate.[1,2] Recently, an emerging epitaxy has been reported, which is the so-called remote epitaxy.[3,4] The remote epitaxy enables to produce single crystalline overlayer on graphene layer because the crystallographic registrations of overlayer can be copied from a underlying single crystalline substrate across graphene layer.[4,5] In the remote epitaxy of microrods (MRs), graphene thickness that is the remote epitaxial gap is critical to determine growth density of MR overlayer because penetrated field strength given from substrate leading to nucleation–growth is attenuated as the graphene thickness increases.[4] This implies that as we use graphene interlayer with spatially different thicknesses can result in different growth regimes of i) remote epitaxy or ii) non-growth, depending on graphene thickness.

We present how the remote epitaxy can be applied to selective-area growth using graphene pattern layer. Position-controlled remote heteroepitaxy was performed by hydrothermal growth of ZnO MRs on intaglio-patterned graphene (IPG)-coated c-plane GaN substrate. The IPG layer consists of two graphene parts of (I) perforated-hole-patterned multilayer graphene (MLG) that prevents the remote epitaxy, which act as a growth mask layer, and (II) single-layer graphene (SLG) penetrating the potential field from underlying GaN substrate to allow remote heteroepitaxy of ZnO through the hole aperture of mask layer, which is embedded between GaN and MLG mask layer. The hole-aperture SLG area yielded remote heteroepitaxial ZnO MRs, whereas MLG area inhibited growth. Diameter and spacing of ZnO MRs are controlled by changing the hole pattern parameters. Transmission electron microscopy revealed the remote heteroepitaxial relationship between ZnO and GaN across the SLG area. According to density-functional theory calculations, the orbitals of SLG transfer the charge from the underlying GaN to the SLG surface leading to remote epitaxy, but the thick MLG was not capable of charge transfer in a long range. The weak van der Waals adhesion of ZnO/IPG/GaN was applied to exfoliate the ZnO MRs overlayer by a thermal release tape-assisted exfoliation technique and to recycle the original substrate. Our results readily open an opportunity to utilize the remote epitaxy for transfer of arrayed epitaxial structures in the designed size and arrangement for device manufacturing.

**Reference**

Recent Progress of Remote Epitaxy of III-Nitride System
Wei Kong, Kuan Qiao, Yunpeng Liu, Chansoo Kim and Jeehwan Kim; Massachusetts Institute of Technology, United States

III-nitride materials including GaN, InN, AlN, and their ternary alloys have been one of the key materials to realize advanced electronic and optoelectronic devices, such as high electron mobility transistors, light emitting diodes and lasers. The device performance heavily depends on defect density of III-nitride materials. However, the lack of native substrates leads to the challenges in fabricating defect-free III-nitride materials, severely limiting the implementation of variety of new devices utilizing III-nitride materials. Additionally, the attachment of III-nitride thin film to its substrate poses challenges of heterointegration of III-nitrides with other material systems. Separation of III-nitride thin films from the substrate while maintaining the pristine material quality is highly favorable.

We have previously shown the synthesis of GaAs on two dimensional materials followed by the separation of GaAs epitaxial thin film from its substrate [1], by utilizing the process so-called “remote-epitaxy”. Such discovery reveals the possibilities towards the fabrication of defect-free semiconductor materials without the constriction of substrate availability. In this report, we demonstrate the remote-epitaxy process to fabricate thin film GaN [2], as well as its ternary InGaN. The remote-epitaxial materials have been characterized by X-ray diffraction, atomic force microscopy and transmission electron microscopy, rendering device grade material quality. Additionally, the thin film III-nitrides can be peeled off from the substrates, and subsequently bonded to a foreign material surface, including Si and SiO2. Based on GaN/Si heterostructure, III-nitride based photonic/phononic cavity is demonstrated. This work has demonstrated a promising path for the integration of III-nitride with an arbitrary material system.

Reference:

Enhanced Heavy Metals Removal Using a New Bucky-Paper Membrane Containing MWCNTs and Two Biopolymers—Chitosan and Carrageenan
Sara S. Alnasser, Afnan Alharbi, Ahmad alshahrani, Mohammed Alsuhaihani, Bandar Atoibai and Mihdar almihdar; KACST, Saudi Arabia

Due to the current global water crisis, wastewater treatment requires considerable attention and development. Dissolved heavy metals in water trigger serious alerts and can have lethal effects on various components of the environment including water resources, soil, plants, animals, and can also be threatening the health of human beings. In this study, we addressed the issue by introducing novel bucky-paper membranes that were fabricated using a combination of biopolymers (i.e., chitosan and carrageenan) and multi-walled carbon nanotubes (MWCNTs). Three dispersions of MWCNTs with chitosan, carrageenan, and chitosan-carrageenan with 0.1% v/w were prepared using vacuum filtration. The removal of six heavy metals (i.e., cobalt, nickel, copper, cadmium, barium, and lead) was investigated in this study. The water permeability and the removal of heavy metals were evaluated using a dead-end (DE) filtration system. Heavy metals removal was studied at pH 7 and under a range of varying applied pressures (1 to 6 bar). At an applied pressure of 1 bar, the removal of lead and copper by the MWCNTs/carrageenan membrane reached 99% and 88%, respectively. However, MWCNTs/carrageenan membrane was found to be fragile. Nevertheless, adding chitosan to carrageenan had significantly improved the mechanical strength of the membrane while sustain the excellent removal properties of the heavy metals. That is, MWCNT/chitosan-carrageenan membrane significantly exceeds MWCNTs/carrageenan membrane in tensile strength, tensile strain and young’s modules by 400%, 17%, and 6%, respectively. On the other hand, the MWCNTs/chitosan membrane showed a high water permeate flux that reached up to 200 L/h.m². Also, the electrical conductivity of all membranes varied from 37 S/CM to 57 S/CM. Additional characterization techniques on the three membranes were conducted in this study as well.
New materials and device integration demands motivate the ability to lift off and transfer epitaxial material. We use a Van der Waals-bonded 2D boron nitride (BN)-on-sapphire template to grow GaN by MOCVD then subsequently separate the GaN using a stress-induced lift-off method. This method has potential for wafer-scale heterogenous integration since large crack-free areas can be separated and the bottom epi-layer surface has sub-nanometer roughness. In this method a tensilely-stressed Ni layer deposited on the GaN acts to separate the epi-layer at the 2D BN interface allowing us to lift off whole wafer-sized GaN layers which are crack-free. Although large crack-free areas of GaN can be separated, the residual compressive strain in the GaN can cause cracks if the strain is inhomogeneously relaxed as the layer is transferred to the new substrate. By varying the stress and thickness of the Ni layer we can homogeneously relax some of the GaN strain upon separation and reduce the resulting crack density. We report on our development of this process including modeling and measurement of the GaN strain by Raman spectroscopy throughout the process.

**S.EL02.04.20**

Remote Epitaxy of ZnO Microrod Arrays across Graphene Junseok Jeong¹² and Young Joon Hong¹²; ¹Sejong University, Korea (the Republic of); ²Graphene Research Institute–Texas Photonics Center International Research Center (GRI–TPC IRC), Korea (the Republic of)

Two-dimensional atomic materials are emerging as epitaxial substrates for transferrable and flexible device application.[1] Graphene has excellent properties for the use as a substrate, such as high electrical conductivity, excellent mechanical strength, and optical transparency.[2,3] Nevertheless, since the difficulties of producing single crystalline thin film and crystallographically aligned nano/microstructures on graphene, due to the use of poly-domain graphene, there remains a challenge to utilize the graphene as a substantially epitaxial substrate. This obstacle can be overcome by the remote epitaxy.[4] The remote epitaxy enables to grow single crystalline overlayer on graphene regardless of the graphene domain because crystallographic registration can be dictated from underlying substrate through graphene. Here, we demonstrate remote homoepitaxy of ZnO microrods (MRs) on different crystal planes of apolar a-plane and polar c-plane ZnO substrates across graphene using hydrothermal growth method.

Despite of the presence of poly-domain graphene intermediate layer, the ZnO MRs were epitaxially grown on a-plane and c-plane ZnO substrates, which were found to be homogeneous in-plane orientation over the entire surface of graphene-coated ZnO substrates. Such homoepitaxial relationship across graphene between ZnO MR and substrate was revealed through transmission electron microscopic and selected area electron diffraction analyses. The density-functional theory calculations suggested that the charge redistribution occurring near graphene induces the electric dipole formation, so the attracted adatoms lead to nucleation-growth of the remote-epitaxial overlayer. Because of a strong potential field caused by long-range charge transfer given from the substrate, even the use of bi-layer and tri-layer graphene resulted in the remote-epitaxial ZnO MRs. The effect of substrate crystal planes is also theoretically and empirically demonstrated. The ability of the graphene, which can be released from the host substrate without covalent bonds, was adapted to transfer the overlayer MR arrays. After the delamination, the host substrate was reused by repeating the process of remote epitaxy over again. This unconventional epitaxy technique offers an opportunity of the producing well aligned, transferrable and flexible epitaxial nano/microstructure arrays templates for epitaxial electronics and optoelectronics applications and regenerating the substrate for cost-saving device manufacturing.

**Reference**


**S.EL02.04.27**

Remote Epitaxy of III-V Semiconductors on CVD-Graphene for Wafer Re-Usability and Flexible Electronics Kuangye Lu, Hyunseok Kim, Sanghoon Bae, Sangho Lee and Jeehwan Kim; Massachusetts Institute of Technology, United States

III-V compound semiconductors offer outstanding electronic and photonic properties that outperform silicon, but the cost of III-V wafers is extremely expensive. Although using original wafers can effectively minimize the cost of wafers, current techniques for wafer recycling add significant costs in fabrication, nullifying the cost savings by reusing the wafer. Remote epitaxy is a newly discovered method that enables single-crystal growth of III-V semiconductor thin films and easy exfoliation of the grown film, thus promising for reusing wafers multiple times. It requires an atomically thin spacer layer, such as graphene, to be present on top of III-V substrates, which allows enough field penetration from substrates through the graphene layer to make epitaxial III-V thin films grown on it maintain single-crystallinity. In addition, the graphene layer
provides weak bonding at the III-V/graphene interface, and thus thin films grown on top of graphene can be easily exfoliated, leading to a cost-effective way of wafer reuse and flexible thin film production. However, previous methods of transferring graphene onto III-V wafers, which use polymethyl methacrylate (PMMA) or metal stressor layers to transfer graphene grown on foreign substrates like copper or SiC, introduce defects and damages on graphene and/or substrates during the transfer process. Remote epitaxial films grown on the damaged graphene/substrate suffer from lower crystal quality and imperfect exfoliation, which undermines wafer reusability and device performance.

Here we report the CVD growth of amorphous graphene on III-V wafers at low temperature that enabled improved quality of remote epitaxial films and their perfect exfoliation. By introducing toluene as a carbon source which cracks at a relative low temperature for graphene growth, we show fully covered amorphous graphene on AlGaAs/GaAs substrates despite arsenic’s low decomposition temperature. The surface of graphene-coated AlGaAs/GaAs substrate remains smooth with a RMS roughness of around 3Å. We also demonstrate 100% coverage of single-crystalline GaAs thin films grown on amorphous graphene, with the film’s quality significantly improved compared to the case of transferred graphene. In addition, roughness of the substrate’s surface remains the same after exfoliation of grown GaAs film, and the growth and exfoliation were successfully repeated multiple times, proving the feasibility for wafer recycling. Through this low temperature CVD growth approach and remote epitaxy, we successfully demonstrate wafer-scale flexible thin film exfoliation and recycling of substrates, which will lead to new opportunities in III-V thin film-based electronics and novel heterostructures with reduced cost.

SESSION S.LP02.04: Live Poster Session: Electronics and Photonics (S.EL02 and S.EL05)
Session Chairs: Sanghoon Bae, Hyunseong Kum and Aaswath Raman
Monday Afternoon, November 30, 2020
5:15 PM - 7:15 PM
S.EL02

S.EL02.04.09
GaN on 2D BN for Stress-Induced Lift-off Eric Blanton1,2, Timothy Prusnick1,2 and Michael Snure1; 1Air Force Research Laboratory, United States; 2KBR, United States

New materials and device integration demands motivate the ability to lift off and transfer epitaxial material. We use a Van der Waals-bonded 2D boron nitride (BN)-on-sapphire template to grow GaN by MOCVD then subsequently separate the GaN using a stress-induced lift-off method. This method has potential for wafer-scale heterogenous integration since large crack-free areas can be separated and the bottom epi-layer surface has sub-nanometer roughness. In this method a tensile-stressed Ni layer deposited on the GaN acts to separate the epi-layer at the 2D BN interface allowing us to lift off whole wafer-sized GaN layers which are crack-free. Although large crack-free areas of GaN can be separated, the residual compressive strain in the GaN can cause cracks if the strain is inhomogeneously relaxed as the layer is transferred to the new substrate. By varying the stress and thickness of the Ni layer we can homogeneously relax some of the GaN strain upon separation and reduce the resulting crack density. We report on our development of this process including modeling and measurement of the GaN strain by Raman spectroscopy throughout the process.

S.EL02.04.11
Enhanced Heavy Metals Removal Using a New Bucky-Paper Membrane Containing MWCNTs and Two Biopolymers—Chitosan and Carrageenan Sara S. Alnasser, Afnan Alharbi, Ahmad alshahrani, Mohammed Alsuhaibani, Bandar Alotaibi and Mihdar almihdar; KACST, Saudi Arabia

Due to the current global water crisis, wastewater treatment requires considerable attention and development. Dissolved heavy metals in water trigger serious alerts and can have lethal effects on various components of the environment including water resources, soil, plants, animals, and can also be threatening the health of human beings. In this study, we addressed the issue by introducing novel bucky-paper membranes that were fabricated using a combination of biopolymers (i.e., chitosan and carrageenan) and multi-walled carbon nanotubes (MWCNTs). Three dispersions of MWCNTs with chitosan, carrageenan, and chitosan-carrageenan with 0.1% v/w were prepared using vacuum filtration. The removal of six heavy metals (i.e., cobalt, nickel, copper, cadmium, barium, and lead) was investigated in this study. The water permeability and the removal of heavy metals were evaluated using a dead-end (DE) filtration system. Heavy metals removal was studied at pH 7 and under a range of varying applied pressures (1 to 6 bar). At an applied pressure of 1 bar, the removal of lead and copper by the MWCNTs/carrageenan membrane reached 99% and 88%, respectively. However, MWCNTs/carrageenan membrane was
found to be fragile. Nevertheless, adding chitosan to carrageenan had significantly improved the mechanical strength of the membrane while sustain the excellent removal properties of the heavy metals. That is, MWCNT/chitosan-carrageenan membrane significantly exceeds MWCNTs/carrageenan membrane in tensile strength, tensile strain and young’s modules by 400%, 17%, and 6%, respectively. On the other hand, the MWCNTs/chitosan membrane showed a high water permeate flux that reached up to 200 L/h.m². Also, the electrical conductivity of all membranes varied from 37 S/CM to 57 S/CM. Additional characterization techniques on the three membranes were conducted in this study as well.

S.EL02.04.12
Radiofrequency-Transparent Electrode for Device Integration Taehoon Kim, Gwangmook Kim and Wooyoung Shim; Yonsei University, Korea (the Republic of)

When an electromagnetic wave impinges on a conductor, most of the incident wave is reflected, which makes metals and transparent conducting oxides (TCOs), such as tin-doped indium oxide (ITO), opaque to visible light (429–750 THz) and far-infrared (FIR) (< 20 THz). This incompatibility between optical transparency and electrical conductivity is well-defined fundamental material properties, but this is often not easy to enhance both simultaneously. Opacity due to electrical conductivity is more pronounced in the lower frequency range. This fundamental incompatibility creates a barrier for the realization of enhanced user-interface and device integration. We present a design strategy for preparing megahertz-range transparent conductor and a concept towards ‘device-to-device integration’ enabled by electromagnetic wave transmittance. The approach to the properties of conductors is verified using a conducting polymer, Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), whose microstructure is effectively controlled by solution process. The use of a transparent conducting polymer as an electrode enables the fabrication of a fully functional touch-controlled display device and magnetic resonance imaging (MRI)-compatible biomedical monitoring device, which would open up a new paradigm for transparent conductors.

S.EL02.04.13
Sodium-Sparked Reduced Graphene Oxide Composite for Low-Temperature Sodium-Beta Alumina Batteries Dana Jin¹, MinJung Kim², Yoon-Cheol Park³, Keeyoung Jung³ and Wooyoung Shim¹; ¹Yonsei University, Korea (the Republic of); ²Research Institute of Industrial Science & Technology, Korea (the Republic of)

Among all the anode materials, Li and Na have the highest capacity and great potential to increase the energy density of batteries. Unfortunately, dendrite growth in metal anodes is one of the safety concerns in current battery devices. One approach to address this issue is to use molten or liquid-metal electrodes. This concept has been applied to sodium-beta alumina batteries (NBBs), which are based on a liquid-Na anode and β″–Al₂O₃ solid electrolyte. Consequently, NBBs, such as Na-metal halide (ZEBRA) batteries, are among the most promising technologies for large-scale renewable energy storage because of their high theoretical specific energy, high energy efficiency, and good cycle life.

Interestingly, in the initial stages of sodium-beta alumina batteries (NBBs) development, it was not anticipated that the low performance would rise from the Na/β″–Al₂O₃ interface. Liquid Na metal should be an ideal reversible electrode, provided that it can be maintained in contact with the whole operating area of the β″–Al₂O₃ throughout the discharging and charging of the cell. It was expected to be the least problematic component of the cell. In reality, liquid Na does not fully wet the surface of the β″–Al₂O₃. Although early observations revealed that incomplete wetting of the β″–Al₂O₃ surface by Na and consequent interfacial impedance problems were likely in NBBs, little was reported for numerous years. Ideally, full contact with liquid Na should be achieved, which provides a large active interface area and thus leads to high NBB performance at low temperatures.

We propose a simple approach to achieve unprecedented NBB performance with a capillary-induced wetting concept that significantly improves the Na wetting on β″–Al₂O₃. In this study, we adopted sparked reduced graphene oxide (rGO) loaded on the surface of the β″–Al₂O₃ as an ideal “wetting sheet,” compared with previous metal (Li or Na)-ion batteries where sparked rGO layers have been used for such metal reservoirs as an anode. The sparked rGO layers with nanogaps exhibited complete liquid-Na wetting, regardless of the surface energy between the liquid Na and graphene oxide, which originated from the capillary force in the gaps (see the figures). This indicated (i) that the Na nucleation and growth were sufficiently rapid to form liquid Na when the battery was charged and (ii) that the area of the Na⁺ passway at the Na (anode)/β″–Al₂O₃ (electrolyte) interface was maximized when the battery was discharged. Thus, a high state-of-charge for potential state-of-art low-temperature NBBs was obtained. This cell-stacking architecture is simple and scalable and addresses the fundamental limitations of NBBs by allowing Na wetting at low temperatures.

S.EL02.04.14
**FeAs van der Waals Crystal** Jongbum Won¹, Hyesoo Kim¹, Eunsil Lee², Jongyoung Kim² and Wooyoung Shim¹; ¹Yonsei University, Korea (the Republic of); ²Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of)

Van der Waals (vdW) materials are composed of two-dimensional planes that are held together by weak interlayer interaction. VdW crystals have attracted increasing attention in the past couple of decades because of their significantly different properties from three-dimensional materials. However, it is a small class of materials, with fewer than 100 layered compounds catalogued in the Inorganic Crystal Structure Database (ICSD), including graphite, h-BN, transition metal dichalcogenides, metal halides, metal pnictides, and metal oxides. Here, we present a topochemical redox concept to prepare a new binary vdW materials by structure control from ternary parent compounds. The vdW crystals obtained had the same chemical composition as known three-dimensionally bonded compounds, but exhibited layered crystal structures. In our vdW crystal design strategy, we synthesized LiFeAs and CaFe₂As₂ as parent compounds. We then selectively removed Li and Ca from parent materials by topochemical redox to obtain FeAs vdW crystals with various crystal structures. We confirmed crystal structure of FeAs vdW crystal by X-ray diffraction (XRD), transmission electron microscope (TEM), scanning transmission electron microscope (STEM) and X-ray photoemission spectroscopy (XPS) and measured electrical property and mechanical property to identify the difference FeAs vdW crystal with three-dimensional orthorhombic FeAs.

**S.EL02.04.19**

**Patterned All-Graphene Surface Enables Position-Controlled Remote Heteroepitaxy of ZnO Microrods** Junseok Jeong¹,², Daekwon Jin¹,² and Young Joon Hong¹,²; ¹Sejong University, Korea (the Republic of); ²Graphene Research Institute–Texas Photonics Center International Research Center (GRI–TPC IRC), Korea (the Republic of)

Heteroepitaxy of semiconductor on two-dimensional atomic layered materials (2d-ALMs) has been promising for fabricating transferrable and flexible devices, because the use of 2d-ALMs allows to easily exfoliate overlayer device from host substrate.[1,2] Recently, an emerging epitaxy has been reported, which is the so-called remote epitaxy.[3,4] The remote epitaxy enables to produce single crystalline overlayer on graphene layer because the crystallographic registrations of overlayer can be copied from a underlying single crystalline substrate across graphene layer.[4,5] In the remote epitaxy of microrods (MRs), graphene thickness that is the remote epitaxial gap is critical to determine growth density of MR overlayer because penetrated field strength given from substrate leading to nucleation–growth is attenuated as the graphene thickness increases.[4] This implies that as we use graphene interlayer with spatially different thicknesses can result in different growth regimes of i) remote epitaxy or ii) non-growth, depending on graphene thickness. We present how the remote epitaxy can be applied to selective-area growth using graphene pattern layer. Position-controlled remote heteroepitaxy was performed by hydrothermal growth of ZnO MRs on intaglio-patterned graphene (IPG)-coated c-plane GaN substrate. The IPG layer consists of two graphene parts of (I) perforated-hole-patterned multilayer graphene (MLG) that prevents the remote epitaxy, which act as a growth mask layer, and (II) single-layer graphene (SLG) penetrating the potential field from underlying GaN substrate to allow remote heteroepitaxy of ZnO through the hole aperture of mask layer, which is embedded between GaN and MLG mask layer. The hole-aperture SLG area yielded remote heteroepitaxial ZnO MRs, whereas MLG area inhibited growth. Diameter and spacing of ZnO MRs are controlled by changing the hole pattern parameters. Transmission electron microscopy revealed the remote heteroepitaxial relationship between ZnO and GaN across the SLG area. According to density-functional theory calculations, the orbitals of SLG transfer the charge from the underlying GaN to the SLG surface leading to remote epitaxy, but the thick MLG was not capable of charge transfer in a long range. The weak van der Waals adhesion of ZnO/IPG/GaN was applied to exfoliate the ZnO MRs overlayer by a thermal release tape-assisted exfoliation technique and to recycle the original substrate. Our results readily open an opportunity to utilize the remote epitaxy for transfer of arrayed epitaxial structures in the designed size and arrangement for device manufacturing.

**Reference**


**S.EL02.04.20**

**Remote Epitaxy of ZnO Microrod Arrays across Graphene** Junseok Jeong¹,² and Young Joon Hong¹,²; ¹Sejong University, Korea (the Republic of); ²Graphene Research Institute–Texas Photonics Center International Research Center (GRI–TPC IRC), Korea (the Republic of)
Two-dimensional atomic materials are emerging as epitaxial substrates for transferrable and flexible device application.[1] Graphene has excellent properties for the use as a substrate, such as high electrical conductivity, excellent mechanical strength, and optical transparency.[2,3] Nevertheless, since the difficulties of producing single crystalline thin film and crystallographically aligned nano/microstructures on graphene, due to the use of poly-domain graphene, there remains a challenge to utilize the graphene as a substantially epitaxial substrate. This obstacle can be overcome by the remote epitaxy.[4] The remote epitaxy enables to grow single crystalline overlayer on graphene regardless of the graphene domain because crystallographic registration can be dictated from underlying substrate through graphene. Here, we demonstrate remote homoepitaxy of ZnO microrods (MRs) on different crystal planes of apolar \( a \)- and polar \( c \)-plane ZnO substrates across graphene using hydrothermal growth method. Despite of the presence of poly-domain graphene intermediate layer, the ZnO MRs were epitaxially grown on \( a \)-plane and \( c \)-plane ZnO substrates, which were found to be homogeneous in-plane orientation over the entire surface of graphene-coated ZnO substrates. Such homoepitaxial relationship across graphene between ZnO MR and substrate was revealed through transmission electron microscopic and selected area electron diffraction analyses. The density-functional theory calculations suggested that the charge redistribution occurring near graphene induces the electric dipole formation, so the attracted adatoms lead to nucleation-growth of the remote-epitaxial overlayer. Because of a strong potential field caused by long-range charge transfer given from the substrate, even of bi-layer and tri-layer graphene resulted in the remote-epitaxial ZnO MRs. The effect of substrate crystal planes is also theoretically and empirically demonstrated. The ability of the graphene, which can be released from the host substrate without covalent bonds, was adapted to transfer the overlayer MR arrays. After the delamination, the host substrate was reused by repeating the process of remote epitaxy over again. This unconventional epitaxy technique offers an opportunity of the producing well aligned, transferrable and flexible epitaxial nano/microstructure arrays templates for epitaxial electronics and optoelectronics applications and regenerating the substrate for cost-saving device manufacturing.

Reference

S.EL02.04.26
Recent Progress of Remote Epitaxy of III-Nitride System Wei Kong, Kuan Qiao, Yunpeng Liu, Chansoo Kim and Jeehwan Kim; Massachusetts Institute of Technology, United States

III-nitride materials including GaN, InN, AlN, and their ternary alloys have been one of the key materials to realize advanced electronic and optoelectronic devices, such as high electron mobility transistors, light emitting diodes and lasers. The device performance heavily depends on defect density of III-nitride materials. However, the lack of native substrates leads to the challenges in fabricating defect-free III-nitride materials, severely limiting the implementation of variety of new devices utilizing III-nitride materials. Additionally, the attachment of III-nitride thin film to its substrate poses challenges of heterointegration of III-nitrides with other material systems. Separation of III-nitride thin films from the substrate while maintaining the pristine material quality is highly favorable.

We have previously shown the synthesis of GaAs on two dimensional materials followed by the separation of GaAs epitaxial thin film from its substrate [1], by utilizing the process so-called "remote-epitaxy". Such discovery reveals the possibilities towards the fabrication of defect-free semiconductor materials without the constriction of substrate availability. In this report, we demonstrate the remote-epitaxy process to fabricate thin film GaN [2], as well as its ternary InGaN. The remote-epitaxial materials have been characterized by X-ray diffraction, atomic force microscopy and transmission electron microscopy, rendering device grade material quality. Additionally, the thin film III-nitrides can be peeled off from the substrates, and subsequently bonded to a foreign material surface, including Si and SiO\(_2\). Based on GaN/Si heterostructure, III-nitride based photonic/phononic cavity is demonstrated. This work has demonstrated a promising path for the integration of III-nitride with an arbitrary material system.

Reference:
III-V compound semiconductors offer outstanding electronic and photonic properties that outperform silicon, but the cost of III-V wafers is extremely expensive. Although reusing original wafers can effectively minimize the cost of wafers, current techniques for wafer recycling add significant costs in fabrication, nullifying the cost savings by reusing the wafer. Remote epitaxy is a newly discovered method that enables single-crystal growth of III-V semiconductor thin films and easy exfoliation of the grown film, thus promising for reusing wafers multiple times. It requires an atomically thin spacer layer, such as graphene, to be present on top of III-V substrates, which allows enough field penetration from substrates through the graphene layer to make epitaxial III-V thin films grown on it maintain single-crystallinity. In addition, the graphene layer provides weak bonding at the III-V/graphene interface, and thus thin films grown on top of graphene can be easily exfoliated, leading to a cost-effective way of wafer reuse and flexible thin film production. However, previous methods of transferring graphene onto III-V wafers, which use polymethyl methacrylate (PMMA) or metal stressor layers to transfer graphene grown on foreign substrates like copper or SiC, introduce defects and damages on graphene and/or substrates during the transfer process. Remote epitaxial films grown on the damaged graphene/substrate suffer from lower crystal quality and imperfect exfoliation, which undermines wafer reusability and device performance.

Here we report the CVD growth of amorphous graphene on III-V wafers at low temperature that enabled improved quality of remote epitaxial films and their perfect exfoliation. By introducing toluene as a carbon source which cracks at a relative low temperature for graphene growth, we show fully covered amorphous graphene on AlGaAs/GaAs substrates despite arsenic’s low decomposition temperature. The surface of graphene-coated AlGaAs/GaAs substrate remains smooth with a RMS roughness of around 3Å. We also demonstrate 100% coverage of single-crystalline GaAs thin films grown on amorphous graphene, with the film’s quality significantly improved compared to the case of transferred graphene. In addition, roughness of the substrate’s surface remains the same after exfoliation of grown GaAs film, and the growth and exfoliation were successfully repeated multiple times, proving the feasibility for wafer recycling. Through this low temperature CVD growth approach and remote epitaxy, we successfully demonstrate wafer-scale flexible thin film exfoliation and recycling of substrates, which will lead to new opportunities in III-V thin film-based electronics and novel heterostructures with reduced cost.

**S.E.L05.06.02**

**Random Nanoparticle Films for Efficient Radiative Emission and Daytime Cooling Based on a Generalized Effective Medium Theory**

Parker Wray, Magel Su and Harry A. Atwater; California Institute of Technology, United States

We investigate nanoparticle film structures as components for daytime radiative cooling, using a generalized effective medium theory which is capable of recovering the Maxwell-Garnett, Bruggeman, and Coherent Potential mixing formulas. We show that, in all cases, nanoparticle fill fraction is a degree of freedom which can be used to improve free space coupling and spectrally tune the emissivity and absorptivity curves so as to optimize radiative emission within the atmospheric transmission window (8 – 14 μm). Based on this theory, we design different radiative cooling structures from composites of SiO<sub>2</sub> and Si<sub>n</sub>N<sub>4</sub> nanoparticle films, which were chosen as the example emissive materials because of their strong absorption peaks within the atmospheric transmission window. Our results show that two-layer nanoparticle films of these materials outperform all thin-film analogs and are sufficient to achieve cooling performances comparable to leading reports in literature. Further research will explore how the low thermal conductivity of nanoparticle films could be used to further enhance daytime radiative cooling performance. This research supports the idea that simple nanoparticle films couple provide a viable method for designing radiative cooling structures, provided scalable methods are identified for nanoparticle fabrication.

**S.E.L05.06.09**

**Scalable, Multi-Functional Covert Polarization Display with Colorimetric Detection**

Joo Hwan Ko, Young Jin Yoo and Young Min Song; Gwangju Institute of Science and Engineering, Korea (the Republic of)

The history of coloration has been proceeded by trials and development of many technologies for selectively splitting the light. Structural coloration, among them, has grown up as a potential candidate alternating traditional pigments/dyes coloration since their great durability, sustainable production, and fine color tuning by controlling materials and dimension. As this property, structural color facilitates the creation of security features for anti-counterfeiting. However, conventionally, most of them have used metal/dielectric materials to make a resonating system at a specific wavelength and polarization condition which demands complex fabrication processes such as e-beam lithography or ion beam lithography technology. Even though this system can be suitable to an ultra-high definition structural color display, it is limited to only a few
millimeter scales or less. To apply into a realistic application such as banknote, luxury products, or customer goods, it is necessary to make it over centimeter scale with a flexible medium.

In this work, to break through these significant flexibility/scalability limitations, we developed polarization distinguishable covert display with ultrathin porous nanocolumns (PNCs) on a metal film by glancing angle deposition (GLAD) method. Particularly, the unique property of this covert display showed powerful functions which provide a hurdle to the inadvertent viewing of stored optical information without compromising their aesthetic. This structure with lossy PNCs on a metal film makes a non-trivial phase shift at the interfaces causing short reflection path and finally shows strong resonance [1]. Furthermore, the PNCs fabricated with GLAD produce anisotropic media and has different effective complex refractive index causing different resonating condition depending on polarization direction [2]. Using this concept, we designed polarization distinguishable color filters with a variety of materials and dimensions with rigorous coupling wave analysis (RCWA) method. In this process, we obtained an enlarged color range occupying over 80% of standard RGB area. In this color response, some showed a small color difference ($\Delta E$), the other showed a large color difference following polarization angle. Additionally, we confirmed this result is originated from human eye’s spectral responses according to between tristimulus value and reflectance spectra having a single minimum. Using these results, we designed optical data label (i.e., QR code) which shows inadvertent viewing in the naked eye (under unpolarized light), on the other hand, this label can be selectively detected by polarized light. For practical application, we designed this label into daily consumer goods with the color matching between labels and products to avoid compromising aesthetics of products and successfully demonstrated onto wine bottleneck, food packaging with confirming the authentication process. As a multi-functional color display, we demonstrated a colorimetric detection. Due to the low complex refractive index of porous medium, PNCs are sensitive to subtle external environment change. Consequently, PNCs reveal a sensitive color change according to background refractive index or additional layer thickness change. Using this unique property, we presented colorimetric detection with external change for volatile organic compounds (VOCs) and humidity.

Hybrid Monolithic Plasmonic Materials for Nonlinear Absorption from the Visible to the NIR

Stephane Parola1, Carole Vaillant1, Denis Chateau1, Anthony Desert1, Frederic Lerouge1, Frederic Chaput1, Sylvain David1, Olivier Maury1, Chantal Andraud1, Gerard Berginc2, Mikael Lindgren3, Hampus Lunden4 and Cesar Lopes4; 1ENS Lyon, France; 2THALES, France; 3NTNU, Norway; 4FOI, Sweden

Hybrid materials are commonly used for wide range of optical applications (sensors, filters, imaging, photocatalysis...).[1] The use of interactions between emitting or absorbing systems and plasmonic nanostructures have also been an intensive field of research due to the possibility to tune and optimize the optical responses using the local electromagnetic field. The synthesis of gold nanostructures combining high yield, purity, large scale and plasmon resonance spreading from the visible to the NIR wavelengths was developped.[2,3] These nanostructures were functionalized in order to allow their homogeneous incorporation in transparent hybrid silica matrices using the sol-gel process.[4,5] Co-dispersion of the metallic structures with nonlinear dyes was successfully achieved.[6] The role of the concentration, shape and size of the metal nanoparticles on the optical response was evaluated. The respective impact on the nonlinear optical response of the dyes will be discussed both in the visible and the near infrared wavelengths.

References


New Ligands and Approaches to RSA Materials

Emigdio Turner1, Sebastian Vittardi1, Ryan O'Donnell2 and Jeffrey Rack1; 1The University of New Mexico, United States; 2U.S. Army Research Laboratory, United States

Reverse Saturable Absorption (RSA) is a nonlinear optical effect in which the excited state of a molecule or material exhibits greater absorptivity than its corresponding ground state. Traditional approaches to optimize this effect in transition metal compounds and materials are to employ extended aromatic rings to enhance absorption at longer wavelengths and to increase the excited state lifetime. In contrast, we have created a new class of chelating ligands comprising phosphorous and sulfur donor atoms. These types of ligands impart beneficial non-emissive properties to transition metal complexes. Complexes of Ir containing these new P,S ligands with derivatives of phenylpyridine will be prepared. In addition to standard characterization techniques (absorption spectroscopy, electrochemistry, NMR spectroscopy, crystallography, etc), these complexes will be interrogated by transient absorption spectroscopy from the femtosecond to the millisecond time scale. These data will determine the excited state spectra and RSA response as a function of wavelength. These data and others will be presented.

Sensitized Photon Upconversion in Metal Organic Frameworks—The Role of 3D Structure

Stefan Illic, Jennifer Rowe and Amanda J. Morris; Virginia Polytechnic Institute and State University, United States

Metal-organic frameworks (MOFs) are a diverse class of highly ordered and tunable nanoscale materials that are increasingly employed in several solar energy conversion schemes. Investigation of light-harvesting and energy transfer processes within the three-dimensional framework of such nanoscopic materials results in more efficient design of biomimetic chromophore arrays for artificial photosynthesis. Here we present the synthesis and photophysical investigation of three anthracenic MOFs. The MOFs were synthesized by following a one-pot solvothermal synthetic protocol, and the powders were structurally characterized with the help of X-ray powdered diffraction (PXRD) patterns and scanning electron microscopy (SEM) images. Steady-state and time-resolved spectroscopic techniques aided in exploring the photophysical behavior in MOFs as a function
of 3D structure. Upon surface functionalization of a sensitizing palladium porphyrin, excitation of the composite with green light resulted in upconverted emission. The role of the 3D incorporation of the anthracenes and resultant spacing of the anthracene units dictates the efficiency of the upconversion process.

**9:45 AM SESSION Q&A WRAP UP**

SESSION S.EL04.06: Live Keynote II: Materials for Nonlinear and Nonreciprocal Photonics  
Session Chairs: Thomas Cooper and Ryan O'Donnell  
Monday Afternoon, November 30, 2020  
S.EL04

**7:30 PM S.EL04.02.01**  
Controlling Nonlinear Generation via Multipolar Interference Ekaterina Poutrina¹,² and Augustine Urbas¹; ¹Air Force Research Laboratory, United States; ²UES, Inc., United States

Probing the nonlinear response in light-matter interactions offers the advantage of lifting some fundamental limitations existing within the scope of linear operations. One of the most striking examples is the ability of breaking the reciprocity of light transmission. Transmission through a medium characterized by a symmetric, time-independent, and linear permittivity tensor stays the same when reversing the excitation direction, or interchanging the source and the detector. While serving as an innate foundation in any optical design, it presents a fundamental challenge for applications requiring a non-reciprocal directionality of light propagation.

Here, we show that the option of non-reciprocity in the directionality and the efficiency of nonlinear generation is inherently incorporated in the response of nanoelements exhibiting magnetic dipolar (or higher-order multipolar) Mie resonance(s) in their linear response. In particular, we show that nonlinear generation from a nanoelement, where it regularly occurs nearly isotropically in all directions (due to the lack of phase matching constraints within nanoscale interaction volumes), can be made both unidirectional and non-reciprocal, such that the generation occurs predominantly in a single direction which, additionally, remains unchanged with respect to a fixed laboratory coordinate system when reversing the direction of the fundamental beam(s). In contrast with the previous studies, the proposed approach does not require asymmetry in either the geometry or the material composition of the nanoelement. Rather, it relies on the multiplicative nature of the nonlinear response which, in turn, allows a simultaneous change in phase of both the electric and the magnetic, nonlinearly induced, dipolar modes, when switching the phase of a single (either electric or magnetic) vector of the fundamental field.

Furthermore, the interference can occur between various pathways within the electric and magnetic (nonlinearly produced) dipolar modes. As a result, non-reciprocity in terms of just a change in the efficiency of nonlinear generation when reversing the direction of any subset of the fundamental beams is inherent to and expected in the nonlinear response of most nanoelements, even the symmetric ones, and for most of the nonlinear processes. Targeted engineering of the relative strengths of various pathways within each (nonlinearly produced) multipolar mode may then allow an interferometric cancellation of the generated field for a given nonlinear process, for certain respective directions of the fundamental beams.

Reliance on multipolar interference in the suggested approach inherently assumes the manifestation of the described phenomena on the nanoscale, through the response of subwavelength-scale elements. These nanoelements can thus be used as building blocks to construct a metasurface or a medium with similar unique features in its nonlinear response. As an example, we present a metasurface operating as a one-way nonlinear mirror, where the image is formed by a process of difference frequency generation on one and the same side of the metasurface independently of the object location.

Both non-reciprocal directionality and inhibition of the nonlinear response require, however, a careful engineering of the respective strengths of various pathways within each (electric or magnetic) type of the nonlinearly produced multipolar partial wave. As such, these phenomena are not expected to manifest in natural nonlinear materials, even those possessing natural magnetic dipolar transitions. They, however, can be achieved via a tailored design of the effective magneto-electric nonlinear polarizabilities of a nanoelement.

**7:50 PM S.EL04.02.04**  
High-Energy Nonreciprocal Directional Dichroism in a Chiral Magnet Janice Musfeldt¹, Michael O. Yokosuk¹; Heung-Sik Kim², Scott Crooker¹, Sang-Wook Cheong³, Kristjan Haule³ and David Vanderbilt¹; ¹University of Tennessee, United
Nonreciprocal directional dichroism is an unusual light-matter interaction that gives rise to diode-like behavior in low symmetry materials. The chiral varieties are particularly scarce due to the requirements for strong spin-orbit coupling, broken time reversal symmetry, and a chiral axis. We bring together magneto-optical spectroscopy and first principles calculations to reveal high energy, broad band nonreciprocal directional dichroism in Ni$_3$TeO$_6$ with special focus on behavior in the metamagnetic phase above 52 T. In addition to demonstrating this effect in the magnetochiral configuration, we explore the transverse magnetochiral orientation in which applied field and light propagation are orthogonal to the chiral axis and by so doing, uncover an additional configuration with a nonreciprocal response in the visible part of the spectrum. In a significant conceptual advance, we use first-principles methods to analyze how the Ni$^{2+}$ d-to-d on-site excitations develop magnetoelastic character and present a microscopic model that unlocks the door to theory-driven discovery of chiral magnets with nonreciprocal properties.

8:10 PM *S.EL04.03.07
Hot-Electron Dynamics in Quantum Dots Manipulated by Spin-Exchange Auger Interactions Victor I. Klimov; Los Alamos National Laboratory, United States

Colloidal semiconductor quantum dots (QDs) are attractive materials for realizing highly flexible, solution-processable optical gain media with readily tunable operational wavelengths [1, 2]. However, QDs are difficult to use in lasing due to extremely short optical gain lifetimes limited by nonradiative multielectron Auger recombination [3]. This, in particular, is a serious obstacle for realizing cw optically and electrically pumped lasing devices. Recently, we have explored several approaches for mitigating the problem of Auger decay by taking advantage of a new generation of core/multi-shell QDs with a radially graded composition that allow for considerable (nearly complete) suppression of Auger recombination [4, 5]. Using these specially engineered QDs, we have been able to realize optical gain with direct-current electrical pumping [6], which has been a long-standing goal in the field of colloidal nanostructures. Further, we have applied these dots to practically demonstrated the viability of a ‘zero-threshold optical gain’ concept using not neutral but negatively charged particles wherein the pre-existing electrons block either partially or completely ground-state absorption [5, 6]. Such charged QDs are optical-gain-ready without excitation, which allows us to reduce the lasing threshold to record-low values that are well below a fundamental single-exciton-per-dot limit [6]. Most recently, we have developed QD devices that operate as both an electroluminescent (EL) structure and a distributed feedback optically pumped laser [7]. By carefully engineering a refractive-index profile across the device stack, we have been able to demonstrate low-threshold lasing even with a very thin EL-active region, which comprises only three monolayers of the QDs. All of these recent developments demonstrate a considerable promise of colloidal QDs for implementing solution-processable optically and electrically pumped lasers operating across a wide range of wavelengths.


8:30 PM *S.EL04.03.01
Strong Coupling and Induced Transparency with Single Quantum Dots and Plasmons—Towards Ultrafast All-Optical Nonlinearities at the Nanoscale Matthew Pelton; University of Maryland-Baltimore County, United States

Achieving room-temperature quantum-mechanical strong coupling, or vacuum Rabi splitting, between a single emitter and a plasmon resonance has been a longstanding goal. Recently, two peaks have been observed in the scattering spectra of plasmonic metal nanostructures coupled to single molecules and single quantum dots, and this was taken as evidence of strong coupling. However, a two-peak scattering structure can also arise at intermediate coupling strengths, below the strong-coupling threshold, due to Fano-like interference between the plasmon and emitter dipole. We unambiguously distinguish between intermediate and strong coupling by measuring both the scattering spectra and the photoluminescence spectra of coupled plasmon-emitter structures. Specifically, we couple single colloidal quantum dots to a plasmon resonator by placing them in the gap between a gold nanoparticle and a silver film. We observe weak, intermediate,
and strong coupling in these hybrid metal-semiconductor structures at room temperature, depending on the detailed nanoscale structure of the metal nanoparticle. These structures have the potential to provide ultrafast, low-power optical nonlinearity on the nanoscale. Both induced transparency and strong coupling can be canceled by absorbing a photon in the quantum dot, leading to a strong change in extinction at the quantum dot transition frequency. Since only a single photon must be absorbed by the QD for this to happen, the energy needed for modulation has the potential to be extremely low, and the structure has the potential to enable all-optical information processing, possibly including neuromorphic computation and quantum information processing. One limitation to the practical application of these structures, however, is the random nature of their assembly and the resulting low yield of structures exhibiting the desired transparency or strong coupling. One approach we have taken to this low yield is to replace the metal nanoparticle with a metal scanning-probe tip. In this way, we are able to achieve reversible, controllable strong coupling to several individual quantum dots, one at a time. Our current efforts are focused on developing bottom-up techniques of chemical synthesis and assembly for the high-yield production of strongly-coupled metal-semiconductor hybrid nanostructures.

8:50 PM BREAK

8:55 PM *S.EL04.03.05
Nanoparticle Materials for Photonics Jake Fontana; Naval Research Laboratory, United States

In this talk, we will describe a materials self-assembly approach to controllably weld gold nanorods end-to-end, forming much higher aspect ratio dimers in macroscopic quantities, linking the nanorods using unfocused femtosecond light. Electrostatic-based molecular assembly controls the discrete selection of end-to-end dimer assemblies, preventing larger structures. Large, high-quality yields of welded dimers can be produced by illuminating these dimer suspensions at their capacitively coupled plasmon resonance wavelength using femtosecond light pulses. In-situ absorbance measurements demonstrate an isosbestic point which results from the conversion of single nanorods to capacitively coupled plasmon dimers, indicative of direct population conversion. We will discuss the underlying physical mechanisms for the welding process as well as the optical properties of the newly formed high aspect ratio dimers.

9:15 PM SESSION Q&A WRAP UP

SESSION S.EL04.01: Organic Nonlinear Optical Materials
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

5:00 AM S.EL04.01.01
A Comparison of the Photophysical Properties of Pt(II) and Au(I) Substituted Fluorene-Benzothiazole Chromophores and their Impact on Nonlinear Optical Performance Tod Grusenmeyer1, Alexis T. Phillips1, Joseph J. Mihaly2, Christopher L. McCleese1, David J. Stewart1, Thomas G. Gray2, Thomas M. Cooper1 and Joy E. Haley1; 1Air Force Research Laboratory, United States; 2Case Western Reserve University, United States

Our research group has a long history of developing chromophores that exhibit non-linear absorption. Substantial progress was made to this end with the synthesis of two-photon chromophores substituted with transition metals. The inclusion of the metal center facilitates the formation of triplet excited-states in the two-photon chromophore. If this leads to a triplet state with strong excited-state absorption at wavelengths where two-photon absorption is active, the nonlinear optical performance of the chromophore is enhanced. The champion molecule from these initial studies was found to be bis(phenylethynyl)bis(tributylphosphine)platinum (II) bearing two alkynyl-benzothiazolylfluorene ligands. Recently, Au(I) analogs of this complex containing fluorene-benzothiazole and alkynyl-fluorene-benzothiazole ligands have been synthesized with differing ancillary ligands attached to the Au(I) center. Varying the ancillary ligand on Au(I) from a phosphate to a N-heterocyclic carbene alters the photophysical properties of the chromophoric ligand. UV-vis, steady-state and time-resolved luminescence, and transient absorption results will be discussed. This talk will compare the photophysical properties and their impact on the nonlinear performance of the original platinum (II) alkynyl-fluorene-benzothiazole complex and the Au(I) fluorene-diphenylamine and Au(I) alkynyl-fluorene-diphenylamine complexes.
Hybrid Monolithic Plasmonic Materials for Nonlinear Absorption from the Visible to the NIR

Stephane Parola\textsuperscript{1}, Carole Vaillant\textsuperscript{1}, Denis Chateau\textsuperscript{1}, Anthony Desert\textsuperscript{1}, Frederic Lerouge\textsuperscript{1}, Frederic Chaput\textsuperscript{1}, Sylvain David\textsuperscript{1}, Olivier Maury\textsuperscript{1}, Chantal Andraud\textsuperscript{1}, Gerard Bergine\textsuperscript{2}, Mikael Lindgren\textsuperscript{1}, Hampus Lunden\textsuperscript{1} and Cesar Lopes\textsuperscript{1}; \textsuperscript{1}ENS Lyon, France; \textsuperscript{2}THALES, France; \textsuperscript{3}NTNU, Norway; \textsuperscript{4}FOI, Sweden

Hybrid materials are commonly used for wide range of optical applications (sensors, filters, imaging, photocatalysis…).[1] The use of interactions between emitting or absorbing systems and plasmonic nanostructures have also been an intensive field of research due to the possibility to tune and optimize the optical responses using the local electromagnetic field. The synthesis of gold nanostructures combining high yield, purity, large scale and plasmon resonance spreading from the visible to the NIR wavelengths was developed.[2,3] These nanostructures were functionalized in order to allow their homogeneous incorporation in transparent hybrid silica matrices using the sol-gel process.[4,5] Co-dispersion of the metallic structures with nonlinear dyes was successfully achieved.[6] The role of the concentration, shape and size of the metal nanoparticles on the optical response was evaluated. The respective impact on the nonlinear optical response of the dyes will be discussed both in the visible and the near infrared wavelengths.

References

Triplet Excited State Derived Excimer Formation in a Solid State Matrix

Joy E. Haley\textsuperscript{1}, Douglas Krein\textsuperscript{1,2}, Jonathan E. Slagle\textsuperscript{1}, Matthew J. Dalton\textsuperscript{1}, David J. Stewart\textsuperscript{1,2}, Rachel Renkel\textsuperscript{1,3}, Jonathan Flikkema\textsuperscript{1,3}, Weijie Su\textsuperscript{1,2}, Loon-Seng Tan\textsuperscript{1} and Thomas M. Cooper\textsuperscript{1}; \textsuperscript{1}Air Force Research Laboratory, United States; \textsuperscript{2}General Dynamics Information Technology, United States; \textsuperscript{3}Southwestern Ohio Council for Higher Education, United States

It is well known in the literature that for a two photon nonlinear absorbing dye to be the most effective, high concentrations are needed. The problem is that most photophysical studies are done at low concentration and in a solution. These low concentration studies are important for understanding inherent materials properties but it is also important to understand what happens in a material at high concentration. In addition to this, efforts have been made to study the effects of incorporating a dye into a solid matrix environment to better understand the constraints this environment has to a given material. Here we present the results of a study of a two photon absorbing platinum dye, E1-BTF, incorporated into various hosts including PMMA, epoxy, polyurethane, and sol gel. Similar results were found in all hosts that a triplet excited state derived excimer forms at the highest concentrations. This is due to close packing of the E1-BTF molecule where both static and dynamic quenching may occur. The host material defined the highest achievable concentrations for each polymer host. We will report on the overall photophysical properties of E1-BTF in these polymer hosts.

Finding Polaritonic Signatures in Complex Spectra via Two-Dimensional Infrared Spectroscopy

Andrea Grafton, Adam Dunkelberger, Blake S. Simpkins and Jeffrey C. Owratucky; US Naval Research Lab, United States
Optical modes can couple to sufficiently strongly absorbing vibrational transitions to create new polaritonic states in the mid-infrared. Transient infrared spectroscopy of these new states reveals rich spectra that report on coherences between and population of both the polaritons and so-called reservoirs of uncoupled modes. Our previous work, focusing on one-dimensional, pump-probe spectroscopy has shown that cavity-coupled vibrations have potential for photonic devices and can exhibit modified relaxation dynamics compared to uncoupled systems. Here, we present new results from two dimensional infrared spectroscopy (2D IR) and pump filtering experiments that give deeper insight into the spectroscopic responses of the vibrationally excited polaritonic system. We report on the spectroscopic polaritonic signatures in cavity-coupled systems and the influence of the homogeneous linewidth of the vibrational mode on the population dynamics of coupled systems.

6:45 AM S.EL04.01.06
Is DBP an Unwanted Guest in Lead-Halide Perovskite Sensitized Upconversion? Alexander S. Bieber, Zachary VanOrman, Sarah Wieghold and Lea Nienhaus; Florida State University, United States

Infrared-to-visible upconversion (UC) bears the potential to surpass the Shockley Queisser limit for single junction photovoltaics. Here, bulk-perovskite sensitized UC has been shown to be a promising approach in which free electrons and holes can be injected into the triplet state of the upconverting semiconductor. In these UC systems, a bulk-perovskite thin film is employed as the absorber layer and rubrene, a p-type tetraphenyl derivative of tetracene, is used as the annihilator layer. To boost the UC quantum yield, the rubrene layer is usually doped with dibenzotetraphenylperiflanthene (DBP) in a commonly used host-guest/annihilator-emitter approach. DBP is used to harvest the singlet excited state from rubrene through a Förster resonance energy transfer, which prevents rubrene from undergoing the reverse process of singlet fission. To understand and optimize the role of DBP in the upconversion devices, we fabricate bilayer devices consisting of a lead halide perovskite sensitizer followed by a layer of rubrene/DBP with varying concentrations of DBP. Steady state and time resolved spectroscopy are then used to study the energy transfer processes in the bilayer devices. As expected, an increase in the DBP concentration results in the reduction of the rubrene emission, indicating a higher transfer efficiency. In addition, we observe an increase in the upconverted light emission when the rubrene/DBP ratio is varied. However, the time-resolved dynamics indicate that DBP may not merely be a guest in the system, but rather directly influences the observed upconversion dynamics and the device performance. These insights provide a path to further optimize and improve the efficiencies of bulk-perovskite sensitized UC devices.

References:

7:30 AM S.EL04.01.08
Cavity-Modified Non-Linear Optical Response and Chemical Reaction Kinetics Blake S. Simpkins1, Wonmi Ahn2, Igor Vurgaftman2, Adam Dunkelberger1, Andrea Grafton1 and Jeffrey C. Owrutsky1; 1U.S. Naval Research Laboratory, United States; 2Excet, United States; 3Naval Research Laboratory, United States

Quantum emitters placed in resonant optical cavities have shown modified spontaneous emission rates and frequency when they are coupled in the weak coupling regime. In the so-called strong coupling regime, however, the coupled oscillators, i.e., emitters and optical modes, exchange energies inextricably, creating new hybrid states called polaritons. Recently, this half-light half-matter quasi-state has been demonstrated in a system where molecular vibrations are coherently coupled to optical cavity modes. In this talk, we will focus on non-linear transient response probed in the ultrafast regime, cavity-modified saturable absorption, and cavity-modified chemical reactivity. Specifically, we find excited-state spectra that reveal coherences between populations of both cavity polaritons and so-called dark states and explore the influence of the homogeneous linewidth of the vibrational modes. Our recently published results[1] show that the saturation fluence (typically, an intrinsic parameter of a material) can be tailored via cavity coupling and exhibits a counterintuitive scaling with system parameters (cavity length and molecular concentration). Lastly, we monitor transmission spectra of the Fabry-Pérot microcavity filled with species that participate in a simple addition reaction. Both reactants and products have strong molecular vibrations that couple to the optical cavity modes, resulting in quantifiable vacuum Rabi splittings. We examine the reaction rates in and out of the cavity to expose the influence of vibrational strong coupling on reaction kinetics. Our results will extend the potential of cavity-modified material properties, which will have important implications for ultrafast optical devices and chemical synthesis and catalysis.
Reverse Saturable Absorption (RSA) is a nonlinear optical effect in which the excited state of a molecule or material exhibits greater absorptivity than its corresponding ground state. Traditional approaches to optimize this effect in transition metal compounds and materials are to employ extended aromatic rings to enhance absorption at longer wavelengths and to increase the excited state lifetime. In contrast, we have created a new class of chelating ligands comprising phosphorous and sulfur donor atoms. These types of ligands impart beneficial non-emissive properties to transition metal complexes. Complexes of Ir containing these new P,S ligands with derivatives of phenylpyridine will be prepared. In addition to standard characterization techniques (absorption spectroscopy, electrochemistry, NMR spectroscopy, crystallography, etc), these complexes will be interrogated by transient absorption spectroscopy from the femtosecond to the millisecond time scale. These data will determine the excited state spectra and RSA response as a function of wavelength. These data and others will be presented.

Sensitized Photon Upconversion in Metal Organic Frameworks—The Role of 3D Structure
Stefan Illic, Jennifer Rowe and Amanda J. Morris; Virginia Polytechnic Institute and State University, United States

Metal-organic frameworks (MOFs) are a diverse class of highly ordered and tunable nanoscale materials that are increasingly employed in several solar energy conversion schemes. Investigation of light-harvesting and energy transfer processes within the three-dimensional framework of such nanoscopic materials results in more efficient design of biomimetic chromophore arrays for artificial photosynthesis. Here we present the synthesis and photophysical investigation of three anthracenic MOFs. The MOFs were synthesized by following a one-pot solvothermal synthetic protocol, and the powders were structurally characterized with the help of X-ray powdered diffraction (PXRD) patterns and scanning electron microscopy (SEM) images. Steady-state and time-resolved spectroscopic techniques aided in exploring the photophysical behavior in MOFs as a function of 3D structure. Upon surface functionalization of a sensitizing palladium porphyrin, excitation of the composite with green light resulted in upconverted emission. The role of the 3D incorporation of the anthracenes and resultant spacing of the anthracene units dictates the efficiency of the upconversion process.

Controlling Nonlinear Generation via Multipolar Interference
Ekaterina Poutrina and Augustine Urbas; 1Air Force Research Laboratory, United States; 2UES, Inc., United States

Probing the nonlinear response in light-matter interactions offers the advantage of lifting some fundamental limitations existing within the scope of linear operations. One of the most striking examples is the ability of breaking the reciprocity of light transmission. Transmission through a medium characterized by a symmetric, time-independent, and linear permittivity tensor stays the same when reversing the excitation direction, or interchanging the source and the detector. While serving as an innate foundation in any optical design, it presents a fundamental challenge for applications requiring a non-reciprocal directionality of light propagation.

Here, we show that the option of non-reciprocity in the directionality and the efficiency of nonlinear generation is inherently incorporated in the response of nanoelements exhibiting magnetic dipolar (or higher-order multipolar) Mie resonance(s) in their linear response. In particular, we show that nonlinear generation from a nanoelement, where it regularly occurs nearly isotropically in all directions (due to the lack of phase matching constraints within nanoscale interaction volumes), can be made both unidirectional and non-reciprocal, such that the generation occurs predominantly in a single direction which,
Additionally, remains unchanged with respect to a fixed laboratory coordinate system when reversing the direction of the fundamental beam(s). In contrast with the previous studies, the proposed approach does not require asymmetry in either the geometry or the material composition of the nanoelement. Rather, it relies on the multiplicative nature of the nonlinear response which, in turn, allows a simultaneous change in phase of both the electric and the magnetic, nonlinearly induced, dipolar modes, when switching the phase of a single (either electric or magnetic) vector of the fundamental field. Furthermore, the interference can occur between various pathways within the electric and magnetic (nonlinearly produced) dipolar modes. As a result, non-reciprocity in terms of just a change in the efficiency of nonlinear generation when reversing the direction of any subset of the fundamental beams is inherent to and expected in the nonlinear response of most nanoelements, even the symmetric ones, and for most of the nonlinear processes. Targeted engineering of the relative strengths of various pathways within each (nonlinearly produced) multipolar mode may then allow an interferometric cancellation of the generated field for a given nonlinear process, for certain respective directions of the fundamental beams.

Reliance on multipolar interference in the suggested approach inherently assumes the manifestation of the described phenomena on the nanoscale, through the response of subwavelength-scale elements. These nanoelements can thus be used as building blocks to construct a metasurface or a medium with similar unique features in its nonlinear response. As an example, we present a metasurface operating as a one-way nonlinear mirror, where the image is formed by a process of difference frequency generation on one and the same side of the metasurface independently of the object location.

Both non-reciprocal directionality and inhibition of the nonlinear response require, however, a careful engineering of the respective strengths of various pathways within each (electric or magnetic) type of the nonlinearly produced multipolar partial wave. As such, these phenomena are not expected to manifest in natural nonlinear materials, even those possessing natural magnetic dipolar transitions. They, however, can be achieved via a tailored design of the effective magneto-electric nonlinear polarizabilities of a nanoelement.

5:30 AM S.EL04.02.02
First-Principles Simulation of Nonreciprocal Directional Dichroism in Correlated Materials Heung-Sik Kim1, Michael O. Yokosuk1,2,3, Kiman Park3, Janice L. Musfeldt2,3, Kristjan Haule4 and David Vanderbilt4; 1Kangwon National University, Korea (the Republic of); 2Pacific Northwest National Laboratory, United States; 3The University of Tennessee, Knoxville, United States; 4Rutgers, The State University of New Jersey, United States

Computation of response functions, based on linear response theory and first-principles electronic structure methods, has been extensively utilized for analyses and predictions of various functional materials such as ferroelectrics, piezoelectrics, and multiferroics. For the study of strongly correlated materials, however, methods based on standard density functional theory need substantial improvement; because of the need of incorporating the so-called two-particle vertex correction in evaluating response functions, which is computationally demanding, an extensive study of functional and correlated materials has remained a challenging task. To mitigate this difficulty and facilitate investigations of correlated functional materials, we propose a new theoretical method to compute linear response functions of strongly correlated Mott insulators. Our approach starts from the strongly correlated atomic regime, unlike other first-principles-based methods, which circumvents evaluating vertex correction terms and enables computationally cheap evaluation of material properties in Mott systems. As an example, we present our simulation results of nonreciprocal directional dichroism in Ni3TeO6, which is a wide-gap Mott insulator, showing a promising agreement with experimental observations.

5:45 AM S.EL04.02.04
High-Energy Nonreciprocal Directional Dichroism in a Chiral Magnet Janice Musfeldt1, Michael O. Yokosuk1, Heung-Sik Kim2, Scott Crooker1, Sang-Wook Cheong3, Kristjan Haule4 and David Vanderbilt4; 1University of Tennessee, United States; 2Kangwon University, United States; 3Los Alamos National Laboratory, United States; 4Rutgers, The State University of New Jersey, United States

Nonreciprocal directional dichroism is an unusual light-matter interaction that gives rise to diode-like behavior in low symmetry materials. The chiral varieties are particularly scarce due to the requirements for strong spin-orbit coupling, broken time reversal symmetry, and a chiral axis. We bring together magneto-optical spectroscopy and first principles calculations to reveal high energy, broad band nonreciprocal directional dichroism in Ni3TeO6 with special focus on behavior in the metamagnetic phase above 52 T. In addition to demonstrating this effect in the magneto-chiral configuration, we explore the transverse magneto-chiral orientation in which applied field and light propagation are orthogonal to the chiral axis and by so doing, uncover an additional configuration with a nonreciprocal response in the visible part of the spectrum. In a significant conceptual advance, we use first-principles methods to analyze how the Ni2+ d-to-d on-site excitations develop magneto-electric character and present a microscopic model that unlocks the door to theory-driven discovery of chiral.
magnets with nonreciprocal properties.

SESSION S.EL04.03: Inorganic Nonlinear Optical Materials
On Demand Abstracts Available for Viewing Starting Saturday
Morning, November 21, 2020
S-EL04

5:00 AM *S.EL04.03.01
Strong Coupling and Induced Transparency with Single Quantum Dots and Plasmons—Towards Ultrafast All-Optical Nonlinearities at the Nanoscale Matthew Pelton; University of Maryland-Baltimore County, United States

Achieving room-temperature quantum-mechanical strong coupling, or vacuum Rabi splitting, between a single emitter and a plasmonic resonance has been a longstanding goal. Recently, two peaks have been observed in the scattering spectra of plasmonic metal nanostructures coupled to single molecules and single quantum dots, and this was taken as evidence of strong coupling. However, a two-peak scattering structure can also arise at intermediate coupling strengths, below the strong-coupling threshold, due to Fano-like interference between the plasmon and emitter dipole. We unambiguously distinguish between intermediate and strong coupling by measuring both the scattering spectra and the photoluminescence spectra of coupled plasmon-emitter structures. Specifically, we couple single colloidal quantum dots to a plasmon resonator by placing them in the gap between a gold nanoparticle and a silver film. We observe weak, intermediate, and strong coupling in these hybrid metal-semiconductor structures at room temperature, depending on the detailed nanoscale structure of the metal nanoparticle.

These structures have the potential to provide ultrafast, low-power optical nonlinearities on the nanoscale. Both induced transparency and strong coupling can be canceled by absorbing a photon in the quantum dot, leading to a strong change in extinction at the quantum dot transition frequency. Since only a single photon must be absorbed by the QD for this to happen, the energy needed for modulation has the potential to be extremely low, and the structure has the potential to enable all-optical information processing, possibly including neuromorphic computation and quantum information processing. One limitation to the practical application of these structures, however, is the random nature of their assembly and the resulting low yield of structures exhibiting the desired transparency or strong coupling. One approach we have taken to this low yield is to replace the metal nanoparticle with a metal scanning-probe tip. In this way, we are able to achieve reversible, controllable strong coupling to several individual quantum dots, one at a time. Our current efforts are focused on developing bottom-up techniques of chemical synthesis and assembly for the high-yield production of strongly-coupled metal-semiconductor hybrid nanostructures.

5:30 AM *S.EL04.03.05
Nanoparticle Materials for Photonics Jake Fontana; Naval Research Laboratory, United States

In this talk, we will describe a materials self-assembly approach to controllably weld gold nanorods end-to-end, forming much higher aspect ratio dimers in macroscale quantities, linking the nanorods using unfocused femtosecond light. Electrostatic-based molecular assembly controls the discrete selection of end-to-end dimer assemblies, preventing larger structures. Large, high-quality yields of welded dimers can be produced by illuminating these dimer suspensions at their capacitively coupled plasmon resonance wavelength using femtosecond light pulses. In-situ absorbance measurements demonstrate an isosbestic point which results from the conversion of single nanorods to capacitively coupled plasmon dimers, indicative of direct population conversion. We will discuss the underlying physical mechanisms for the welding process as well as the optical properties of the newly formed high aspect ratio dimers.

6:00 AM *S.EL04.03.07
Hot-Electron Dynamics in Quantum Dots Manipulated by Spin-Exchange Auger Interactions Victor I. Klimov; Los Alamos National Laboratory, United States

Colloidal semiconductor quantum dots (QDs) are attractive materials for realizing highly flexible, solution-processable optical gain media with readily tunable operational wavelengths [1, 2]. However, QDs are difficult to use in lasing due to extremely short optical gain lifetimes limited by nonradiative multielectron Auger recombination [3]. This, in particular, is a serious obstacle for realizing cw optically and electrically pumped lasing devices. Recently, we have explored several
approaches for mitigating the problem of Auger decay by taking advantage of a new generation of core/multi-shell QDs with a radially graded composition that allow for considerable (nearly complete) suppression of Auger recombination [4, 5]. Using these specially engineered QDs, we have been able to realize optical gain with direct-current electrical pumping [4], which has been a long-standing goal in the field of colloidal nanostructures. Further, we have applied these dots to practically demonstrated the viability of a ‘zero-threshold optical gain’ concept using not neutral but negatively charged particles wherein the pre-existing electrons block either partially or completely ground-state absorption [5, 6]. Such charged QDs are optical-gain-ready without excitation, which allows us to reduce the lasing threshold to record-low values that are well below a fundamental single-exciton-per-dot limit [6]. Most recently, we have developed QD devices that operate as both an electroluminescent (EL) structure and a distributed feedback optically pumped laser [7]. By carefully engineering a refractive-index profile across the device stack, we have been able to demonstrate low-threshold lasing even with a very thin EL-active region, which comprises only three monolayers of the QDs. All of these recent developments demonstrate a considerable promise of colloidal QDs for implementing solution-processable optically and electrically pumped lasers operating across a wide range of wavelengths.


6:30 AM S.EL04.03.08
Exciton-Polaritons in a Tunable Microcavity with 2D-Peroxvskite Based on Free-Standing Thin Films Karolina Lempicka1, Magdalena Furman1, Marcin Muszynski1, Mateusz Krol3, Adam Wincukiewicz1, Rafał Mazur2, Maria Kaminska1, Wiktor Piecek2, Paweł W. Majewski2, Jacek Szczytko1 and Barbara Pietka1; 1University of Warsaw, Poland; 2Institute of Applied Physics, Military University of Technology, Poland; 3Faculty of Chemistry, University of Warsaw, Poland

Recently, interest in organic-inorganic perovskites has increased due to their application in photovoltaics, photonics and optoelectronics. They have also been used as a strong light emitters in the microcavities, due to the possibility of obtaining strong light-matter coupling regime, and the occurrence of coherent macroscopic effects, such as Bose-Einstein condensation of exciton-polaritons. Compared with multi quantum wells heterostructures produced by epitaxial growth of inorganic semiconductors, 2D perovskites displays stronger dielectric confinement in the inorganic layers, whereas excitons in such materials are characterized by a higher binding energy and exhibits strong nonlinearities. It indicates that the devices based on polaritons in 2D perovskite layers can work stable at room temperature. In our work we present a novel construction of a tunable planar dielectric cavity containing free standing layers of 2D-perovskite. Perovskites are deposited on thin films obtained from solution P2611:NMP.

The realization of such microcavity is innovative due to specific and unique technique of preparing emitter from thin films of layered perovskite-type semiconductor (Cs4H8(CH2)3NH3)2PbI4. The frame of free-standing films from polyimide solution were deposited by spin-coating technique on silica substrate. After heating, obtained structure served as matrix to deposit 2D-layered perovskite. Fabrication of ultrathin polyimide films allows to isolate lots of arbitrary materials from the substrate. Obtained thin film of perovskite were placed between dielectric mirrors controlled through piezo positioners, which allowed to shift photonic mode over the range of 100 meV. Such 2D perovskites can be considered as spontaneous realizations of a quantum well, in which organic material is sandwiched between organic cations acting as a potential barrier. The advantage of an emitter based 2D perovskites strongly coupled to the cavity field is its enhanced emission rate. Moreover, the regime of exciton-polaritons condensate compared to typical lasers is the ability to obtain laser action without the need to create population inversion. The additional advantage of our tuneable structure is the possibility to adjust the emission wavelength. A strong coupling regime between the perovskite exciton and the confined photon mode is evidenced at room temperature from angular-resolved reflectivity and photoluminescence experiments. The observed exciton-photon coupling strength is of Ω~110 meV.

The scientific meaning of this work is concentrated on the realization of new approach to obtain efficient, thin layer of organic-inorganic materials in a microcavity and developing a room-temperature devices for the observation of strong light-matter coupling and lasing phenomena.
Effects of Disorder on Two-Photon Absorption in Chalcogenide Glass

Nikita Dutta¹, Juliana M. Almeida², Cleber Mendonca² and Craig B. Arnold¹; ¹Princeton University, United States; ²University of São Paulo, Brazil

Chalcogenide glasses (ChGs) have long been of interest to the photonics community for their unique properties like high refractive index, photo-induced phase changes, and high optical nonlinearities. The latter are essential for all-optical systems but can be difficult to tailor due to a lack of understanding of their complex origins. Here we use open-aperture Z-scan to compare the two-photon absorption (2PA) spectra of arsenic (III) sulfide ChG samples with different levels of local bonding disorder. We find that the difference between the 2PA coefficients of the samples depends on the ratio of the photon energy to the band gap energy, giving rise to two distinct regions in the spectra. We then explain these observations using an effective mass model that links the 2PA coefficient of a glass to its level of structural disorder. Our results offer a generalized structure-property relation for semiconducting glasses that can be used to enhance optical nonlinearities for photonic applications.

Exploring I-II-IV-VI₄-Type Materials beyond Cu₂BaSnS₄ for Energy Applications

Garrett C. McKeown Wessler, Jon-Paul Sun, Tianlin Wang, Tong Zhu, Volker Blum and David B. Mitzi; Duke University, United States

Recently, Cu₂BaSnS₄ (CBTS) and its mixed-chalcogen analog Cu₂BaSn(S,Se)₄ (CBTSSe) have emerged as promising new semiconductors for photovoltaic (PV) and photoelectrochemical (PEC) applications. This potential is due to CBTS and CBTSSe having high absorption coefficients, abundant and non-toxic elemental makeups, and reduced tendency for antisite disorder between cations. Beyond CBTS and CBTSSe, various other compounds within the I₂-II-IV-VI₄ family have drawn attention for applications in thermoelectrics (e.g. Ag₂BaSnSe₄), nonlinear optics (Li₂BaSnSe₄), and solar energy conversion (Cu₂SrSnS₄). Therefore, it is useful to explore the larger I₂-II-IV-VI₄ space beyond CBTS for promising semiconductors. This talk will explore several new compounds within this space. Cu₂BaGeSe₄ (CBGSe) has been shown theoretically and experimentally to have favorable solar-energy conversion prospects and the material properties of this compound can be tuned through cationic alloying (namely Sn for Ge) similar to substituting Se for S in CBTSSe. Close examination of the crystal structures of CBGSe and the fully-Sn substituted Cu₂BaSnSe₄ reveals related structural moieties upon which the lattices are built. This has led to the design and discovery of three new semiconductors Ag₂SrSiS₄, Ag₂SrGeS₄, and Ag₂SrSnS₄. These compounds have band gaps within relevant ranges for single- and multi-junction PV as well as PEC applications. Future work will investigate further the properties of these compounds and hypothetical related semiconductors for solar-energy conversion applications.


Strong Coupling of Light and Matter Observed in a Tunable Microcavity with 2D-Peroxskites at Room Temperature

Magdalena Furman¹, Marcin Muszynski¹, Karolina Lempicka², Mateusz Krol¹, Adam Wincukiewicz¹, Rafal Mazur², Maria Kaminska¹, Wiktor Piecêk², Jacek Szczypko¹ and Barbara Pietka¹; ¹Faculty of Physics, University of Warsaw, Poland; ²Military University of Technology, Poland

In recent years hybrid-organic inorganic perovskites have become a very promising materials for photonic applications and optical devices. Special attention is given to the two-dimensional (2D) perovskites. In the two-dimensional crystalline form
these materials behave as a self-organized multiple quantum-well heterostructures. Compared to analogous semiconductor heterostructures 2D-layered perovskites displays stronger dielectric confinement in the inorganic layers, whereas excitonic resonances in such materials are characterized by a high binding energy and large oscillator strengths which leads to a great stability even at room temperatures, as well as exhibit strong non-linearities. We report the realization of a tunable planar dielectric microcavities containing a 2D-layered perovskite-type semiconductor, CH$_3$NH$_3$PbI$_3$, showing the strong-coupling regime at both room and liquid helium temperatures. 2D-layered perovskite structure was synthesized from the organic solution which was deposited by spin-coating on a dielectric mirror. The tunable cavity was constructed of two dielectric mirrors. The distance between the mirrors was controlled through piezo positioners. It allow, at the same time, for the realization of high fineness open micro-cavities (high Q) with tunable photonic mode and to avoid deterioration of perovskite crystals caused by the growth of the upper mirror. A strong coupling regime between the perovskite exciton and the confined photon mode is evidenced at room and liquid-helium temperatures from angular-resolved reflectivity and photoluminescence experiments. The observed exciton-photon coupling strength is of $W\sim 110$ meV and photonic mode can be tuned over the range of 100 meV. The scientific significance of this work is based on the realization of a room-temperature new material platform allowing for the observation of phenomena previously carried out at cryogenic temperatures.

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**SESSION S.LP03.05: Live Poster Session: Electronics and Photonics (S.EL04, S.EL06, S.EL09, S.EL12 and S.EL15)**

**Session Chair:** Hongping Zhao

**Tuesday Afternoon, December 1, 2020**

**5:15 PM - 7:15 PM**

**S.EL04.04.04**

**Strong Coupling of Light and Matter Observed in a Tunable Microcavity with 2D-Perovskites at Room Temperature**

*Magdalena Furman*, Magdalena Furman$^1$, Marcin Muszynski$^1$, Karolina Lempicka$^2$, Mateusz Krol$^1$, Adam Wincukiewicz$^1$, Rafał Mazur$^1$, Maria Kamińska$^1$, Wiktor Piecck$^2$, Jacek Szczytko$^1$ and Barbara Pietka$^1$; 1Faculty of Physics, University of Warsaw, Poland; 2Military University of Technology, Poland

In recent years hybrid organic-inorganic perovskites have become a very promising materials for photonic applications and optical devices. Special attention is given to the two-dimensional (2D) perovskites. In the two-dimensional crystalline form these materials behave as a self-organized multiple quantum-well heterostructures. Compared to analogous semiconductor heterostructures 2D-layered perovskites displays stronger dielectric confinement in the inorganic layers, whereas excitonic resonances in such materials are characterized by a high binding energy and large oscillator strengths which leads to a great stability even at room temperatures, as well as exhibit strong non-linearities. We report the realization of a tunable planar dielectric microcavities containing a 2D-layered perovskite-type semiconductor, CH$_3$NH$_3$PbI$_3$, showing the strong-coupling regime at both room and liquid helium temperatures. 2D-layered perovskite structure was synthesized from the organic solution which was deposited by spin-coating on a dielectric mirror. The tunable cavity was constructed of two dielectric mirrors. The distance between the mirrors was controlled through piezo positioners. It allow, at the same time, for the realization of high fineness open micro-cavities (high Q) with tunable photonic mode and to avoid deterioration of perovskite crystals caused by the growth of the upper mirror. A strong coupling regime between the perovskite exciton and the confined photon mode is evidenced at room and liquid-helium temperatures from angular-resolved reflectivity and photoluminescence experiments. The observed exciton-photon coupling strength is of $W\sim 110$ meV and photonic mode can be tuned over the range of 100 meV. The scientific significance of this work is based on the realization of a room-temperature new material platform allowing for the observation of phenomena previously carried out at cryogenic temperatures.

**S.EL06.11.01**

**(Si)GeSn Semiconductors for Integrated MIR Opto-Electronics**

*Simone Assali*$^1$, Alain Dijkstra$^2$, Anis Attiaoui$^1$, Mahmoud Atalla$^1$, Aashish Kumar$^1$, Samik Mukherjee$^1$ and Oussama Moutanabbir$^1$; 1Ecole Polytechnique de Montreal, Canada; 2Technische Universiteit Eindhoven, Netherlands

Sn-containing group IV semiconductors (Si)GeSn represent a versatile platform to implement a variety of Si-compatible photonic, optoelectronic, and photovoltaic devices. This class of semiconductors provides two degrees of freedom, strain and composition, to tailor the band structure and lattice parameter thus enabling a variety of heterostructures and low-dimensional...
systems on a Si substrate. In this presentation, we will discuss the recent progress in controlling and understanding the opto-electronic properties of metastable (Si)GeSn semiconductors. The relevance of these semiconductors for Si-compatible mid-infrared optoelectronics will be discussed from both materials and device perspectives. The growth of the (Si)GeSn multilayer heterostructure with Sn contents up to ~20at.% is currently performed using a chemical vapor deposition (CVD) reactor on a Silicon wafer. By reducing the growth temperature, the Sn content in the alloy is increased, while preserving a high degree of crystal purity for the heterostructure in the topmost Sn-rich layer.[2,3] Atom probe tomography (APT) measurements will be discussed to address the abruptness of the interfaces in the GeSn multi-layer heterostructure and the uniform composition in the 18 at.% GeSn layer grown on top.[2] Positron annihilation lifetime spectroscopy (PAS) and depth-profiled Doppler broadening measurements will be discussed to enrich the understanding of point defects in these semiconductors. Based on these analyses, we found that divacancies are the predominant type of point defects in GeSn with composition in the 6.5-13 at.% range.[4]

Photoluminescence (PL) emission studies will be presented and discussed. In a GeSn layer with a Sn content of 18 at.% the room temperature PL emission was found to be centered at 0.36 eV (i.e. 3.5 μm wavelength).[2] However, the compressive in-plane strain (-1.3 %) in these GeSn layers reduces the directness of the alloy, leading to a higher energy gap value. By releasing the strain down to -0.2% in the 18 at.% Sn layer using a fully-underetched micro-disk geometry, a 50 meV red-shift of the PL emission energy down to 0.31 eV (i.e. 4.0 μm wavelength) is obtained. Moreover, the strained and relaxed PL emission and absorption measurements ranging from 300K down to 4K will be shown.[5] These observations will be discussed in the light of photocurrent measurements and photodetectors operating at MIR wavelengths.


S.ELO6.11.02
Epitaxial Growth of Atomically-Sharp GeSn/Ge/GeSn Tensile Strained (≥1.5 %) Quantum Well on Si Simone Assali, Aashish Kumar, Jérôme Nicolas, Samik Mukherjee, Anis Attiaoui, Patrick Del Vecchio and Oussama Moutanabbir; Ecole Polytechnique de Montreal, Canada

In a full-group IV integrated semiconductor platform for tensile-strained Ge the direct-band gap can be obtained when the Ge is grown on a lattice-mismatched Ge0.87Sn0.13 substrate. With this approach the main challenge is to increase the incorporation of Sn in Ge above the ~1 at.% equilibrium composition. Major developments were recently achieved in the epitaxial growth of random GeSn alloys with composition above 16 at.%. A biaxial tensile strain in a Ge layer up to ~1.5% was demonstrated when growing on a Ge0.88Sn0.12 substrate.[2-3] However, despite the large amount of tensile strain in Ge, no information is available on the abruptness of the Ge-GeSn interface and on the possibility of the subsequent GeSn growth on top. Here, we discuss the epitaxial growth of a tensile-strained GeSn/Ge/GeSn (s-Ge) QW heterostructure with sharp interfaces and in-plane biaxial strain above 1.5 % grown on lattice-matched Ge0.88Sn0.12 substrate.[2-3] However, despite the large amount of tensile strain in Ge, no information is available on the abruptness of the Ge-GeSn interface and on the possibility of the subsequent GeSn growth on top. Here, we discuss the epitaxial growth of a tensile-strained GeSn/Ge/GeSn (s-Ge) QW heterostructure with sharp interfaces and in-plane biaxial strain above 1.5 % grown on lattice-matched Ge0.90Sn0.10.[4] The sharpness of the Ge/GeSn heterostructure interfaces will be addressed using TEM-EELS and atom probe tomography (APT) measurements. A coherent s-Ge epityaxy with a tunable layer thickness in the sub-20 nm range is achieved. The pseudomorphic nature of the s-Ge layer will be discussed by combining cross-sectional STEM measurements and XRD-RSM measurements performed at a synchrotron radiation facility.

The s-Ge QW platform is a new versatile platform to investigate light-hole (LH) spin-based qubits and 2D high hole mobility electronics. Under tensile in-plane biaxial strain, LH occupies the top of the valence band and the LH-HH splitting can exceed 100s meV. Moreover, when the tensile in-plane biaxial strain approaches 2 % only LH are confined in the QW, thus minimizing LH-HH interactions

S.ELO6.11.04
Homogeneous Cooling Dynamics in Laser Enhanced-Direct Print Additive Manufacturing of Circular Optical Fiber Interconnects Roger B. Tipton1, Dianhao Hou1, Thomas Weller2 and Venkat Bhethanabotla1; 1University of South Florida, United States; 2Oregon State University, United States

Integrated photonics have many compelling advantages for computing and communication applications, including high-speed
and extremely wide bandwidth operations. When fused deposition printing (FDM) a PMMA plastic optical fiber on a surface the bottom of the fiber is flat due to non-uniform cooling and the force of gravity on the fiber during solidification. Here we show that by embedding the fiber in a urethane optical cladding material, the fiber cools homogeneously and retains its round ship which is optimum for light transmission. This homogeneous cooling allows the use of a flexible, low cost additive and subtractive assembly method called laser enhanced-direct print additive manufacturing (LE-DPAM) to produce plastic optical fiber interconnects for photonic systems we have enabled higher transmission rates, lower power requirements, improve signal integrity and timing, less heat generation, and improve security of communication signals.

S_ELO6.11.05
Eldred Lee1,2, Zhehui Wang2, Michael James2, Eric Fossum1, Kaitlin Anagnost1 and Jifeng Liu1; 1Dartmouth College, United States; 2Los Alamos National Laboratory, United States

Since the discovery of X-rays, the continuous expansion of X-ray technology has transformed our society. However, the capability gap for hard X-ray detectors in the 10-100 keV range is problematic. Even though scintillator-based methods are widely used, they are limited by their decay time response, light yield, and spatial resolution, which may prevent them from being effective in the next generation of light source facilities, the generic platform of imaging sensor technology, and quantum image computing.

One class of X-ray detection primarily focuses structured photocathode designs that rely on external photoemission and collecting electrons converted from photons using an external electric field. This research only demonstrated up to 5% photon-to-electron conversion efficiency (electron generation) at 7.5keV incident photon energy, which is still commendable as this value has been roaming around the 1-1.5% area for external photoemission for a few decades [1, 2]. However, we believe that there is a potential to significantly increase this 5% electron generation even beyond 7.5keV incident photon energy via X-ray photon emission from high-Z materials.

Here, we present the Monte Carlo simulation results and analyses via Monte Carlo N-Particle Software (MCNP) that demonstrate a tremendous potential of revolutionizing the advancement of X-ray imaging with a two-layer design that consists of a high-Z semiconductor material on top of a Si layer. The high-Z layer is called photon attenuation layer (PAL), and the Si layer the electron detection layer (EDL). PAL-EDL latticed multi-pixel X-ray detector can also lead to low inter-pixel scattering with significant electron and photoelectron generation. The underlying principle of this design is photon energy down conversion, where the top high-Z PAL leads to an effective X-ray photon energy attenuation down to a few keV and allows Si to absorb them with a much higher absorption coefficient. This approach is distinct from scintillators in that the attenuated photons remain in X-ray spectral regime instead of visible regime. For instance, with PbTe, CdTe or CZT PAL and the Si EDL, we have observed >22% electron generation at 10keV X-ray photon energy and >2.8% electron generation at 40 keV incident photon energy with minimum inter-pixel scattering effects. The average electron energy lies between a few hundred eV and a couple keV.

At 30-40keV, we observed that adding a high-Z PAL on top of Si EDL can lead up to 13x higher electron generation than the typical Si direct-detection method seen in commercial products such as photomultipliers. Furthermore, because MCNP does not include the “avalanche gain” process in Si, the observed efficiencies may be underestimated. The MCNP results will be coupled with models that take the avalanche gain process into consideration (e.g. TCAD). In addition, this high-Z PAL-Si EDL configuration can be integrated to regular backside illumination (BSI) CMOS image sensor or quanta image sensor-based devices, paving the way towards a billion-pixel X-ray camera design for wide field-of-view applications in light sources [3].


S_ELO6.11.07
Study of Space Charge Limited Conduction Mechanism and Effect of In Situ Annealing on the Trap Distribution in...
GaAsSb Nanowires Mehul K. Parakh, Sean Johnson, Rabin Pokharel, Priyanka Ramaswamy, Surya Nalamati, Jia Li and Shanthi Iyer; North Carolina A&T State University, United States

This work presents the first observation of space charge limited conduction (SCLC) mechanism in intrinsic GaAsSb nanowires (NWs) grown by Ga-assisted molecular beam epitaxy and the effect of post-growth in-situ annealing in an ultra-high vacuum on trap concentration and its energy distribution in the NWs. Current-voltage (I-V) measurements on single NW (using conductive atomic force microscopy) and ensemble NWs (using two probe method) exhibited linear behavior at lower bias transitioning to a power-law behavior at higher bias, where the dominance of injected carriers over thermally generated charge carriers was observed. Temperature-dependent I-V analysis (I-V-T) on as-grown ensemble NW device in SCLC region yielded a trap concentration of $10^{16}$ cm$^{-3}$ distributed over a wide energy distribution in the bandgap as opposed to the reduced trap concentration of $7 \times 10^{14}$ cm$^{-3}$ in in-situ annealed NW ensemble confined to a narrower energy distribution of 0.12 eV located below the band edge, suggesting that annealing in ultra-high vacuum is an effective approach for the annihilation of the traps. The trap energy level in in-situ annealed NWs is speculated to be originating from Ga vacancy, and Ga$_{As}$ anti-site defect level during growth. Observations of increased PL intensity with reduced full-width half maxima at 4K and lower LO mode in corresponding Raman spectra for in-situ annealed NWs compared to as-grown NWs further attest to the annihilation of traps on in-situ annealing. Further, AFM current mapping also exhibited a considerable increase in several conducting NWs in in-situ compared to as-grown NWs. Hence, I-V-T analysis of the SCLC mechanism has been demonstrated to be a simple approach to obtain information on growth induced traps in the NWs.

S.E.L06.11.08

Photonic CMOS Field Effect Transistor Fabricated with an Ultra-Low Resistance Built-in Laser, Nonlinear Optical Films, and Multiple Photon Sensors for Very High Resolution, Low Dark Current CCD and CMOS Imaging Applications James Pan$^{1,2}$; 1Advanced Enterprise and License Company, United States; 2Northrop Grumman Electronic Systems, United States

Photon-generated carriers may substantially improve the output current, and reduce series resistance of CMOSFETs. Photonic devices, such as Multiple Quantum Well Lasers, Quantum Dots Lasers, Vertical Cavity Surface-Emitting Lasers (VCSEL), Light Emitting Diodes (LEDs) have been reported for various applications. With modulation doped laser junctions, and bandgap engineered tunneling mechanisms, ultra-low resistivity and laser diode forward voltage can be achieved. These laser diodes can be fabricated in the drain region of a MOSFET. A photon sensor, such as avalanche photo diode (APD), can be included in the channel / well regions. The laser, APD, and MOSFET are fabricated as one integral transistor. When the MOSFET is turned off, the laser is also turned off. The laser is switched on only when a gate voltage and a drain voltage are applied to the MOSFET. Light emitted from the laser is absorbed by the APD. Light current produced by the built-in photon sensors or APD reduces series resistance and may substantially improve the output current and switching speed.

Indium Tin Oxide (ITO) is commonly used in Charge Coupled Devices (CCD) receiving front illumination. The gate electrode material can be replaced with ITO, which is transparent for specific light spectrums. The new Photonic CMOS transistor, including nonlinear optical films and multiple photon sensors (for various light spectrums) can be used for CCD (with ITO) or CMOS image products (without ITO) for front or back illumination.

When external light is absorbed in the depleted channel and well regions (where the multiple photon sensors or APDs are located) of a Photonic MOSFET, light electrons are generated. These light electrons produce a drain current, which turns on the built-in laser in the drain region. The result is not only a light current, but also a new beam of a laser light are generated. Much higher resolution may be achieved with multiplexing of the light signals and specially designed ROIC (Read Out Integrated Circuit), which may also include Photonic CMOSFETs.

Nonlinear Optics have been reported for various products and applications. The nonlinear crystal films change the input light signal and produces an output light signal of a different frequency or color. In the new Photonic CMOS transistor, in addition to the built-in laser in the drain, there are multiple avalanche photo diodes in the channel / well regions, nonlinear crystal films below the APDs, and a reflector (metal or multiple indices total reflection film stack) in the bottom of the device. The APDs are designed to absorb lights from various bands of spectrums. When light passes through the Photonic CMOS Transistor, some APD films absorb lights of specific frequencies, and other APD films absorb the reflected light of different frequencies through the nonlinear crystal layers. This feature enhances the absorption rate and external quantum efficiency of the Photonic MOSFET, and may significantly improves the quality and resolution of the images from the CCD or CMOS.
imaging devices.

In this paper we will discuss Photonic MOSFET drain current (IDS) vs. spectral characteristics of nonlinear optical films. With the nonlinear optical films, it is possible to substantially improve the CMOS performance according to these data. Dark current density and resolution using a Photonic CMOS image sensor vs. traditional CMOS image sensor are analyzed. The advantages of a Photonic CMOS image sensor are lower dark current, and higher light sensitivity, due to the built-in lasing device and multiple photon sensing films, and nonlinear optical features.

Information regarding incident light spectrums vs. Ion / Ioff ratio for a Photonic CMOS image sensor will presented. Comparison of the speeds of CMOS image sensors with and without the built-in nonlinear optics films will be discussed.

We will also introduce various types of crystals of nonlinear optics suitable for the Photonic CMOS image sensing applications.

S.EL09.07.01
Comparison between Silicon and Silicon Nitride Platform for Nonvolatile Phase Change Photonic In-Memory Computing

Xuan Li1, Nathan Youngblood2, Zengguang Cheng1 and Harish Bhaskaran1; 1University of Oxford, United Kingdom; 2University of Pittsburgh, United States

Demands for applying silicon photonics to high-performance computing systems have grown significantly in recent years due to the breakdown of Dennard scaling and information transfer bottlenecks in the conventional von Neumann architecture. Data processing on photonic platforms is a promising approach because of the potential advantages over electrical approaches where large bandwidth, high efficiency, ultrafast modulation speed, and low crosstalk are crucial. Critical photonic components, such as lasers, modulators, switches, filters, multiplexers, photodetectors, and memory cells, have been developed on different material platforms, such as silicon nitride (SiN), GeSi, III-V semiconductors, and others, with silicon on insulator (SOI) being the dominant platform. Owing to its compatibility with mature CMOS processes and integration with electrical devices, fabless and large scale silicon photonic integrated circuits (PICs) are available and thus offer a promising route to future commercialization.

Recently fully integrated photonic memory devices have been demonstrated on silicon nitride and silicon. This approach not only enables photonic data storage on-chip, but also shows multilevel storage, improved SNR, and reduced switching energy over available optical storage technology. Previous work on silicon nitride waveguides demonstrated both multilevel storage (> 32 levels) and computation in a fully optical framework. This was despite the fact that silicon nitride does not benefit from a high refractive index contrast (~2/1.5 in Si3N4/SiO2 vs 3.5/1.5 in Si/SiO2) or the ability to integrate active photonics (such as modulators and photodetectors) directly in the waveguide. Silicon-On-Insulator (SOI), on the other hand, has both these advantages, leading to smaller footprint devices and easy integration with high-speed, CMOS-based electronics. In spite of rapid advances of demonstrations in this field on both silicon and silicon nitride platforms, a clear pathway towards choosing between the two has been lacking.

Here, we systematically evaluate and compare the computation performance of phase change photonics on a silicon platform and a silicon nitride platform. Our experimental results show that whilst Silicon platforms are superior to Silicon Nitride in terms of potential for integration, modulation speed, and device footprint, it requires trade-offs in terms of energy efficiency. We then successfully demonstrate single-pulse modulation using phase-change optical memory (PCOM) on silicon photonic waveguides and demonstrate efficient programming, memory retention, and readout of > 4bits of data per cell. This decreased the device footprint compared with silicon nitride photonics and reduced both the energy and time required for reaching arbitrary memory levels. We have characterized the reliability of this approach and outlined a comparison with other state-of-the-art programming methods. The use of silicon demonstrates a major step toward making phase-change photonic memory a viable and integrable technology. Our results have potential applications like deep learning based on vector-matrix multiplication and neuromorphic computing. Our approach paves the way for the in-memory computing on the silicon photonic platform.

S.EL09.07.03
TEM and EDX Analyses of Thermally Improved Phase-Change Memory by Optimized Encapsulation Layer

Gauthier Lefèvre1, Anna-Lisa Serra2, Olga Cueto3, Nicolo Castellani2, Guillaume Bourgeois2, Nicolas Bernier2, Marie Claire Cyrille2, Mathieu Bernard2, Virginie Beugin2, Christophe Vallée1, Sylvain David1, Christelle Charpin2, Etienne Nowak2 and Gabriele Navarro2; 1LTM-CNRS, France; 2CEA-LETI, France
Phase-Change Memory (PCM) is a promising candidate for next generation of non-volatile memory [1]. PCM operations rely on the reversible phase transition between the amorphous and the crystalline phase, which occurs upon current-induced joule heating. Therefore, the reliability of the programming operation depends also on the thermal efficiency of the device [2]. Heat retention is thus essential in PCM and in complete contradiction with usual conception of electronic devices where thermal dissipation is a key point.

In this context, optimized thermal encapsulation in Ge-rich Ge-Sb-Te based PCM devices enables programming current reduction and improved data retention [3]. Indeed, an SiC encapsulation layer provides a more uniform heating of the active volume of the PCM cell, with respect to a standard SiN layer. Thanks to TEM and EDX analyses performed on state-of-the-art PCM heater-based devices, we demonstrate the higher uniformity of the heating process in the PCM cell during the programming operation achieved by optimized SiC encapsulation. Moreover, nano-diffraction patterns analysis highlights the crystalline morphology of the programmed active volume and of the surrounding material. Finally, we show the agreement between experimental data and TCAD simulations.


S.E.L09.07.04

Structural Transitions and Switching Effect in Nanoscaled Ge2Sb2Te5 Films Modified by Bismuth Impurity

Nurlan Almassov¹, Andrei Sazonov², Sanzhar Dyussembayev³, Oleg Prikhodko⁴, Nazim Guseinov⁴, Zhandos Tolepov⁴ and Sergei Kozhukhin⁵; ¹Nazarbayev University, Kazakhstan; ²University of Waterloo, Canada; ³University of Al-Farabi Kazakhstan National University, Kazakhstan; ⁴Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Russian Federation

The design of non-volatile memory cells based on phase change materials (PCM) is the subject of many studies. And one of the most promising materials are the films of Ge₂Sb₂Te₅ chalcogenide glassy semiconductor (CGS). The operation of memory cell is based on a reversible glass-crystal phase transition, which occurs when a current pulse passes through the film's nano-volume. The embedding of metal impurity in the films can improve the property of memory cells. However, the features of phase transition in the metal-modified Ge₂Sb₂Te₅ films are poorly understood. This work presents the results of the study of the structure observed in nanoscale films of Ge₂Sb₂Te₅ modified by Bi (Ge₂Sb₂Te₅<Bi>). By the method of HR-TEM imaging it was found that the structure of Ge₂Sb₂Te₅<Bi> films presents the amorphous matrix with isolated crystalline nanoregions (nanoclusters) of metallic bismuth with average size ~ 8 nm. Local atomic structure of the films was studied by Raman spectroscopy. It was found that under the laser irradiation there is the structure transition of nanoscale Ge₂Sb₂Te₅ films from amorphous into polycrystalline hexagonal stable state through metastable polycrystalline cubic phase. In contrast, in the Ge₂Sb₂Te₅<Bi> films the transition from amorphous to polycrystalline hexagonal stable state under the laser irradiation occurs without intermediate metastable cubic phase.

S.E.L09.07.05

Analysis of the Limitation of the JMAK Equation for Crystallization of GST Based Phase Change Materials (PCMs)

Kazimierz J. Plucinski; Military University of Technology, Poland

An investigation into the relationship between crystal fraction and electrical conductivity for GST materials was performed. Transition from amorphous to conduction state for homogeneous nucleation of conductive crystallites in the resistive amorphous layer and limitation of the JMAK equation to modeling this transition is analyzed. In particular, the analysis relate to the validity of the model in terms of time-temperature description of crystallization and dependencies between minimum amount of crystal during nucleation and percolative threshold

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S.E.L12.05.01

Multi-level Tactile Ferroelectric Field Effect Transistor Sensing Memory

Kyuho Lee and Cheolmin Park; Yonsei University, Korea (the Republic of)
A tactile memory, which can sense and memorize the external stimuli, has been reported up to date with great potential in emerging wearable electronics. To realize bi-functional systems for sensing and memorizing, two device platforms integrated with tactile sensor and memory have drawbacks from physically bulky systems as well as increase of circuit resistance from wire connection, giving rise to low sensing sensitivity. In particular, a binary memory with bi-level state of ON/OFF has limitation in storing multi-level sensing information that requires multiple memory array. A multi-level memory-based single device platform without the integration is, therefore, on demand.

Herein, we demonstrate a non-volatile multi-level tactile memory based on a single ferroelectric-gate field-effect transistor (Fe-FET) allowing for intelligent electronic skins (e-skins), which can sense, memorize, and then retrieve the tactile information. Pressure-sensitive top-gate shape formation can precisely sense and memorize the external pressure stimuli by making an underlying ferroelectric film polarized according to the size of the contact area between top-gate and ferroelectric film, giving rise to variation of gate voltage supply. Our tactile 1-transistor memory exhibits high sensitivity of >90 kPa⁻¹ at making an underlying ferroelectric film polarized according to the size of the contact area between top-gate and ferroelectric crystals. For lead-based relaxor-PbTiO₃ crystals, nanosized polar regions are believed to be the origin of giant piezoelectricity. For lead-free systems such as [111]-poled tetragonal ferroelectric BaTiO₃ crystals, enhanced piezoelectricity has been reported by reducing the domain size from hundreds to several microns. These examples lead to a long-standing belief that the smaller the domain size, the higher the piezoelectricity. Our recent study reveals an alternative route to enhancing piezoelectricity by increasing the size of domains through AC poling in relaxor-PbTiO₃. In this poster, we will discuss the general domain size effect on piezoelectricity in prototypical non-lead perovskites in tetragonal, orthorhombic, and rhombohedral ferroelectric phases, such as BaTiO₃, K₀.₅Na₀.₅NbO₃, and BiFeO₃, by examining the effective piezoelectric

**S.E.L12.05.05**

**Effect of Sintering Temperature/Particle Size on Structural, Magnetic and Transport Properties of Polycrystalline Nd₀.₅Ca₀.₅MnO₃ Manganites**

Dhararendra Raghav¹, Harikrishna Singh₂ and Ghanshyam D. Varma¹; ¹Indian Institute of Technology Roorkee, India; ²C.S.I.R. N.P.L., India

Nanosized materials, such as nanoparticles, nanowires, nanotubes, and nanocomposites are currently the focus of intense investigations due both to the physics they involve and to their potential for revolutionary technological applications. The applications are expected to be in a wide variety of diverse areas, such as logic circuits, magneto-electronic devices, magnetic data storage, medicine, and biotechnology. The phenomena and properties behind these applications are unique to nanodimensions, such as quantum confinement effects and enhanced surface to volume ratio. So, we have investigated the effect of particle size/sintering temperature on structural, magnetic and transport properties in Nd₀.₅Ca₀.₅MnO₃ system. Different size materials have been synthesized using Sol-gel method and sintered at 900 , 1100 and 1300 degree Centigrade to get the samples of different particle sizes. Phase pureness of the samples has been confirmed by Rietveld refinement of the powder X-Ray diffraction (XRD) data, which authenticates orthorhombic structure with Pnma space group. All three lattice constants (a, b and c), bond lengths and bond angles decrease with increasing particle size. The magnetization measurements (H@500 Oe) as a function of temperature exhibit paramagnetic (PM) to ferromagnetic (FM) transition and also brings out that (i) the divergence between the zero field cooled (ZFC) and field cooled cooling (FCC) magnetization decreases with increasing particle size, (ii) all samples show charge ordering at 250 K, (iii) the sharp drop of ZFC magnetization for all samples. At low temperatures a glassy behaviour is visible at higher particle size. The isothermal magnetization loops confirm the increase in the FM component at higher particle size at low temperature (20 K). The temperature dependent resistivity of all samples have been measured without magnetic field and resistivity measurements show no insulator to metal transition at lower sintering temperature but at higher sintering temperature the metal to insulator transition has been found. The data of resistivity have been fitted by using variable range hopping model (VRH). Characteristic temperature (Tᵥ), localization length (1/α) and average hopping distance (R) have been calculated by using this model. X-ray photoemission spectra of Mn2p and Mn2s core-level confirm dual valence state of Mn (Mn³⁺ and Mn⁵⁺), which is responsible for the magnetic behaviour of NCMO system. The correlation between the transport and observed magnetic properties of sintered NCMO samples will be described and discussed in paper. 

**S.E.L12.05.14**

**Domain Size Effects on Piezoelectricity in Lead-Free Ferroelectric Single Crystals**

Bo Wang¹, J.J. Wang¹, Fei Li²,¹ and Long-Qing Chen¹; ¹Pennsylvania State University, University Park, United States; ²Xi’an Jiaotong University, China

Domain size is known to play a critical role in electromechanical properties of domain-engineered ferroelectric single crystals. For lead-based relaxor-PbTiO₃ crystals, nanosized polar regions are believed to be the origin of giant piezoelectricity. For lead-free systems such as [111]-poled tetragonal ferroelectric BaTiO₃ crystals, enhanced piezoelectricity has been reported by reducing the domain size from hundreds to several microns. These examples lead to a long-standing belief that the smaller the domain size, the higher the piezoelectricity. Our recent study reveals an alternative route to improve piezoelectricity by increasing the size of domains through AC poling in relaxor-PbTiO₃. In this poster, we will discuss the general domain size effect on piezoelectricity in prototypical non-lead perovskites in tetragonal, orthorhombic, and rhombohedral ferroelectric phases, such as BaTiO₃, K₀.₅Na₀.₅NbO₃, and BiFeO₃, by examining the effective piezoelectric
coefficients of engineered domain structures using a combination of thermodynamic analysis and phase-field simulations. We find that the domain size effect on piezoelectricity depends on the symmetry of the ferroelectric phase. The size effect becomes significant when the domain is reduced to a critical size (~ sub-100 nm) which depends on the proximity to a ferroelectric-ferroelectric phase transition and on the width of domain walls. Moreover, the domain size effect has a strong anisotropy, giving rise to opposite trends for different piezoelectric tensor components as well as varying along different probing directions. By separating the contributions from domains and domain walls, we reveal that the size effect is majorly originated from the modification of thermodynamic states of domains due to the presence of domain walls. We also reveal that the domain size effect on piezoelectricity can be understood as a competition between the domain size effects on the dielectric permittivity and on the polarization rotation. The former is related to the flattening of free energy landscapes, while the latter is due to the built-in fields between domain walls. Besides, we predict a convenient way of controlling the domain size by poling via an alternating electric field. This work offers a thermodynamic-based understanding of the domain size effect and brings new insights into the fundamental knowledge of the processing-microstructure-property relationship in piezoelectric single crystals.

S.EL15.08.01
PEALD and Band Alignment of AlF3 on Polycrystalline Diamond
Robert D. Mecham, Daniel C. Messina, Jesse Brown and Robert J. Nemanich; Arizona State University, United States

Metal-fluoride thin films have previously been investigated as gate insulators in MISFETs (CaF2/Au/Diamond) and this work expands upon that investigation. AlF3 is an ultra-wide-bandgap (10.8 eV) material with a low dielectric constant (2.2). These properties indicate that AlF3 may be a suitable insulator for high power high frequency devices. AlF3 films have been deposited on hydrogen terminated boron-doped polycrystalline diamond in a plasma enhanced atomic layer deposition (PEALD) process. PEALD is an emerging energy enhanced ALD technique that utilizes plasma radicals to drive surface reactions rather than thermal energy. PEALD allows for lower impurities, increased growth rates, improved stoichiometry, and lower deposition temperatures. The reactants used were trimethylaluminum, pyridine-hydrogen fluoride, and a hydrogen plasma. In-situ X-ray photoelectron spectroscopy was used to determine the band alignment of AlF3 films on polycrystalline diamond. The valence band maxima are measured at 9.15 eV and 0.05 eV for AlF3 and diamond, respectively. A type II staggered gap is formed with a conduction band offset of 3.77 eV and a valence band offset of 9.1 eV. The results indicate that AlF3 should be appropriate as a dielectric on p-type diamond.

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S.EL15.08.03
Investigations of Ultrawide Bandgap (AlIn)xO3 Alloy for AlInN / GaN Devices
Xiaoli Liu and Chee-Keong Tan; Clarkson University, United States

Recent progress in wide band gap semiconductor based power electronics technology sparked humongous interest in the development of the semiconductor materials. With the aim of further reducing the cost, size, compactness while improving energy efficiency and performance of electrical systems, semiconductor materials of larger energy bandgap have been highly sought after. Recent studies show that ternary AlInN material grown lattice-matched with GaN provides access of energy bandgap of ~4.5 eV, allowing theoretically higher Baliga figure of merit than GaN-based devices and similar to that of β-Ga2O3 based devices. However, it also poses some difficulty in controlling the field effect since insulating material with larger energy bandgap is required to create conducting channel and block electron leakage from devices. Finding an insulator material with energy bandgap larger than 4.5eV that can be grown on AlInN material is thus important towards realizing the AlInN / GaN field effect transistor based devices. Most recently, AlInO material has been proposed as a viable material that can serve as the insulator through thermal oxidation of the AlInN material. While the AlInO material is expected to exhibit chemical formula of (Al1-xIn)xO3, it is unclear if the AlInO material is thermodynamically stable and the information of AlInO material is extremely limited to date. Understanding the material properties of AlInO material from the viewpoint of structural and electronic properties is therefore critical for AlInN / GaN devices.

In this work, (Al1-xIn)xO3 alloys covering complete In compositions are investigated using Density Functional Theory (DFT) calculations. Two different phases of AlInO alloys will be investigated: corundum and hexagonal. The effect of In atoms on the electronic properties of AlInO alloys is investigated. For structural properties, lattice constants and equilibrium volume of (Al1-xIn)xO3 alloys are analyzed. Moreover, band alignment between AlInO and AlInN is studied, exploring possible heterojunction lineups in various orientations.

For DFT calculation, supercell approach is implemented in which a 60-atom AlInO crystal is constructed. The In composition is varied through the number of Al atoms being replaced in the crystal structure. DFT calculations were carried out using commercial package MedeA-VASP software. Band structure calculations were performed by using projector augmented wave (PAW) method, with the use of semilocal generalized gradient approximation (GGA-PBE) functional to
Vertical diamond P-I-N diodes were fabricated with an n+-i-p++ structure consisting of a heavily phosphorus-doped n-type capability that can protect sensitive RF front-end components from high power incident signals. The wide bandgap of diamond coupled with its higher thermal conductivity give it a superior RF power handling resistance much smaller than the 50 Ω characteristic impedance and the majority of the input power is reflected away from the receiver input. P-I-N diodes made of Si and GaAs used in today’s conventional RP systems have limitations at high-power levels in the material. According to the X-ray diffraction analysis the Ti clusters in a-Ga2O3 matrix helps in reducing the change was confirmed by SEM studies producing octahedral shape nanocrystallites with sizes from ~5 to 50 nm. 

In this work an experimental study to characterize titanium (Ti) doped amorphous-Gallium Oxide (Ga2O3) nano-films (a-Ga2O3:Ti) produced by magnetron sputtering at 300K is reported. The nano-films were deposited by the co-sputtering process using Ti and Gallium oxide (Ga2O3) targets with a two magnetron system; the films were deposited over glass substrates covered with a 20 nm of non-doped buffer Ga2O3 layer grown by the same process. The Ga2O3 concentration was changed by varying the RF-power of the Ga2O3 magnetron at 75 or 150 W, while the DC-power for the Ti target was set at 80W. Due to the non-equilibrium character of the sputtering technique the grown films can be considered as a distribution of Ti clusters embedded into an a-Ga2O3 matrix when the growth process is done at low temperatures, therefore post-grown annealing processes can be used to adjust the film properties fixing appropriately the annealing conditions, temperature or atmosphere composition. The annealing temperatures were 400, 450, 500 and 550 ºC by periods of 10 min, in a high purity N2 atmosphere. When the samples were annealed at low temperatures the resistivity of the films were varied from 5.74x10^4 to 134.63 Ω-cm, electron concentration from 10^22 to 10^19 cm^-3 and mobility of 0.475 to 6.689 cm²/V-s. by annealing the samples at 550ºC electrical insulating nano-films were produced by the complete oxidation of the Ti clusters. The relatively low mobility of the doped nano-films suggests the Ti dopant produces carrier dispersion suggesting the presence of Ti deep levels in the material. According to the X-ray diffraction analysis the Ti clusters in a-Ga2O3 matrix helps in reducing the required temperature to transform amorphous films to β-Ga2O3 at ~400 ºC. The required temperature to produce the phase change was confirmed by SEM studies producing octahedral shape nanocrystallites with sizes from ~5 to 50 nm.

**S.EL15.08.09**

Morphological and Electrical Study of Ga2O3-Ti Nanofilms Processed by Co-Sputtering Lucia Ivonne Juárez Amador1, Karen A. Neri2, Laura Hill-Pastor3, Miguel Galvan Arellano1, Mario Zambrano-Serrano1, Jose Alberto Andracca2, Gabriel Romero-Paredes1 and Ramón Peña-Sierra1; 1CINVESTAV-IPN, Mexico; 2Instituto Politécnico Nacional, Mexico; 3Centro de Investigación en Dispositivos Semiconductores, BUAP, Mexico

In this work an experimental study to characterize titanium (Ti) doped amorphous-Gallium Oxide (Ga2O3) nano-films (a-Ga2O3:Ti) produced by magnetron sputtering at 300K is reported. The nano-films were deposited by the co-sputtering process using Ti and Gallium oxide (Ga2O3) targets with a two magnetron system; the films were deposited over glass substrates covered with a 20 nm of non-doped buffer Ga2O3 layer grown by the same process. The Ga2O3 concentration was changed by varying the RF-power of the Ga2O3 magnetron at 75 or 150 W, while the DC-power for the Ti target was set at 80W. Due to the non-equilibrium character of the sputtering technique the grown films can be considered as a distribution of Ti clusters embedded into an a-Ga2O3 matrix when the growth process is done at low temperatures, therefore post-grown annealing processes can be used to adjust the film properties fixing appropriately the annealing conditions, temperature or atmosphere composition. The annealing temperatures were 400, 450, 500 and 550 ºC by periods of 10 min, in a high purity N2 atmosphere. When the samples were annealed at low temperatures the resistivity of the films were varied from 5.74x10^4 to 134.63 Ω-cm, electron concentration from 10^22 to 10^19 cm^-3 and mobility of 0.475 to 6.689 cm²/V-s. by annealing the samples at 550ºC electrical insulating nano-films were produced by the complete oxidation of the Ti clusters. The relatively low mobility of the doped nano-films suggests the Ti dopant produces carrier dispersion suggesting the presence of Ti deep levels in the material. According to the X-ray diffraction analysis the Ti clusters in a-Ga2O3 matrix helps in reducing the required temperature to transform amorphous films to β-Ga2O3 at ~400 ºC. The required temperature to produce the phase change was confirmed by SEM studies producing octahedral shape nanocrystallites with sizes from ~5 to 50 nm.

**S.EL15.08.10**

Diamond P-I-N Diodes for Receiver Protectors Mohammad Faizan Ahmad1, Harshad Sureti1, Franz A. Koeck1, Robert J. Nemani1, Stephen M. Goodnick1, Trevor J. Thornton1 and Josephine Chang2; 1Arizona State University, United States; 2Northrop Grumman Mission Systems, United States

The intrinsic properties of diamond are attractive for use in high power receiver protector (RP) systems such as those required at the input of radar systems. At low input power, the RP device presents a low capacitance and high resistance so that it adds negligible insertion loss to the desired signals. However, at high input power levels the RP turns on with a resistance much smaller than the 50 Ω characteristic impedance and the majority of the input power is reflected away from the receiver input. P-I-N diodes made of Si and GaAs used in today’s conventional RP systems have limitations at high-power. The wide bandgap of diamond coupled with its higher thermal conductivity give it a superior RF power handling capability that can protect sensitive RF front-end components from high power incident signals. Vertical diamond P-I-N diodes were fabricated with an n⁺-i-p⁻ structure consisting of: a heavily phosphorus-doped n-type diamond layer with a doping concentration >1x10¹⁹ cm⁻³ and a thickness of approximately 300 nm; an intrinsic diamond layer of thickness approximately 0.5 μm; and a heavily boron-doped diamond <111> substrate with doping concentration of 5x10²⁰ cm⁻³ and a thickness of 300 μm. The sample was patterned by photolithography and Ti/Pt/Au contacts were deposited on both top and bottom surfaces of the diode. The PIN test structures consist of a total of 144 diodes with diameters of 50 μm, 100 μm, 200 μm, and 400 μm. A SiO₂ hard mask of thickness 2 μm was deposited on the diamond surface prior to the isolation etch step. Reactive ion etching was used to define electrically isolated mesa regions etched to a depth of ~600 nm. The SiO₂ etching was carried out using fluorine RIE with 25 sccm of CHF₃ and Ar at a chamber pressure of 30 mTorr at 200
The electrical characteristics of the P-I-N diodes were measured using DC and RF probe stations. The diodes show significant forward current starting at around 10 V. The lowest specific on-resistivity at high forward bias was measured using the DC probe station and found to be 4.5x10^{-4} \, \text{\Omega} \cdot \text{cm}^2. The capacitance of the diodes at zero bias was extracted from small-signal S-parameter measurements in the frequency range 0.1 – 10 GHz and found to be 7.6 nF/cm². Taken together these values suggest a figure of merit, \( \text{FOM} = \frac{R_{\text{on}}}{C_{\text{eff}}} = 6.81 \, \text{ps} \), corresponding to a frequency of 23.37 GHz.

A 200 μm diameter PIN diode was attached to a coplanar waveguide (CPW) for RF small-signal measurements as follows. The p-type substrate of the diode was soldered onto the ground plane of the ground-signal-ground strip-line of the CPW while the n-type top contact was wire bonded to the signal line. The diode was DC biased with a bias-T connected to the input of the CPW. S-parameters were measured at no bias and 12 V of forward bias, over a frequency range of 0.5 to 5 GHz at 10 dBm power. \( S_{11} \) and \( S_{21} \) were found to be -15 dB and -0.4 dB respectively with no bias at 500 MHz, confirming negligible insertion loss with no forward bias applied. At 12 V of forward bias, \( S_{11} \) and \( S_{21} \) were found to be -2.5 dB and -13 dB respectively at the same frequency, confirming that up to 95% of the input power is reflected by the forward biased PIN diode. With further optimization of the diode growth and fabrication it will be possible to reduce the on-resistance and the associated \( R_{\text{on}} \cdot C_{\text{eff}} \) figure of merit with the goal of achieving PIN diodes that provide > 30 dB isolation for high power receiver protection applications.

This research is supported by a contract from Northrop Grumman Corporation. One of us (Mohammad Faizan Ahmad) acknowledges support from NSF contract ECCS-1542160.

S.EL.15.08.11
Defect Structure and Distribution of Electrons in Ga2O3 and IGZO Stack Yong-Seok Lee, Min-Ju Choi, Yonghee Lee, Ho Won Jang and Young-Woon Kim; Seoul National University, Korea (the Republic of)

Epitaxial Ga2O3 film was grown on the Al2O3 substrate using magnetron sputtering. Because of the lattice mismatch between Ga2O3 and substrate, epitaxial films reveal mosaic domain structure with high number density of interfacial dislocations. Interfacial Domain size has an average diameter of ~ 40 nm. On the top of the Ga2O3, without additional treatment, semiconducting indium gallium zinc oxide (IGZO) was stacked to obtain the oxide/semiconductor structure. An external electron beam control system for SEM and TEM was designed and built in house to acquire position specific physical properties – direct measurement for the electron density and luminescence characteristics from the optical energy states. External control system was successfully adopted to Electron Beam-Induced Current Imaging (EBIC) to visualize 2-dimensional distribution of electrons at the interface, which can be indirect indication of preferred electron conduction paths. Cathodoluminescence in TEM was also adopted to identify the 2-dimensional distribution of optical bandgap. Defects, originated from the interface, works as dead centers of luminescence, not wavelengths shifters as can be typically seen from the partial dislocation in GaN/InGaN lighting emitting diode structure.

S.EL.15.08.13
Exploring the Role of Defects Produced by Ion Irradiation on Near and Sub-Surface GaN Thomas W. Pfeifer¹, Ethan A. Scott²,¹, David Olson¹, Patrick E. Hopkins¹, Khalid Hattar² and Stuart Van Deusen²; ¹University of Virginia, United States; ²Sandia National Laboratories, United States

The wide band gap and high thermal conductivity of gallium nitride semiconductors makes them ideal for high power and high frequency applications. These properties however are dependent upon the order and impurity concentration of the crystalline structure. In this study, we use Time Domain Thermoreflectance (TDTR) to investigate the role of defects on the thermal performance of GaN semiconductors. He atoms were implanted into GaN, with dosing concentrations varying between 1x10^{13} and 1x10^{19} cm^{-2} and implantation energies at both 400eV and 400keV. TDTR is a pump-probe technique that measures the change in thermoreflectance on the surface of a sample as a function of pump-probe delay time from picoseconds to nanoseconds; this change in thermoreflectance is related to both the temporal temperature decay from impulse heating driven by the sub-picosecond pump pulse and the frequency-dependent temperature rise induced from the modulated pump pulse train. Thus, TDTR is well suited to measure both the thermal conductance across near surface interfaces along with thermal property changes of buried damaged regions from the ion irradiation. Our TDTR apparatus includes an 800nm 80MHz femtosecond pulsed laser, the pump is modulated at 8.4MHz, and all samples included an aluminum transducer deposited on the surface. Ions implanted at low powers localize near the surface of the GaN, and their effect can be observed when measuring the Aluminum-GaN thermal boundary conductance. Ions implanted at higher powers penetrate to a depth greatly exceeded the thermal penetration depth of the TDTR measurement technique. Here, the role of defects due to the passage of the ions is observed and measured. We believe the results and trends observed in this study are not limited to GaN, and a deeper understanding of the effects of doping on thermal properties could assist in cooling of doped semiconductor
Crystal Defects in GaN and Diamond Transistor Structures
Aris Christou; University of Maryland, United States

The state-of-the-art power switching devices made from SiC and GaN semiconductors contain a high density of crystal defects. Most of these defects are present in starting wafers and some are generated during device processing. There is little conclusive evidence so far on the exact role that the crystal defects play on device performance, manufacturing yield, and more importantly, long-term field-reliability especially when devices are operating under extreme stressful environments. This paper provides a review of the current state-of-the-art of Diamond and GaN power semiconductor material technology, and the potential impact crystal defects may have on power switching electronics. UWBG Nitride materials suffer from both extended and point defects, each of which will challenge the material’s application in both vertical and lateral power devices. The extended defects include vertical threading dislocations of both edge and screw type. The latter defects have been shown to be correlated to leakage in vertical two terminal device structures while the influence of the former is still undetermined and remains a critical research issue. Channel surfaces in vertical three terminal devices will also degrade due to vertical threading dislocations. These extended defects occur in all epitaxial layers grown on c-plane substrates (the predominant and largest area substrate type) and are the result of the lack of a high quality substrate bulk material as well as substrate surface. Diamond faces the challenge of achieving n type doping. We report our results on delta doped channels in diamond CVD epitaxial layers and the achievement of delta doped field effect transistors. Finally, our recent experiments of proton and gamma radiation effects show that diamond transistors transfer characteristics do degrade as a result of radiation induced defects.

Investigating F-Doped MZO as the Emitter in CdTe Solar Cells
Manoj K. Jamarkattel, Adam Phillips, Jacob Gibbs, Kamala Khanal Subedi, Fadhil K. Alfaadhili, Randy J. Ellingson and Michael Heben; University of Toledo, United States

Recently, incorporation of Mg$_{x}$Zn$_{1-x}$O (MZO) as the emitter in CdSeTe solar cells has resulted in improved open circuit voltage and efficiency. However, the MZO layer appears to be sensitive to subsequent device processing, possibly due to unoptimized conduction band alignment or insufficient doping in the MZO layer. Unfortunately, the carrier concentration in the MZO is dominated by oxygen vacancies, which is difficult to control. Here we investigate how doping MZO films with F affect the CdSeTe properties. We deposit the MZO:F in two ways. The first method is by depositing an MZO/MgF stack followed by high temperature anneal, while the second method will be cosputtering ZnO, MgO, and MgF. Our preliminary results on the bilayer stack show that, peak PL intensity and bulk carrier lifetime of MZO:F/CdTe device increased after annealing. There is evidence of intermixing of the MZO and MgF after annealing, suggesting that the Fermi level of the MZO is closer to the conduction band at the film interface. If this is the case, band bending in the CdSeTe layer will be enhanced, leading to reduced interface recombination. Further investigation into the cause of these results will be presented, as will the results obtained when a cosputtered MZO:F emitter is used. The findings of this study may lead to higher efficient CdTe devices.
10:15 AM PANEL DISCUSSION

10:40 AM REBBECCA SAIVE, PANELIST

10:40 AM YUAN YANG, PANELIST

10:40 AM PO-CHUN HSU, PANELIST

10:40 AM S.EL05.01.08
Broadband Thermal Beaming Using Multiple Epsilon Near Zero Materials Jin Xu and Aaswath P. Raman; University of California, Los Angeles, United States

Controlling the propagation, absorption and emission of light has been a topic of fundamental interest in contemporary photonics research. In the context of controlling the emission of light from thermal sources, a central challenge is that of angular selectivity. Over the past two decades, a range of photonic strategies, including using surface phonon-polariton modes, have enabled anomalous angular ‘beaming’ of thermal radiation, albeit only at narrow ranges of wavelengths. However, thermal radiation is inherently a broadband phenomenon. We currently lack the ability to constrain broad-spectrum thermal emission over a narrow range of angles of incidence, but consistently over a broad range of wavelengths. This form of broadband thermal beaming would be a fundamentally enabling capability for a range of applications, including infrared imaging and camouflage, thermophotovoltaics and radiative cooling.

Here, we employ multiple epsilon-near-zero (ENZ) materials in a layered configuration to realize a broadband angularly selective thermal emitter. ENZ materials can fulfill high absorption and emission of incident light at wavelengths where the epsilon is near zero. Aluminum oxide (Al₂O₃), Silicon monoxide (SiO) and Silica (SiO₂) are all polariton materials with different ENZ wavelength. When combining them on top of each other into a multilayer thin film structure, we can obtain broadband near-blackbody emission from 7 to 11 μm at a certain range of angles of incidence in the p polarization. We demonstrate this broadband angularly selective thermal emitter through theory, simulations, and an experimentally fabricated structure.

By employing transfer matrix method, we analytically solve the dispersion relation of this multilayer thin film structure and able to observe the EM field using the simulation tool. Following that, experimental results are compared with the analytical models with excellent agreement. The ENZ multilayer stack was coated on a Φ=100mm wafer via electrical beam evaporation method on CHA MARK 40. First, a 100nm Aluminum layer was deposited on the silicon wafer and then with 200nm Al₂O₃, 300nm SiO and 100nm SiO₂ on top of each other. Then the sample was characterized by a Fourier-transform infrared spectroscopy (FTIR)-Jacob 6100. The strongest emission occurs at an AOI around θ = 70° and can be tuned from 65°to 80° by just varying the thickness of the layers. Outside of this AOI range the multilayer film is highly reflective which allows a switch between emission and reflection mode by changing the AOI. The materials used and structure designed in our research are cheap and easy to fabricate and fully compatible with wafer-scale manufacturing. Overall, this thin film based ENZ approach opens a path towards broadband thermal beaming and angular selectivity at low cost, at large scale and with simple structures.

10:50 AM S.EL05.01.07
Cool White Polymer Coatings Based on Hollow Glass Microspheres for Radiative Cooling Xiao Nie¹, Youngjae Yoo², Hasitha Hewakuruppu¹, Ziqi Yu¹, Jonathan Sullivan¹, Anirudh Krishna¹ and Jaeho Lee¹; ¹University of California, Irvine, United States; ²Korea Research Institute of Chemical Technology, Korea (the Republic of)

While selective emitters can lead to significant radiative cooling by reflecting sunlight and emitting heat to the surroundings, current materials solutions such as multilayer structures or metallic reflectors are inadequate for large-scale radiative cooling.
systems that require lightweight, flexible and low-cost materials. Commonly used coatings for scalable applications, including commercial pigment-embedded white paints, suffer from strong ultraviolet absorption from embedded high-refractive-index (n~2.5) TiO₂ particles and a low near-infrared reflectivity. The strong ultraviolet absorption induces severe photocatalytic degradation for the organic binder components in TiO₂-based paints. Integrating low refractive index particles such as SiO₂ microspheres can be used to avoid high ultraviolet absorption because the extinction coefficient of SiO₂ remains approximately zero throughout the ultraviolet/visible/near-infrared spectrums. Here we create a lightweight, flexible and scalable polymer coating by integrating controlled volume concentrations of hollow glass microspheres within a polydimethylsiloxane (PDMS) matrix since PDMS is a commonly used low-cost polymer with little solar absorption and easy accessibility. We utilize hollow SiO₂ microspheres instead of solid microspheres as they provide a higher interfaces-to-volume ratio and a much smaller density. Our size analysis shows that the diameter of the hollow glass microspheres ranges from 2 µm to over 40 µm and the shell thickness are roughly 0.05 times the diameter (0.1 µm to 2 µm). The prepared polymer coating offers a maximum mass density of 681 kg/m³ and the corresponding areal density of 0.885 kg/m². The polymer coating also shows excellent flexibility and scalability which is beneficial for large-scale applications. As the volume concentration of hollow glass microspheres increases from 0 to 70%, the average reflectivity in the visible spectrum accordingly increases from 0.06 to 0.92 while the emissivity in the mid-infrared remains above 0.85. We use computations based on rigorous coupled-wave analysis to explain the role of hollow glass microspheres in increasing the solar reflectivity. The high solar reflectivity is attributed to the strong backscattering of sunlight enabled by refractive index difference between PDMS matrix (n~1.4) and SiO₂ shell (n~1.45), as well as between SiO₂ shell and air void (n~1) inside the microsphere. Our computation based on the Finite-difference time-domain method shows that hollow glass microspheres with a hierarchical arrangement of diameters are more efficient in scattering the sunlight and thus the polymer coating composed of large numbers of such hierarchical systems randomly distributed in a PDMS matrix can provide high solar reflectivity. The high mid-infrared emissivity is attributed to multiple extinction peaks of PDMS in the mid-infrared wavelength caused by different vibrational modes of its molecular structures. Our outdoor temperature measurement shows that the polymer coating on a concrete surface can lead to a temperature reduction of 25°C during the day, which is also 9°C below ambient temperature when conduction and convection are limited. Our building energy analysis shows the potential impact of the polymer coating on common buildings in Phoenix and estimates annual cooling energy savings of 6-38 MJ/m². The demonstrated ultraviolet-resistant property shows that the polymer coating exhibits great reliability and thus outperforms commercially available white paints. The selectively reflective polymer coating material based on hollow glass microspheres presents optimal material solutions for large-scale radiative cooling applications in buildings.

10:55 AM OPEN DISCUSSION

11:00 AM S.ELO5.01.03
Comparison of Simulated and Measured Light Emission Spectra from Solid State Incandescent Light Emitting Devices Yue Kuo¹, Abhinav Shukla¹ and Tyler W. Kuo²; ¹Texas A&M University, United States; ²The University of Texas at Austin, United States

The warm white light emission phenomena from a single solid state incandescent light emitting device (SSI-LED) was reported by Kuo's group (1,2). This device is composed of a very large number of nano-resistors formed from the breakdown of a MOS capacitor with a nm-thick high-k gate dielectric on a p-type Si wafer. Light is emitted during the passage of the current thorough the nano-resistors, i.e., following the Planck's law on blackbody emission. The light emission phenomena can last for more than 20,000 hours under the continuous operation condition in air without a passivation layer (3). The emitted light can be narrowed down to a narrow wavelength width near 850 nm (4), which is a potential light source in an on-chip optical interconnect system.

In this paper, the light emission phenomena over a SSI-LED has been simulated. The emission spectra from the thermal excitation of the nano-resistor at different temperatures with and without inclusion of an ITO or a-Si thin film filter are simulated and compared with that measured from the actual device. The device size effect on the distribution of nano-resistors and therefore the distribution of light dots is estimated and compared with that of the actual device, which will be correlated to the measured current density of the device.

11:05 AM BREAK

SESSION S.EL05.08: Live Panel Discussion and Lightning/Flash II: Nanoimprint and Nanomanufacturing  
Session Chairs: Austin Howes and Aaswath Raman  
Sunday Morning, November 29, 2020  
S.EL05

11:15 AM PANEL DISCUSSION

11:50 AM MARC VERSCHUUREN, PANELIST

11:50 AM BARBARA STADLOBER, PANELIST

11:50 AM PAUL BRAUN, PANELIST

11:50 AM CHRISTOPHER SPADACCINI, PANELIST

11:50 AM S.EL05.03.01
Atmospheric Pressure Plasma Synthesis and Aerodynamic Focusing of Silicon Nanoparticles for Additive Manufacturing  
Alexander Ho and Rebecca J. Anthony; Michigan State University, United States

The use of nonthermal plasmas has emerged as an effective method for the synthesis of high-quality nanoparticles. Extensive study of nonthermal plasma reactors under low pressure conditions has been conducted which has yielded systems capable of producing nanoparticles with size tunable properties. Miniaturization to a microscale reactor allows for effective operation of a RF nonthermal plasma reactor at atmospheric pressure. The reduced scale of the reactor also provides the opportunity for combining nanoparticle synthesis and deposition into a single system for manufacturing with nanoparticles. Presented here is our work on the additive manufacturing of silicon nanoparticles synthesized at atmospheric pressure with a nonthermal plasma. The plasma was generated with a 13.56 MHz RF power supply inside a glass capillary tube between two external ring electrodes. A silane precursor gas together with an argon background gas were flown to the reactor for the synthesis of silicon nanoparticles. The reactor was attached to a motorized system responsible for controlled deposition of the nanoparticles in predetermined geometries. TEM and XRD has shown that control between crystalline and amorphous particles can be achieved by controlling the applied power. Control over the nanoparticle size has also been demonstrated by varying the overall gas flow rate to the reactor. In efforts to increase the capability of this system for manufacturing processes we have investigated methods to control the deposition resolution. Spreading of the particles after exiting the reactor leads to wide linewidths which can limit the performance of this tool for manufacturing. Manipulation of the gas flow with aerodynamic lenses allows for reduced expansion of the particles and improved resolution. With this method we have been able to reduce the spot size to 1.3 times the size of the reactor tube outlet diameter.

11:55 AM S.EL05.02.04
Direct Optical Lithography of Transparent Metal Oxide Nanomaterials for Optical and Optoelectronic Applications  
Jia-Ahn Pan1, Yuanyuan Wang1,2 and Dmitri V. Talapin1; 1University of Chicago, United States; 2Nanjing University, China

Colloidal nanoparticles have been established as a diverse class of material with many interesting and useful properties. However, their practical application often requires some form of patterning procedure such as photolithography, ink-jet printing and nanoimprint lithography. Direct optical lithography of functional inorganic nanomaterials (DOLFIN) is a solution-processed additive patterning technique that utilizes a photosensitive colloidal nanomaterial ink. Here we engineer ligand-colloid interactions to be optically sensitive, allowing us to achieve micron-resolution patterning of metal oxide nanomaterials. Using this approach, we demonstrate the facile lithography of thick (>500 nm) metal oxide structures, which have a high-refractive index (n > 1.8) and are highly transparent. As a proof of concept, we manufacture diffractive optical elements (e.g. gratings) to show that significant phase modulation of light is attainable. Unlike polymer-based optical elements, our optical devices are more robust and can tolerate high temperatures due to its primarily inorganic content. We
also show the patterning of conductive colloidal oxide nanomaterials (e.g. ITO), which facilitates its implementation as a transparent conductive electrode. These advances aim to facilitate the integration of colloidal nanomaterials in real-world applications.

12:00 PM S.EL05.02.03
Polymer Blend Lithography—Bioinspired Scalable Fabrication of Disordered Photonic Nanostructures for Biosensing Radwanul H. Siddique1,2, Vinayak Narasimhan1, Shailabh Kumar1 and Hyuck Choo1,2; 1California Institute of Technology, United States; 2Samsung Advanced Institute of Technology, Korea (the Republic of)

Millions of years of evolution in the biological world has developed a plethora of micro- and nanoscopic photonic structures that are frequently superior to synthetic analogs. These biophotonic materials show interesting novel and tunable unforeseen properties with deliberately introduced disorder in their respective geometries and compositions. Over the last decade, photonic materials with tailored -i.e. with deliberately introduced- structural disorder have also attracted considerable interest in various optical applications due to their extended spectral and angular range of effectiveness. Most bio-inspired nanostructured devices or optical metamaterials designed to date have been demonstrated at small-scales using expensive top-down techniques. However, biological structure formation in nature utilizes several bottom-up self-assembly approaches for manufacturing hierarchical mesoscopic nanostructures (100 – 550 nm) with immense diversity. Despite recent efforts aimed at increasing top-down fabrication writing speed, alternative routes based on self-assemblies still possess major advantages for industrial implementation of disordered structures as they allow rapid processing over large areas (> cm²).

In this communication, we show that up-scalable polymer blend lithography technique can be used as a versatile platform for fabricating 2D planar, disordered nanostructures that can be exploited in both top-down and bottom-up strategies. Polymer blend lithography utilizes the polymer-phase separation process following nature’s way of forming nanostructures. The tailored disorder is achieved here by adjusting the process parameters (polymer blend composition and deposition conditions), enabling us to tune the morphology and the spatial distribution of the nanostructures produced, and in turn their light management properties.

First, we use our approach to pattern a resist etching mask, employed for transferring disordered nanopillars by dry etching (top-down route) onto a Fabry-Perot-resonator-based intraocular pressure (IOP) sensor for glaucoma management. The nanostructure integration onto the IOP sensor led to a 2.5-fold improvement in readout angle allowing easy handheld monitoring and in a one-month in vivo study conducted in rabbits, showed a 3-fold reduction in IOP error and 12-fold reduction in tissue encapsulation and inflammation, compared to an IOP sensor without nanostructures. Second, we demonstrate that similar structures can serve as a template in a bottom-up configuration, whereby aluminum thin film is directly deposited into the disordered nanoholes to form scalable plasmonic metasurfaces. These metasurfaces generate hybrid multipolar lossless plasmonic modes resulting in a broadband fluorescence-enhancement factor above 1000 for visible wavelengths with respect to glass chips commonly used in bioassays. Using the metasurface and a multiplexing technique involving three visible wavelengths, we successfully detected three biomarkers, insulin, vascular endothelial growth factor, and thrombin relevant to diabetes, ocular and cardiovascular diseases, respectively, in a single 10-μL droplet containing only 1 femtomole of each biomarker.

References

SESSION S.EL05.09: Live Panel Discussion and Lightning/Flash III: Nanophotonics at Large Scales
Session Chairs: Vivian Ferry and Giulia Tagliabue
Monday Morning, November 30, 2020
S.EL05

8:00 AM PANEL DISCUSSION
During the last decade, III-V semiconductor nanowires (NWs) have received great research interest due to their promising potential for next-generation electronic, optoelectronic, and photonic devices. One of the main challenges for epitaxially-grown III-V NWs, however, is their high manufacturing cost, which can be divided to two individual categories: (1) the cost of starting III-V substrates, and (2) the cost of pre-epitaxy fabrication associated with substrate patterning. Large-scale integration of III-V NW-based technologies requires novel nanofabrication strategies that mitigate both cost streams. Wafer costs can be substantially reduced simply through growth of III-V NWs on foreign substrates such as silicon or graphene, instead of on bulk III-V wafers. One strategy for simultaneously reducing fabrication complexity and pre-growth processing costs is to reuse Si substrates with existing predefined growth masks for selective-area epitaxy (SAE) of III-V NW arrays. Here, we present wafer-scale, bottom-up SAE growth of InAs NW arrays and fabrication of flexible NW-based infrared (IR) photodetectors realized through delamination of embedded NW arrays and reuse of Si substrates with predefined growth masks. Silicon (111) substrates are patterned by conventional photolithography to obtain pores with 0.5 μm diameters and 1 μm pitch in SiO2 growth masks of 55 nm thickness. Next, InAs NW arrays are grown via the SAE approach using metalorganic chemical vapor deposition (MOCVD). Trimethyl-indium (TMIn) and arsine (AsH3) were used as precursor gases for the supply of In and As growth species, respectively, at a set-point growth temperature of 700 °C. A two-step growth technique is introduced, whereby a separate nucleation step using a TMIn flow rate of 16 μmol/min precedes a NW growth step at a TMIn flow rate of 0.77 μmol/min. This procedure is necessary for optimization of pore occupation toward a global NW yield of >85%, with NW aspect ratios of ~15. The InAs NW arrays are embedded in various polymer membranes and mechanically delaminated from their growth substrates, then bonded to carrier substrates for subsequent device fabrication. The polymer-embedded NW array exfoliation process leaves NW bases with heights of ~50 nm below the fracture plane attached to the growth surface. Consequently, five different substrates restoration processes are investigated prior to substrate-reuse. It is observed that the best results for re-growth of daughter generation InAs NW arrays on reused Si substrates can be realized when no additional wet etching, chemical treatment, or mechanical polishing steps are introduced between subsequent re-growth runs, as the remaining NW bases serve as SAE growth sites. Direct re-growth on reused Si substrates results in vertical extension of existing NW bases and growth of InAs NWs with aspect ratios >80 under the same growth conditions as the primary run with comparable global NW yield. For fabrication of flexible IR photodetectors using both primary and subsequent generation InAs NW arrays, a unique process flow is reported, which enables NW transfer yields of ~100% and preserves the original position and orientation of as-grown NWs. This work demonstrates that multiple generations of InAs NW-based devices can be fabricated through reuse of a single, templated Si substrate, without introduction of intermediate substrate restoration processes such as wet etching or chemical mechanical polishing. This approach can serve as an effective strategy toward growth and fabrication of large-area, high-efficiency, low-cost, flexible, and wearable device applications in III-V nanoelectronics, optoelectronics, and photovoltaics.

Planar optical elements with efficient light control at the nanoscale can be designed based on transdimensional photonic lattices that operate in the translational regime between two and three dimensions. Such transdimensional lattices include 3D-engineered nanoantennas supporting multipole Mie resonances and arranged in the 2D arrays to harness collective effects in the nanostructure [1]. Optical antennas made out of van der Waals material with naturally-occurring hyperbolic dispersion is
a promising alternative to plasmonic and high-refractive-index dielectric structures in the practical realization of nanoscale photonic elements. The antenna made out of hexagonal boron nitride (hBN) possesses different multipole resonances enabled by the supporting high-k modes and their reflection from the antenna boundaries. The full range of the resonances is demonstrated for the hBN cuboid antenna, a decrease of reflection from the array, and highly directional resonant scattering from antennas pairs. We show that transdimensional lattices consisting of resonant hBN antennas in the engineered periodic arrays have great potential to serve as functional elements in ultra-thin optical components and photonic devices.

We show that a periodic array of particles with a large imaginary part of their permittivity (LIPP) can support well-defined modes localized within the particle, with the spectral position of the modes mainly defined by the array period. It has been known for a long time that a non-zero imaginary part of the permittivity enables propagating surface modes at the interface of materials with positive permittivities, known as Zenneck modes. Recently, it has been demonstrated that transition metal dichalcogenides (TMDC) layers support different kinds of propagating Zenneck waves defined by the layer thickness and interfaces with air and substrate [2]. Here, we show that localized Zenneck modes are possible on subwavelength particles and that the particles can serve as antennas for direction light scattering, reflection suppression, and Kerker-effect applications. To illustrate a possibility to control light, we show that simultaneous excitation of the several particle multipole resonances (electric dipole and quadrupole) allows for achieving significant reflection suppression and observation of the generalized lattice Kerker effect [3]. Materials with LIPP are common in nature, including TMDCs and lossy metals, titanium, chromium, and others.

Acknowledgment. This material is based upon work supported by the Air Force Office of Scientific Research under Grant No. FA9550-19-1-0032.


8:45 AM S.EL05.04.10
Large-Scale Thermoregulatory Material Inspired by Cephalopods Mohsin Ali Badshah1, Erica M. Leung1, Christopher Moore2, Panyiming Liu1, Marlon Pinedo1 and Alon Gorodetsky1,1,1; 1University of California, Irvine, United States; 2Chapman University, United States

Low-cost, large-area thermal management is desirable for the operation of many modern technologies including smart clothing, electronic circuits, building environments, and outdoor equipment to control heat flow. Inspired by the space blanket and the dynamic skin of cephalopods, we have demonstrated a large-area, highly uniform, low-cost nanostructured material with tunable thermoregulatory and infrared properties. We have implemented scalable nanofabrication processes to achieve a material with an area > 500 cm², a > 40 % change in infrared transmittance and reflectance, and a dynamic environmental setpoint temperature window of ~ 8 °C. Due to characteristics of scalability and associated figures of merit, our material affords new scientific and technological opportunities not only for adaptive optics and thermoregulation but also for any platform that would benefit from dynamic control of infrared radiation and heat.
Periodic Self-Assembled Nanopatterns with Spacings Approaching Visible Wavelengths Using Block Copolymer/Homopolymer Blends

Gregory S. Doerk, Ruipeng Li, Masafumi Fukuto and Kevin Yager; Brookhaven National Laboratory, United States

Bottom up self-assembly of block copolymers (BCPs) offers a scalable, economical alternative to lithography for producing large area, highly uniform nanopatterns required for engineering materials with tailored light-matter interactions. At their typical scales (~20-50 nm feature spacing), thin film BCP nanopatterns may be used to generate deep subwavelength like...
nanotextures that reduce visible reflectance to < 1% [1,2], or nanoholes that improve light trapping in photovoltaics at carrier selective rear contacts [3]. Nevertheless a greater latitude for optical property engineering would be possible using self-assembled BCP patterns at length scales commensurate with visible wavelengths of light in order to exploit optical diffraction and resonance effects. This is prohibited by exponentially slower ordering kinetics in the ultrahigh molecular weight BCPs (> 1000 kg/mol) required for this scaling. Here we report dramatically accelerated ordering afforded by blending in very low molecular weight (~3 kg/mol) homopolymer plasticizers. These formulations enable a 10× reduction in the time required to achieve ordered nanopatterns with periods > 200 nm. Subsequent reactive ion etching demonstrates that these nanopatterns are readily transferrable to other materials. Exemplar applications such as structural colors made possible using these self-assembled patterns will be described.

References:

Research performed at the CFN and NSLS-II, U.S. DOE Office of Science Facilities at Brookhaven National Laboratory under Contract No. DE-SC0012704.

9:40 AM S.EL05.05.08
Physically Assisted Chemical Assembly for Large-Area, Reproducible Near-Field Response Regina Ragan; University of California, Irvine, United States

Single molecule (SM) detection represents the ultimate limit of chemical detection. Over the years, many experimental techniques have emerged with this capacity. Yet, SM detection and imaging methods require large, reproducible spectral datasets in order to benefit from chemometric methods. We will present a scalable chemical assembly platform for plasmonic and metamaterial architectures that yield reproducible optical response. For example, surface enhanced Raman scattering spectroscopy (SERS), with extensive applications in biosensing, is demonstrated to be particularly promising because Raman active molecules can be identified without recognition elements and is capable of SM detection. Yet quantification at ultralow analyte concentrations requiring detection of SM events remains an ongoing challenge, with the few existing methods requiring carefully developed calibration curves that must be redeveloped for each analyte molecule. We will present work where we demonstrate that using 2-dimensional physically activated chemical (2PAC) self-assembly, we can achieve reproducible enhancement factors of 10⁹ over 1 cm². 2PAC crosslinks nanoparticles into discrete assemblies with a small molecule linker, where the crosslinking reaction is driven by electrohydrodynamic flow at on a substrate surface. The hotspots observed in a 2PAC fabricated assembly have gap spacing is 0.9 nm, corresponding to the length of the chemical crosslinker. Large area SERS maps are acquired from these 2PAC assembled surfaces from analyte dissolved in water and even complex biological media.

One of the most important applications of contemporary machine learning, i.e., image analysis, has remained relatively untouched by the SERS community. We will show that a combination of large area and reproducible SERS substrates with a CNN model is used to address the long standing challenge in SERS: quantification of sub-nanomolar analyte concentrations. A convolutional neural network (CNN) model when applied to bundles of reliable SERS spectra yields a robust, facile method for concentration quantification down to 10 fM using SM detection events. The demonstrated limit of blank (LOB) is 1 fM for Rhodamine 800, with a limit of quantification (LOQ) of 10 fM. Furthermore, the model’s predicted concentrations have an average r² value of 0.958 over 6 orders of magnitude as determined by k-folds cross validation. A key advantage of the analysis is its compatibility with transfer learning, the use of large datasets to train a model and then generalize this pretrained model to new molecules quickly with significantly smaller datasets. The uniformity of enhancement factor is essential for our approach, as large variance in the dataset not only increases the variance in predictions, but also requires more data for convergence and prevents a transfer learning approach. Generalization of the CNN model to other analytes using transfer learning is demonstrated with methylene blue. Transfer learning achieves good results with as few as 50 8x8 pixel maps. Thus entire datasets are acquired quickly, requiring just 5.3 minutes of total laser exposure time per concentration to train a robust model that is much faster and more scalable than required for building SM concentration regression models. This demonstrates a proof of concept for hyperspectral CNN image analysis of SERS, which could be broadly applicable within SERS, especially in the biological setting where classification of images could improve analysis of bacteria that are already imaged with SERS. We will also present results showing this approach is able to differentiate susceptible and resistant bacterial strains for rapid antimicrobial susceptibility tests.

9:45 AM S.EL05.05.07
Multi-Layered Nanoparticle Coatings with Tunable Refractive Index and Surface Roughness Deposited with Aerosol Impact Driven Assembly (AIDA) Peter Firth1,2, Zachary C. Holman2,1 and Shannon Poges1,2; 1Swift Coat, United States; 2Arizona State University, United States

The next generation of functional coatings will likely be composed of nanomaterials. At the laboratory scale nanomaterial-based coatings have shown the potential to improve performance and enable completely new functionality in applications like thermal barrier coatings on high-temperature parts, active layers in electronic devices, anti-reflective coatings for PV modules, or biocompatible coatings for medical applications. In all cases, these coatings should be able to be formed over large areas at commercial production rates and have a uniform and controllable thickness, and their constituent particles should retain their nano-properties.

Present nanomaterial films developed in laboratories are often unable to be reproduced on a commercial scale; the manufacturing methods are inherently nanomaterial, substrate, and application specific. This specificity results in manufacturing processes that are expensive or offer limited utility. We propose an advanced nanomaterial film manufacturing technology based on Aerosol Impact Driven Assembly (AIDA) that overcomes these deficiencies.

AIDA begins by aerosolizing a nanomaterial using any desired technique, from atomizing a nanoparticle-laden solution to feeding nanoparticle-precursor gas into a plasma. The aerosolized material is fed into the AIDA system, which consists of two chambers separated by a slit-shaped nozzle, with the bottom chamber held under vacuum (< 1 Torr). The nanomaterial is accelerated to a velocity of several hundred meters/second as it and the aerosol background gas are forced through the nozzle, resulting in the formation of a curtain of nanoparticles directed into the downstream chamber. A substrate is passed through the curtain, and the nanomaterial collisions with and adheres to the substrate, forming a thin coating.

AIDA’s unique approach to film formation enables independent control over nearly every aspect of the coating’s morphology. As a dry spray technique, there are no inherent limitations on the thickness. Coatings ranging in thickness from a sub-monolayer to >1mm have been produced with dynamic deposition rates as high as 6 mm-m/min. By adjusting the particle impact velocity, the porosity of the coating can be controlled between 5% and 95%. This enables control over film properties like the refractive index, heat transfer coefficient, and dielectric constant. By changing the angle of impaction, the surface roughness of the film can be tuned between 0 nm and >100 nm allowing engineers to tune the effective surface energy of the coating. Combining this intimate control of film morphology with the wide range of nanomaterials compatible with AIDA allows engineers to produce complex, multi-layered, multi-component, and multi-functional films using a single platform.

As a case study, we will showcase an AIDA system capable of depositing on 14”x24” substrates that uses an in-situ non-thermal plasma reactor to synthesize metal-oxide nanoparticles (SiO2, TiO2, and ZnO) and produce a multi-layered coating that is simultaneously highly photocatalytic (self-cleaning) and anti-reflective for use in PV module glass. The composition of each layer will be tuned to maximize the photocatalytic self-cleaning effect. The thickness and refractive index of each layer will be tuned to optimize its anti-reflective properties and provide a 3% transmittance gain compared to uncoated glass. The surface roughness of each layer will be tuned to promote adhesion and provide the desired water contact angle on the top surface to enhance self-cleaning.

Effectively Transparent Contacts for Photovoltaic Devices Rebecca Saive1,2,3; 1University of Twente, Netherlands; 2California Institute of Technology, United States; 3ETC Solar, Netherlands

Effectively transparent contacts (ETCs) constitute the only front contact technology to date overcoming the inherent trade-off between grid conductivity and transparency[1]. When applied to solar cells relative efficiency improvements of 4-10% can be achieved. ETCs consist of triangular cross-section microscale silver grids that redirect incoming light towards the absorber material of the photovoltaic (PV) device instead of reflecting it back to the light source. Key features of this technology are the mesoscale structure size leading to ray-optical near-field interaction and low sheet resistivity [2] in combination with a novel fabrication method allowing for mirror-like optical properties. Here, the design of ETCs, their physical and visual [3] properties, application in different solar cell technologies and the principle of residue-free imprint lithography will be presented. Commercialization of the ETC technology is underway and executed by the award-winning Caltech and UTwente.
A Triple-Mode mid-IR Modulator for All-Surface Large-Scale Heat Management

Po-Chun Hsu; Duke University, United States

Radiative heat management is a promising approach for thermoregulation because it is ubiquitous, rapid, lightweight, and energy-efficient. The sensitivity and spectral tunability also make thermal radiation particularly powerful in many energy applications, such as rooftop radiative cooling, solar thermal heating, wearable thermal management, and so on. As the radiative heat management concept becomes more and more prevalent and influential, it also calls for more functions integrated into one single device. In this talk, I will introduce a triple-mode mid-infrared modulator that can switch among transmission, reflection, and emission states. The device is composed of an elastomer/metal thin film with a rationally designed coupling relationship between mechanical and optical properties. The fabrication is highly scalable and does not need any photolithography. By controlling the biaxial strain of the elastomer/metal film, the device can switch among the three modes with unprecedented performance of emittance contrast $|\Delta \varepsilon| = 0.44$, transmittance contrast $|\Delta \tau| = 0.48$, and reflectance contrast $|\Delta \rho| = 0.38$, and these modulation remains stable after 100 cycles. Being able to switch among three modes means the device can perform heating and cooling on objects with all kinds of surface emissivities, no matter it is perfect thermal emitter such as the human body or poor emitters such as metals. We also performed semi-empirical structure optimization to serve as the future pattern design guideline. It provides a new paradigm in the cross-disciplining area of soft and shape-changing photonic materials.

Comparison of Simulated and Measured Light Emission Spectra from Solid State Incandescent Light Emitting Devices

Yue Kuo¹, Abhinav Shukla¹ and Tyler W. Kuo²; ¹Texas A&M University, United States; ²The University of Texas at Austin, United States

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In this paper, the light emission phenomena over a SSI-LED has been simulated. The emission spectra from the thermal excitation of the nano-resistor at different temperatures with and without inclusion of an ITO or a-Si thin film filter are simulated and compared with that measured from the actual device. The device size effect on the distribution of nano-resistors and therefore the distribution of light dots is estimated and compared with that of the actual device, which will be correlated to the measured current density of the device.


Switchable Smart Radiative Heating and Cooling Building Envelope

Po-Chun Hsu; Duke University, United States
Solar thermal energy has been one of the major energy sources to realize zero energy buildings for a sustainable future. The high efficiency and low cost make it particularly attractive to reduce the energy consumption for hot water and space heating. On the other hand, the radiative cooling uses the rest of the sky, i.e. the outer space, as the cold source to generate cooling that can offset the usage of refrigeration and space cooling. Both technologies show rapid and promising improvement in the past decade, which calls for new engineering and design principles to further maximize the energy saving for buildings. In this talk, I will introduce a smart building envelope that can switch between solar heating and radiative cooling, so it can be applied to buildings at various climate zones (spatial variation) under different weather and forms of energy demand (temporal variation). The dual-function material which possesses both heating and cooling property is switched mechanically between ~600 W/m² of solar heating and ~100 W/m² of radiative cooling in less than one minute. This high performance is the outcome of heat transport analysis and engineering. We demonstrate this smart heat managing building envelope can be adopted in all 16 climate zones in the US and produce in more energy-saving on a yearly basis.

6:30 AM S.E.L05.01.07
Cool White Polymer Coatings Based on Hollow Glass Microspheres for Radiative Cooling Xiao Nie¹, Youngjae Yoo², Hasitha Hewakuruppu¹, Ziqi Yu¹, Jonathan Sullivan¹, Anirudh Krishna¹ and Jaeho Lee¹; ¹University of California, Irvine, United States; ²Korea Research Institute of Chemical Technology, Korea (the Republic of)

While selective emitters can lead to significant radiative cooling by reflecting sunlight and emitting heat to the surroundings, current materials solutions such as multilayer structures or metallic reflectors are inadequate for large-scale radiative cooling systems that require lightweight, flexible and low-cost materials. Commonly used coatings for scalable applications, including commercial pigment-embedded white paints, suffer from strong ultraviolet absorption from embedded high-refractive-index (n ~2.5) TiO₂ particles and a low near-infrared reflectivity. The strong ultraviolet absorption induces severe photocatalytic degradation for the organic binder components in TiO₂-based paints. Integrating low refractive index particles such as SiO₂ microspheres can be used to avoid high ultraviolet absorption because the extinction coefficient of SiO₂ remains approximately zero throughout the ultraviolet/visible/near-infrared spectrums. Here we create a lightweight, flexible and scalable polymer coating by integrating controlled volume concentrations of hollow glass microspheres within a polydimethylsiloxane (PDMS) matrix since PDMS is a commonly used low-cost polymer with little solar absorption and easy accessibility. We utilize hollow SiO₂ microspheres instead of solid microspheres as they provide a higher interfaces-to-volume ratio and a much smaller density. Our size analysis shows that the diameter of the hollow glass microspheres ranges from 2 µm to over 40 µm and the shell thickness are roughly 0.05 times the diameter (0.1 µm to 2 µm). The prepared polymer coating offers a maximum mass density of 681 kg/m³ and the corresponding areal density of 0.885 kg/m². The polymer coating also shows excellent flexibility and scalability which is beneficial for large-scale applications. As the volume concentration of hollow glass microspheres increases from 0 to 70%, the average reflectivity in the visible spectrum accordingly increases from 0.06 to 0.92 while the emissivity in the mid-infrared remains above 0.85. We use computations based on rigorous coupled-wave analysis to explain the role of hollow glass microspheres in increasing the solar reflectivity. The high solar reflectivity is attributed to the strong backscattering of sunlight enabled by refractive index difference between PDMS matrix (n ~1.4) and SiO₂ shell (n ~1.45), as well as between SiO₂ shell and air void (n ~1) inside the microsphere. Our computation based on the Finite-difference time-domain method shows that hollow glass microspheres with a hierarchical arrangement of diameters are more efficient in scattering the sunlight and thus the polymer coating composed of large numbers of such hierarchical systems randomly distributed in a PDMS matrix can provide high solar reflectivity. The high mid-infrared emissivity is attributed to multiple extinction peaks of PDMS in the mid-infrared wavelength caused by different vibrational modes of its molecular structures. Our outdoor temperature measurement shows that the polymer coating on a concrete surface can lead to a temperature reduction of 25°C during the day, which is also 9°C below ambient temperature when conduction and convection are limited. Our building energy analysis shows the potential impact of the polymer coating on common buildings in Phoenix and estimates annual cooling energy savings of 6-38 MJ/m². The demonstrated ultraviolet-resistant property shows that the polymer coating exhibits great reliability and thus outperforms commercially available white paints. The selectively reflective polymer coating material based on hollow glass microspheres presents optimal material solutions for large-scale radiative cooling applications in buildings.

6:45 AM S.E.L05.01.08
Broadband Thermal Beaming Using Multiple Epsilon Near Zero Materials Jin Xu and Aaswath P. Raman; University of California, Los Angeles, United States

Controlling the propagation, absorption and emission of light has been a topic of fundamental interest in contemporary photonics research. In the context of controlling the emission of light from thermal sources, a central challenge is that of angular selectivity. Over the past two decades, a range of photonic strategies, including using surface phonon-polariton modes, have enabled anomalous angular ‘beaming’ of thermal radiation, albeit only at narrow ranges of wavelengths.
However, thermal radiation is inherently a broadband phenomenon. We currently lack the ability to constrain broad-spectrum thermal emission over a narrow range of angles of incidence, but consistently over a broad range of wavelengths. This form of broadband thermal beaming would be a fundamentally enabling capability for a range of applications, including infrared imaging and camouflage, thermophotovoltaics and radiative cooling.

Here, we employ multiple epsilon-near-zero (ENZ) materials in a layered configuration to realize a broadband angularly selective thermal emitter. ENZ materials can fulfill high absorption and emission of incident light at wavelengths where the epsilon is near zero. Aluminum oxide (Al$_2$O$_3$), Silicon monoxide (SiO) and Silica (SiO$_2$) are all polariton materials with different ENZ wavelength. When combining them on top of each other into a multilayer thin film structure, we can obtain broadband near-blackbody emission from 7 to 11µm at a certain range of angles of incidence in the p polarization. We demonstrate this broadband angularly selective thermal emitter through theory, simulations, and an experimentally fabricated structure.

By employing transfer matrix method, we analytically solve the dispersion relation of this multilayer thin film structure and able to observe the EM field using the simulation tool. Following that, experimental results are compared with the analytical models with excellent agreement. The ENZ multilayer stack was coated on a Φ=100mm wafer via electrical beam evaporation method on CHA MARK 40. First, a 100nm Aluminum layer was deposited on the silicon wafer and then with 200nm Al$_2$O$_3$, 300nm SiO and 100nm SiO$_2$ on top of each other. Then the sample was characterized by a Fourier-transform infrared spectroscopy (FTIR)-Jacob 6100. The strongest emission occurs at an AOI around $\theta = 70^\circ$ and can be tuned from 65° to 80° by just varying the thickness of the layers. Outside of this AOI range the multilayer film is highly reflective which allows a switch between emission and reflection mode by changing the AOI. The materials used and structure designed in our research are cheap and easy to fabricate and fully compatible with wafer-scale manufacturing. Overall, this thin film based ENZ approach opens a path towards broadband thermal beaming and angular selectivity at low cost, at large scale and with simple structures.

7:00 AM *S.EL05.01.09
Scalable Fabrication of Radiative Cooling Paint Yuan Yang and Jyotirmoy Mandal; Columbia University, United States

Radiative cooling is an attractive method to save energy usage for terrestrial entities, such as buildings and vehicles. To achieve efficient radiative cooling, high solar reflectance and high thermal emittance are needed. In this talk I will present out recent results on developing porous polymer paint for achieving high-performance radiative cooling. Strong sunlight reflectance at the polymer/air interface leads to solar reflectance of 96-99.6% and thermal emittance of 0.97. Sub-ambient cooling of 6 oC is achieved under strong sunlight. Such paint can also be prepared in scalable fashion and applied by wide range of surface with irregular shapes. Moreover, we have achieved dynamic switching inside by wetting/dewetting the porous film by liquid. A bilayer design is also developed for colored cooling paint, which shows 10-30% higher reflectance in the infrared part of solar spectrum.

References:
Jyotirmoy Mandal et al., Joule, online.

SESSION S.EL05.02: Nano-Imprint and Other Lithographic Methods
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL05

5:00 AM *S.EL05.02.01
R2R-UV Nanoimprinting for Large-Area Fabrication of Freeform Micro-Optical Components Barbara Stadlober, Stephan Ruttoloff, Johannes Götz, Dieter Nees, Ladislav Kuna, Ursula Palfinger, Anja Haase, Martin Smolka, Jan Hesse, Claude Leiner and Christian Sommer; Joanneum Research, Austria

Recently, R2R-UV nanoimprinting has proven to be very useful and unrivalled for the large-area fabrication of high-resolution, hierarchical structures at reasonable throughput deployed for mechanically flexible and lightweight functional surfaces in bionic applications like drag-reducing films or transparent conductive electrodes [1], [2].
Here we report on the deployment of our UV-Nanoimprinting pilot line for the manufacturing and upscaling of optical components in lighting and microfluidic applications. This pilot line covers all steps needed for upscaling, namely design & simulation, origination via maskless laser lithography, tooling via Step & Repeat UV-NIL and large area replication via R2R UV-nanoimprinting.

One key prerequisite for the versatile deployment of UV-nanoimprinting is the adjustability of the imprint resin towards the targeted application scenario. It should be tuneable in terms of elasticity and surface tension to account for easy demoulding and for low (water-repellent) as well as high (water-wicking) energy surfaces and it should have low enough viscosity to allow for large-area coating. Special requirements for the channel forming resin in microfluidics are a sufficiently high surface energy to allow for a fast and long distance filling of analytes, the ability to be bio-functionalized and low cytotoxicity. For optical polymer components, the tuneability of the refractive index is important as well. Another key aspect for industrial implementation of disordered structures as they allow rapid processing over large areas (>>cm²).

Increasing top-down fabrication writing speed, alternative routes based on self-assemblies still possess major advantages in various optical applications due to their extended spectral and angular range of effectiveness. Despite recent efforts aimed at increasing top-down fabrication writing speed, alternative routes based on self-assembly still possess major advantages for industrial implementation of disordered structures as they allow rapid processing over large areas (>~cm²). Over the last decade, photonic materials with tailored -i.e. with deliberately introduced- structural disorder have also attracted considerable interest in various optical applications due to their extended spectral and angular range of effectiveness. Most bio-inspired nanostructured devices or optical metamaterials designed to date have been demonstrated at small-scales using expensive top-down techniques. However, biological structure formation in nature utilizes several bottom-up self-assembly approaches for manufacturing hierarchical mesoscopic nanostructures (100 – 550 nm) with immense diversity. Despite recent efforts aimed at increasing top-down fabrication writing speed, alternative routes based on self-assembly still possess major advantages for industrial implementation of disordered structures as they allow rapid processing over large areas (>~cm²).

In this communication, we show that up-scalable polymer blend lithography technique can be used as a versatile platform for fabricating 2D planar, disordered nanostructures that can be exploited in both top-down and bottom-up strategies. Polymer blend lithography utilizes the polymer-phase separation process following nature’s way of forming nanostructures. The tailored disorder is achieved here by adjusting the process parameters (polymer blend composition and deposition conditions), enabling us to tune the morphology and the spatial distribution of the nanostructures produced, and in turn their light management properties.

First, we use our approach to pattern a resist etching mask, employed for transferring disordered nanopillars by dry etching (top-down route) onto a Fabry-Perot-resonator-based intraocular pressure (IOP) sensor for glaucoma management. The nanostructure integration onto the IOP sensor led to a 2.5-fold improvement in readout angle allowing easy handheld monitoring and in a one-month in vivo study conducted in rabbits, showed a 3-fold reduction in IOP error and 12-fold reduction in tissue encapsulation and inflammation, compared to an IOP sensor without nanostructures. Second, we demonstrate that similar structures can serve as a template in a bottom-up configuration, whereby aluminum thin film is directly deposited into the disordered nanoholes to form scalable plasmonic metasurfaces. These metasurfaces generate hybrid multipolar lossless plasmonic modes resulting in a broadband fluorescence-enhancement factor above 1000 for visible wavelengths with respect to glass chips commonly used in bioassays. Using the metasurface and a multiplexing technique involving three visible wavelengths, we successfully detected three biomarkers, insulin, vascular endothelial growth factor, and thrombin relevant to diabetes, ocular and cardiovascular diseases, respectively, in a single 10-μL droplet containing only...
1 femtomole of each biomarker.

References

5:45 AM S.EL05.02.04
Direct Optical Lithography of Transparent Metal Oxide Nanomaterials for Optical and Optoelectronic Applications Jia-Ahn Pan1, Yuanyuan Wang1,2 and Dmitri V. Talapin1; 1University of Chicago, United States; 2Nanjing University, China

Colloidal nanoparticles have been established as a diverse class of material with many interesting and useful properties. However, their practical application often requires some form of patterning procedure such as photolithography, ink-jet printing and nanoimprint lithography. Direct optical lithography of functional inorganic nanomaterials (DOLFIN) is a solution-processed additive patterning technique that utilizes a photosensitive colloidal nanomaterial ink. Here we engineer ligand-colloid interactions to be optically sensitive, allowing us to achieve micron-resolution patterning of metal oxide nanomaterials. Using this approach, we demonstrate the facile lithography of thick (>500 nm) metal oxide structures, which have a high-refractive index (n > 1.8) and are highly transparent. As a proof of concept, we manufacture diffractive optical elements (e.g. gratings) to show that significant phase modulation of light is attainable. Unlike polymer-based optical elements, our optical devices are more robust and can tolerate high temperatures due to its primarily inorganic content. We also show the patterning of conductive colloidal oxide nanomaterials (e.g. ITO), which facilitates its implementation as a transparent conductive electrode. These advances aim to facilitate the integration of colloidal nanomaterials in real-world applications.

SESSION S.EL05.03: Additive Manufacturing and Other Novel Methods
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL05

5:00 AM S.EL05.03.01
Atmospheric Pressure Plasma Synthesis and Aerodynamic Focusing of Silicon Nanoparticles for Additive Manufacturing Alexander Ho and Rebecca J. Anthony; Michigan State University, United States

The use of nonthermal plasmas has emerged as an effective method for the synthesis of high-quality nanoparticles. Extensive study of nonthermal plasma reactors under low pressure conditions has been conducted which has yielded systems capable of producing nanoparticles with size tunable properties. Miniaturization to a microscale reactor allows for effective operation of a RF nonthermal plasma reactor at atmospheric pressure. The reduced scale of the reactor also provides the opportunity for combining nanoparticle synthesis and deposition into a single system for manufacturing with nanoparticles. Presented here is our work on the additive manufacturing of silicon nanoparticles synthesized at atmospheric pressure with a nonthermal plasma. The plasma was generated with a 13.56 MHz RF power supply inside a glass capillary tube between two external ring electrodes. A silane precursor gas together with an argon background gas were flown to the reactor for the synthesis of silicon nanoparticles. The reactor was attached to a motorized system responsible for controlled deposition of the nanoparticles in predetermined geometries. TEM and XRD has shown that control between crystalline and amorphous particles can be achieved by controlling the applied power. Control over the nanoparticle size has also been demonstrated by varying the overall gas flow rate to the reactor. In efforts to increase the capability of this system for manufacturing processes we have investigated methods to control the deposition resolution. Spreading of the particles after exiting the reactor leads to wide linewidths which can limit the performance of this tool for manufacturing. Manipulation of the gas flow with aerodynamic lenses allows for reduced expansion of the particles and improved resolution. With this method we have been
able to reduce the spot size to 1.3 times the size of the reactor tube outlet diameter.

5:15 AM *S.EL05.03.02  
**Additive Manufacturing of 3D Microscale Gradient Refractive Index Polymer Optics in Porous Silicon**  
Paul V. Braun; University of Illinois at Urbana Champaign, United States

Here we present Subsurface Controllable Refractive Index via laser Beam Exposure (SCRIBE), a novel lithographic approach to fabricate polymer optical elements with arbitrary 3D index profiles at precise locations within a mesoporous silicon scaffold. We achieve a broad index range at 633 nm of 1.55 to 2.01 by adjusting the laser exposure. We demonstrate a microscale doublet objective that focuses visible light to 750 ± 20 μm and a smallest-on-record 15-μm diameter spherical Luneburg (gradient index) lens. Finally, we realize integrated photonic devices that use 3D waveguides to couple light vertically from the surface to a horizontally oriented subsurface all-pass microring (Q = 10,000). These demonstrations present a new paradigm for lithographically-aligned 3D fabrication of polymer micro-optics and photonic systems.

5:45 AM *S.EL05.03.03  
**Advances in Additive Manufacturing and Architected Materials for Micro and Nanoscale 3D Structures**  
Christopher M. Spadaccini; Lawrence Livermore National Laboratory, United States

Material properties are governed by the chemical composition and spatial arrangement of constituent elements at multiple length-scales. This fundamentally limits material properties with respect to each other creating trade-offs when selecting materials for specific applications. For example, strength and density are inherently linked so that, in general, the more dense the material, the stronger it is in bulk form. We are combining inverse design methods such as topology optimization, with advanced additive micro- and nanomanufacturing techniques to create new material systems with previously unachievable property combinations – architected mechanical metamaterials. The performance of these materials is fundamentally controlled by geometry at multiple length-scales, from the nano- to the macroscale, rather than chemical composition alone. We have demonstrated designer properties of these mechanical metamaterials in polymers, metals, ceramics and combinations thereof. Properties include ultra-stiff lightweight materials, negative stiffness, and negative thermal expansion to name a few, as well as functional properties such electrical, optical, and even chemical responses. Recently, we have also demonstrated metamaterials which respond to external stimuli; namely magnetic fields. We have primarily utilized our custom developed additive manufacturing techniques to create these structures and materials. These include projection microstereolithography (PuSL), direct ink writing (DIW), and electrophoretic deposition (EPD). I will also touch on new advanced concepts such as volumetric additive manufacturing (VAM), computed axial lithography (CAL), parallel two-photon polymerization, and diode-based additive manufacturing (DiAM) as well as new materials including graphene aerogel and nanoporous gold.

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5:00 AM *S.EL05.04.01  
**Plasmonic Material Platforms for Tunable Nanophotonic Devices**  
Alexandra Boltasseva, Deesha Shah, Soham Saha and Vladimir Shalaev; Purdue University, United States

In the field of tunable optics, transparent conducting oxides (TCOs) have heralded a new generation of all-optical switches. The extraordinary enhancement of reflection modulation by epsilon-near-zero materials has paved the way for lithography-free all-optical switches in the telecommunication regime. We have demonstrated reflection modulation of up to 40% with optical pump-powers in the millijoules/cm² range, utilizing planar films of aluminum-doped zinc oxide [1]. Furthermore, we have demonstrated the addition and subtraction of the optically induced nonlinearities utilizing simultaneous intraband and
interband pumping, performing operations in the sub-picosecond timescale [2]. We have also demonstrated low power optical switching with cadmium oxide in the mid-infrared regime, where the free-carrier-induced changes in the refractive index can achieve reflection modulation up to 135% with pump-powers as low as 1.3 mJ/cm². Finally, we have brought together low-loss dielectrics such as undoped ZnO and metals such as titanium nitride in hybrid metal-dielectric resonators to demonstrate broadband optical switching in the near-infrared wavelengths, achieving reflection modulation over 50% with relaxation times in the order of 2 picoseconds [3].

Transdimensional materials (TDMs) are yet another material platform gaining traction for dynamically tunable nanophotonic devices. The optical responses of atomically thin plasmonic films can be engineered by precise control of their structural and compositional parameters. This unique tailorability establishes TDMs as an attractive material for the design of tailorable and dynamically switchable metasurfaces [4]. Transition metal nitrides (TMNs) are ideal materials to investigate the tailorable properties of plasmonic films with thicknesses of just a few monolayers. The optical and electrical properties of smooth, epitaxial, TiN ranging from 2 to 10 nm have been characterized by ellipsometry and Hall measurements [5]. Although the metallicity decreases in smaller thicknesses, the thinnest film (2 nm) still retains a carrier density of 10^{22}cm^{-3} and is plasmonic at visible wavelengths. We have also explored the role of oxidation, and strain through first principles density functional (DFT) calculations, providing a way to tailor the optical response [6]. Gate dependent Hall measurements on a 1 nm film also reveals extreme tunability of the carrier concentration (up to 8.5%).

TCOs and TMNs have been reported as promising material platforms for actively tunable nanophotonic devices. While our results have long established TCOs as a major player for ultrafast, switchable metasurfaces, our progress in developing tunable atomically thin TiN demonstrates the potential for tunable plasmonics based on TDMs.


5:30 AM S.EL05.04.02
Transdimensional Photonic Lattices of High-Index Nanoantennas and Layered Materials Fatih Ince, Viktoriia Babicheva and Soham Saha; University of New Mexico, United States

Planar optical elements with efficient light control at the nanoscale can be designed based on transdimensional photonic lattices that operate in the translational regime between two and three dimensions. Such transdimensional lattices include 3D-engineered nanoantennas supporting multipole Mie resonances and arranged in the 2D arrays to harness collective effects in the nanostructure [1]. Optical antennas made out of van der Waals material with naturally-occurring hyperbolic dispersion is a promising alternative to plasmonic and high-refractive-index dielectric structures in the practical realization of nanoscale photonic elements. The antenna made out of hexagonal boron nitride (hBN) possesses different multipole resonances enabled by the supporting high-k modes and their reflection from the antenna boundaries. The full range of the resonances is demonstrated for the hBN cuboid antenna, a decrease of reflection from the array, and highly directional resonant scattering from antennas pairs. We show that transdimensional lattices consisting of resonant hBN antennas in the engineered periodic arrays have great potential to serve as functional elements in ultra-thin optical components and photonic devices. We show that a periodic array of particles with a large imaginary part of their permittivity (LIPP) can support well-defined modes localized within the particle, with the spectral position of the modes mainly defined by the array period. It has been known for a long time that a non-zero imaginary part of the permittivity enables propagating surface modes at the interface of materials with positive permittivities, known as Zenneck modes. Recently, it has been demonstrated that transition metal dichalcogenides (TMDC) layers support different kinds of propagating Zenneck waves defined by the layer thickness and interfaces with air and substrate [2]. Here, we show that localized Zenneck modes are possible on subwavelength particles and that the particles can serve as antennas for direction light scattering, reflection suppression, and Kerker-effect applications. To illustrate a possibility to control light, we show that simultaneous excitation of the several particle multipole resonances (electric dipole and quadrupole) allows for achieving significant reflection suppression and observation of the generalized lattice Kerker effect [3]. Materials with LIPP are common in nature, including TMDCs and lossy metals, titanium, chromium, and others.
Acknowledgment. This material is based upon work supported by the Air Force Office of Scientific Research under Grant No. FA9550-19-1-0032.


5:45 AM *S.EL05.04.04
Flat Optics—From Metasurfaces to New Cameras Federico Capasso; Harvard University, United States

Metasurfaces enable arbitrary control of the wavefront of light by locally manipulating amplitude, phase and polarization.\(^1\),\(^2\) I will present advances in components (metalenses and structurally birefringent phase plates) that have enabled the realization of high-performance polarization sensitive cameras and depth cameras. Recent developments have enabled the practical realization of optical elements in which the polarization of light may vary spatially.\(^3\) We recently presented an extension of Fourier optics—matrix Fourier optics—for understanding these devices and apply it to the design and realization of metasurface gratings implementing arbitrary, parallel polarization analysis.\(^4\) We show how these gratings enable a compact, full-Stokes polarization camera without standard polarization optics. Our single-shot polarization camera requires no moving parts, specially patterned pixels, or conventional polarization optics and may enable the widespread adoption of polarization imaging in machine vision, remote sensing, and other areas.\(^5\) We also have demonstrated a compact depth sensor that is inspired by the jumping spider.\(^6\) It combines novel metalens optics, which modifies the phase of incident light at a subwavelength scale, with efficient computations to measure depth from image defocus. The sensor uses a metalens to split the light that passes through an aperture, and concurrently form two differently-defocused images at distinct regions of a single planar photosensor. We have demonstrated a system that deploys a 3mm-diameter metalens to measure depth over a 10cm distance range, using fewer than 700 floating point operations per output pixel., at video rates.\(^7\) Compared with previous passive depth sensors, our metalens depth sensor is compact, single-shot and requires a small amount of computation. This integration of nano-photonics and efficient computation brings artificial depth sensing closer to being feasible on millimeter-scale, micro-Watts platforms such as microrobots and micro-sensor networks.

1. N. Yu and F. Capasso *Nature Materials* 13, 139 (2014)

6:15 AM *S.EL05.04.05
Nanoprinting-Enabled Scalable Metasurfaces for Hyperlens, Metalens and Metahologram in the Visible Junsuk Rho; Pohang University of Science and Technology, Korea (the Republic of)

Metamaterials consist of subwavelength structured units have demonstrated many promising applications in optics and photonics. However, practical applications of metamaterials have been prohibited by low productivity of conventional fabrication methods. Electron beam lithography has been widely used to realize metamaterials which operate in the visible because necessary critical dimension of the unit structure is smaller than the diffraction limit of typical photolithography. Most metamaterials have been demonstrated by electron beam lithography whereas it is not suitable for practical uses due to high cost and ridiculously low throughput. Here, we demonstrate large scale metamaterials operating in the visible based on nanoimprint lithography (NIL) which allows rapid replication of nanostructures. An efficient and convenient new imaging device made of a wafer-scale array of spherical hyperlenses are demonstrated based on NIL. Hyperlens is a metamaterial based imaging device whose super-resolving power comes from the hyperbolic dispersion relation in anisotropic media, which enables the sub-diffraction-limited objects to be resolved in the far-field [1]. However, hyperlenses suffered from the extreme difficulties in fabrication process and objects placement which restrict the practical uses of the hyperlenses devices. To overcome this limitations, direct pattern transfer techniques using NIL is applied as implementing large-scale hyperlenses arrays is desirable [2]. We demonstrate 4-inch wafer-scale array of hyperlenses using NIL and it is integrated into a conventional microscopy system for imaging hippocampal neurons with resolution down to 151 nm, much smaller than the diffraction limit of conventional imaging systems [3]. We also demonstrate one-step fabrication method based on NIL to realize dielectric metasurfaces [4,5]. Despite many advantages of conventional NIL, it is still inefficient to fabricate dielectric metasurfaces because conventional NIL requires
secondary operations such as thin film deposition and etching, which reduce productivity, substrate compatibility and cost competitiveness of NIL. To overcome the limitations, we develop nanoparticle composite (NPC) that consists of high-index nanoparticle inclusions in UV-curable resin. The refractive index of the NPC can be controlled by the volume fraction of the inclusion. Since the transferred pattern by the NPC can itself work as metasurfaces due to sufficiently high refractive index of the NPC, dielectric metasurfaces can be realized by a single step of NIL without any secondary operations. Experimental demonstration of metahologram and metalenses verify the feasibility of our method, thereby we believe our approach provides a promising opportunity to manufacture metamaterials for practical uses.

References

6:45 AM *S.EL05.04.06
Scalable Nanophotonic Methods to Identify Pathogens and Their Interactions Jennifer A. Dionne; Stanford University, United States

Bacterial infections such as pneumonia, staphylococcus, and streptococcus do not often make headlines, yet they are responsible for more deaths than AIDS and many cancers and rank among the most expensive medical conditions to treat. Bacterial identification and antibiotic susceptibility testing can span days, even in state-of-the-art laboratories using the most advanced technologies, delaying the use of targeted antibiotics and accelerating the spread of infectious disease. Here, we present development of scalable, clinically-compatible nanophotonic imaging tools for bacterial pathogen identification, their antibiotic susceptibility, and their interactions with immune cells. First, we combine Raman spectroscopy and deep learning to accurately classify bacteria by both species and antibiotic resistance in a single step. We design a convolutional neural network (CNN) for spectral data and train it to identify 30 of the most common bacterial strains from single-cell Raman spectra, achieving antibiotic treatment identification accuracies exceeding 99% and species identification accuracies similar to leading mass spectrometry identification techniques. Our combined Raman-CNN system represents a proof-of-concept for rapid, culture-free identification of bacterial isolates and antibiotic resistance. Then, we introduce a new class of in vivo optical probes to monitor the forces between pathogens and immune cells with high spatial and temporal resolution. Our design is based on upconverting nanoparticles that, when excited in the near-infrared, emit light of a different color and intensity in response to nano-to-microNewton forces. The nanoparticles are sub-30nm in size, do not bleach or photobleach, and can enable deep tissue imaging with minimal tissue autofluorescence. We present the design, synthesis, and characterization of these nanoparticles both in vitro and in vivo; both chronic and acute cytotoxicity assays are used to confirm biocompatibility. Long-term, our Raman-CNN platform and optical-force sensors could enable several advances for personalized medicine and mitigation of infectious disease, allowing patients to receive the appropriate drug at the appropriate dosage and for the appropriate duration.

7:15 AM S.EL05.04.09
Reuse of Si Substrates for Selective-Area Epitaxy of Large-Area III-V Nanowire Array-Based Flexible Infrared Photodetectors Alireza Abrard, Mohadeseh A. Baboli, Thomas S. Wilhelm and Parsian K. Mohseni; Rochester Institute of Technology, United States

During the last decade, III-V semiconductor nanowires (NWs) have received great research interest due to their promising potential for next-generation electronic, optoelectronic, and photonic devices. One of the main challenges for epitaxially-grown III-V NWs, however, is their high manufacturing cost, which can be divided to two individual categories: (1) the cost of starting III-V substrates and (2) the cost of pre-epitaxy fabrication associated with substrate patterning. Large-scale integration of III-V NW-based technologies requires novel nanofabrication strategies that mitigate both cost streams. Wafer costs can be substantially reduced simply through growth of III-V NWs on foreign substrates such as silicon or graphene, instead of on bulk III-V wafers. One strategy for simultaneously reducing fabrication complexity and pre-growth processing costs is to reuse Si substrates with existing predefined growth masks for selective-area epitaxy (SAE) of III-V NW arrays. Here, we present wafer-scale, bottom-up SAE growth of InAs NW arrays and fabrication of flexible NW-based infrared (IR) photodetectors realized through delamination of embedded NW arrays and reuse of Si substrates with predefined growth masks. Silicon (111) substrates are patterned by conventional photolithography to obtain pores with 0.5 µm diameters and 1 µm pitch in SiO2 growth masks of 55 nm thickness. Next, InAs NW arrays are grown via the SAE approach using
metalorganic chemical vapor deposition (MOCVD). Trimethyl-indium (TMIn) and arsine (AsH₃) were used as precursor gases for the supply of In and As growth species, respectively, at a set-point growth temperature of 700 °C. A two-step growth technique is introduced, whereby a separate nucleation step using a TMIn flow rate of 16 μmol/min precedes a NW growth step at a TMIn flow rate of 0.77 μmol/min. This procedure is necessary for optimization of pore occupation toward a global NW yield of >85%, with NW aspect ratios of ~15. The InAs NW arrays are embedded in various polymer membranes and mechanically delaminated from their growth substrates, then bonded to carrier substrates for subsequent device fabrication. The polymer-embedded NW array exfoliation process leaves NW bases with heights of ~50 nm below the fracture plane attached to the growth surface. Consequently, five different substrates restoration processes are investigated prior to substrate-reuse. It is observed that the best results for re-growth of daughter generation InAs NW arrays on reused Si substrates can be realized when no additional wet etching, chemical treatment, or mechanical polishing steps are introduced between subsequent re-growth runs, as the remaining NW bases serve as SAE growth sites. Direct re-growth on reused Si substrates results in vertical extension of existing NW bases and growth of InAs NWs with aspect ratios >80 under the same growth conditions as the primary run with comparable global NW yield. For fabrication of flexible IR photodetectors using both primary and subsequent generation InAs NW arrays, a unique process flow is reported, which enables NW transfer yields of ~100% and preserves the original position and orientation of as-grown NWs. This work demonstrates that multiple generations of InAs NW-based devices can be fabricated through reuse of a single, templated Si substrate, without introduction of intermediate substrate restoration processes such as wet etching or chemical mechanical polishing. This approach can serve as an effective strategy toward growth and fabrication of large-area, high-efficiency, low-cost, flexible, and wearable device applications in III-V nanoelectronics, optoelectronics, and photovoltaics.

7:30 AM S.EL05.04.10
Large-Scale Thermoregulatory Material Inspired by Cephalopods Mohsin Ali Badshah¹, Erica M. Leung¹, Christopher Moore², Panyiming Liu¹, Marlon Pinedo¹ and Alon Gorodetsky¹,¹,¹; ¹University of California, Irvine, United States; ²Chapman University, United States

Low-cost, large-area thermal management is desirable for the operation of many modern technologies including smart clothing, electronic circuits, building environments, and outdoor equipment to control heat flow. Inspired by the space blanket and the dynamic skin of cephalopods, we have demonstrated a large-area, highly uniform, low-cost nanostructured material with tunable thermoregulatory and infrared properties. We have implemented scalable nanofabrication processes to achieve a material with an area > 500 cm², a > 40 % change in infrared transmittance and reflectance, and a dynamic environmental setpoint temperature window of ~ 8 °C. Due to characteristics of scalability and associated figures of merit, our material affords new scientific and technological opportunities not only for adaptive optics and thermoregulation but also for any platform that would benefit from dynamic control of infrared radiation and heat.

SESSION S.EL05.05: Growth and Solution-Processed Approaches for Scalable Photonics
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

5:00 AM S.EL05.05.01
Effect of Defective Microstructure on the Reflective Structural Color of Self-Assembled Colloidal Crystals Tianyu Liu, Bryan VanSaders, Sharon C. Glotzer and Michael J. Solomon; University of Michigan–Ann Arbor, United States

We report the relationship between measures of the crystal quality of self-assembled colloidal crystal films and the intensity of their structural color. Structural color arises from geometric diffraction; it has potential applications in optical materials because it is more resistant to environmental degradation than coloration mechanisms that are of chemical origin. Structural color can be produced from self-assembled films of colloidal particles. To study the connection between crystal film quality and structural color intensity, we investigate the peak intensity and peak width of structural color reflection spectra as a function of defect density, film thickness and impurity concentration using a combined experimental and computational approach. Polystyrene microspheres are self-assembled into defect-laden colloidal crystals via solvent evaporation. Colloidal crystal growth via sedimentation is simulated with molecular dynamics and the reflection spectrum of simulated crystals is calculated using the finite-difference time-domain method. We examine the impact of several commonly observed defect types (vacancies, stacking fault tetrahedra, planar faults, and microcracks) on structural color peak intensity. We find that the
reduction in peak intensity scales with increased defect density; stacking fault tetrahedra have a particularly detrimental effect. The thickness profiles are characterized by cross-sectional scanning electron microscopy and profilometry. The reflective spectral response of the colloidal crystals is measured with a white light spectrophotometer. Our results show that reflectance of structural color increases as a function of the crystal thickness, until a plateau is reached at thicknesses greater than about 10 μm. The plateau reflection is 83.2 ± 2.8%; this value is significantly less than the 100% reflectivity predicted for a fully crystalline material; the difference is caused by defects present in the experimental crystal structures. Finally, we manipulate the defect structures of colloidal crystals by introducing differently sized particles that function as impurities. As the concentration of the impurity is increased, the measured intensity of structural color reflection decreases by amounts that we correlate with the observed microstructure. These findings can guide the design of optical materials which tune the intensity of structural color.

5:15 AM *S.EL05.05.02
Processes for Hyper-Scaling Electronic and Photonic Device Manufacturing Michael A. Filler; Georgia Institute of Technology, United States

This talk will overview our work toward two general-purpose nanomanufacturing processes for the hyper-scaling of semiconductor nanowire-based electronic and photonic devices: SCALES and Geode. The SCALES process (Selective CoAxial Lithography via Etching of Surfaces) leverages chemical differences between compositionally distinct nanowire segments to yield polymer surface masks with nanoscale precision. The Geode process utilizes an unconventional substrate – the interior surface of hollow silica microcapsules lined with the metal nanoparticles that seed nanowire growth – to increase the throughput of nanowire production by orders-of-magnitude. These processes are part of an emerging platform for the massively scalable fabrication and deployment of high-performance semiconductor materials and devices for applications in electronics and photonics.

5:45 AM *S.EL05.05.03
Scalable Self-Assembly of Nanoparticles into 3D Hierarchal Microspheres Shanying Cui, Xin Guan, Christopher Roper and Adam Gross; HRL Laboratories, United States

Sprayable coatings for frequency-selective reflectors or absorbers in the visible and infrared are enabled by heterogeneous and hierarchal microspheres, such as high index contrast core-shell structures or spherical Bragg stacks. However, such nano- to micron-scale architecture can be difficult to achieve for a wide array of visible and infrared transparent materials. In this talk, we describe a fast, scalable, and material-agnostic process to make heterogeneous structures for omnidirectional IR reflection and scattering. We apply our self-assembly method to multiple nanoparticle compositions (SiO2, TiO2, LiYF4, InP, PbSe) and nanoparticle shapes (spheres, pyramids, hexagonal prisms), yielding smooth and uniform microspheres 10-100 micrometers in diameter. The microspheres have a high nanoparticle packing density and do not contain any IR-active organic ligands or binders. Next, we show control of the microsphere internal structure by co-assembling two materials, yielding structures ranging from core-shell to a periodic mixture. Diffuse reflectance measurements of the assembled microspheres show that MWIR scattering is enhanced for materials with differing refractive indexes (Δn > 1). Our process is capable of making scattering microspheres at a rate of >0.1 grams / minute, thereby leveraging existing nanoparticle capabilities and unique properties and scaling them into macroscale coatings (m² surfaces) for optical and photonics applications.

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6:15 AM S.EL05.05.04
Mechanochemical Conversion Kinetics of Red Phosphorus to Black Phosphorus for Optoelectronic Applications Samuel V. Pedersen1,2, Florent Muramutsa1, Joshua D. Wood1, Chad Husko2, David Estrada1,2 and Brian Jaques1,2; 1Boise State University, United States; 2Center for Advanced Energy Studies, United States; 3Wood Technical Consulting, United States; 4Iris Light Technologies, United States

With the promise of novel optoelectronic devices using black phosphorus (BP), there is a need for a large-scale synthesis method for BP compatible with on-chip integration. Herein, we attain large scale mecanochemical conversion of red phosphorus (RP) to black phosphorus (BP) via high energy ball milling. During the milling process, the collisions of hardened steel media rapidly compress amorphous RP into crystalline, orthorhombic BP flakes, with a conversion yield >95% for up to 5 g of bulk BP powder. Commercial scale-up of BP production can be extrapolated by empirically derived conversion kinetics from lab scale, high energy ball mills. BP’s milling conversion kinetics, as monitored via ex situ XRD,
shows a sigmoidal behavior best described by the Avrami rate model. For <60% conversion, BP is rapidly formed at the expense of RP following an autocatalytic behavior with induction times proportional to the milling intensity. At ≥60% conversion, milling conversion rate suddenly decreases, indicative of a growth mechanism change with presumably a higher activation energy, thereby requiring higher impact energies for complete conversion. Further, by comparing the specific milling dose, namely, the energy input required for the phase transformation to reach completion, versus the conversion progress, we can determine the optimum milling conditions. We therefore ascertain the BP specific milling dose (50 kJ/g) and minimum impact energy (25 mJ/impact), both necessary to scale up production and minimize the power consumed in a tumbler milling vessel. Finally, the as-synthesized BP powder exfoliates more readily than single crystal BP sources in solution, as revealed by concentrations obtained from UV-Vis absorption under the same exfoliation conditions. The milled, converted BP solution is roughly 6-fold the concentration of the single crystal solution. High energy ball milling is demonstrated as a large scale, viable synthesis route for BP.

6:30 AM *S.E.L.05.05.06
Plasmonic Devices Based on Collapsible Nanofingers Wei Wu; University of Southern California, United States

Nano-gap structure has attracted great scientific interests. For example, plasmonic nanostructures with nano-gaps concentrate light to a small volume, which can lead to many potential applications. While it is theoretically predicted that the optimal plasmonic hot spot is a gap of less than 1 nanometer between two metallic particles, there is still no manufacturing technology to reliably fabricate it with high-precision and controllability at practical cost. In this work, we present a novel fabrication technique that combines both top-down and bottom-up process to produce large-area nanogap structures with atomic-precision gap size control. First, two layers of photoresist and one liftoff layer were spin-coated on substrates, then Nanoimprint (NIL)\(^1\), Reactive Ion Etching (RIE) and Metal Deposition were utilized to achieve desired metal patterns. Afterwards, uncovered areas were etched by RIE to form high aspect ratio nanofingers and Atomic Layer Deposition was used to grow selected thin dielectric layer outside nanofingers. After dripping ethanol onto samples, high aspect ratio nanofingers would be driven to collapse by capillary force during ethanol evaporation. By manipulating nanofinger heights and dielectric thicknesses, gap size down to 0.8 nm can be precisely defined after finger collapsing and such structure can be utilized as an ideal platform to study the rich sciences of plasmon and quantum effect. For example, we experimentally demonstrated that tunneling barrier height across the gap can be adjusted by using appropriate gap spacer materials and gap sizes.\(^2\) As a result, plasmonic enhancement can be strongly affected since the electron tunneling mechanism is the most essential part in determining the plasmonic enhancement factor. It was found that as the tunneling barrier height is decreased, the enhancement of electron tunneling manifests itself in a wider optimal gap, a redshift of the plasmon frequency with increasing gap size was also observed when the gaps narrowed to sub-5 nm range\(^2\). Moreover, many photonic applications have been studied and implemented intensively based on our controllable nanogap structures. Those include plasmonic enhanced fluorescence, single-molecule label-free sensing by SERS\(^3\) and plasmonic enhanced photocatalysis.

Reference:
two chambers separated by a slit-shaped nozzle, with the bottom chamber held under vacuum (< 1 Torr). The nanomaterial is accelerated to a velocity of several hundred meters/second as it and the aerosol background gas are forced through the nozzle, resulting in the formation of a curtain of nanoparticles directed into the downstream chamber. A substrate is passed through the curtain, and the nanomaterial collides with and adheres to the substrate, forming a thin coating. AIDA’s unique approach to film formation enables independent control over nearly every aspect of the coating’s morphology. As a dry spray technique, there are no inherent limitations on the thickness. Coatings ranging in thickness from a sub-monolayer to >1mm have been produced with dynamic deposition rates as high as 6 mm-m/min. By adjusting the particle impact velocity, the porosity of the coating can be controlled between 5% and 95%. This enables control over film properties like the refractive index, heat transfer coefficient, and dielectric constant. By changing the angle of impaction, the surface roughness of the film can be tuned between 0 nm and >100 nm allowing engineers to tune the effective surface energy of the coating. Combining this intimate control of film morphology with the wide range of nanomaterials compatible with AIDA allows engineers to produce complex, multi-layered, multi-component, and multi-functional films using a single platform.

As a case study, we will showcase an AIDA system capable of depositing on 14”x24” substrates that uses an in-situ non-thermal plasma reactor to synthesize metal-oxide nanoparticles (SiO₂, TiO₂, and ZnO) and produce a multi-layered coating that is simultaneously highly photocatalytic (self-cleaning) and anti-reflective for use in PV module glass. The composition of each layer will be tuned to maximize the photocatalytic self-cleaning effect. The thickness and refractive index of each layer will be precisely tuned to optimize its anti-reflective properties and provide a 3% transmittance gain compared to uncoated glass. The surface roughness of each layer will be tuned to promote adhesion and provide the desired water contact angle on the top surface to enhance self-cleaning.

7:15 AM S.E.L.05.05.08
Physically Assisted Chemical Assembly for Large-Area, Reproducible Near-Field Response Regina Ragan; University of California, Irvine, United States

Single molecule (SM) detection represents the ultimate limit of chemical detection. Over the years, many experimental techniques have emerged with this capacity. Yet, SM detection and imaging methods require large, reproducible spectral datasets in order to benefit from chemometric methods. We will present a scalable chemical assembly platform for plasmonic and metamaterial architectures that yield reproducible optical response. For example, surface enhanced Raman scattering spectroscopy (SERS), with extensive applications in biosensing, is demonstrated to be particularly promising because Raman active molecules can be identified without recognition elements and is capable of SM detection. Yet quantification at ultralow analyte concentrations requiring detection of SM events remains an ongoing challenge, with the few existing methods requiring carefully developed calibration curves that must be redeveloped for each analyze molecule. We will present work where we demonstrate that using 2-dimensional physically activated chemical (2PAC) self-assembly, we can achieve reproducible enhancement factors of 10⁹ over 1 cm². 2PAC crosslinks nanoparticles into discrete assemblies with a small molecule linker, where the crosslinking reaction is driven by electrohydrodynamic flow at on a substrate surface. The hotspots observed in a 2PAC fabricated assembly have gap spacing is 0.9 nm, corresponding to the length of the chemical crosslinker. Large area SERS maps are acquired from these 2PAC assembled surfaces from analyte dissolved in water and even complex biological media.

One of the most important applications of contemporary machine learning, i.e., image analysis, has remained relatively untouched by the SERS community. We will show that a combination of large area and reproducible SERS substrates with a CNN model is used to address the long standing challenge in SERS: quantification of sub-nanomolar analyte concentrations. A convolutional neural network (CNN) model when applied to bundles of reliable SERS spectra yields a robust, facile method for concentration quantification down to 1 fM using SM detection events. The demonstrated limit of blank (LOB) is 1 fM for Rhodamine 800, with a limit of quantification (LOQ) of 10 fM. Furthermore, the model’s predicted concentrations have an average r² value of 0.958 over 6 orders of magnitude as determined by k-folds cross validation. A key advantage of the analysis is its compatibility with transfer learning, the use of large datasets to train a model and then generalize this pretrained model to new molecules quickly with significantly smaller datasets. The uniformity of enhancement factor is essential for our approach, as large variance in the dataset not only increases the variance in predictions, but also requires more data for convergence and prevents a transfer learning approach. Generalization of the CNN model to other analytes using transfer learning is demonstrated with methylene blue. Transfer learning achieves good results with as few as 50 8x8 pixel maps. Thus entire datasets are acquired quickly, requiring just 5.3 minutes of total laser exposure time per concentration to train a robust model that is much faster and more scalable than required for building SM concentration regression models. This demonstrates a proof of concept for hyperspectral CNN image analysis of SERS, which could be broadly applicable within SERS, especially in the biological setting where classification of images could improve analysis of bacteria that are already imaged with SERS. We will also present results showing this approach is able to differentiate susceptible and
 Bottom up self-assembly of block copolymers (BCPs) offers a scalable, economical alternative to lithography for producing large area, highly uniform nanopatterns required for engineering materials with tailored light-matter interactions. At their typical scales (~20-50 nm feature spacing), thin film BCP nanopatterns may be used to generate deep subwavelength like nanotextures that reduce visible reflectance to < 1% [1,2], or nanoholes that improve light trapping in photovoltaics at carrier selective rear contacts [3]. Nevertheless a greater latitude for optical property engineering would be possible using self-assembled BCP patterns at length scales commensurate with visible wavelengths of light in order to exploit optical diffraction and resonance effects. This is prohibited by exponentially slower ordering kinetics in the ultrahigh higher molecular weight BCPs (> 1000 kg/mol) required for this scaling. Here we report dramatically accelerated ordering afforded by blending in very low molecular weight (~3 kg/mol) homopolymer plasticizers. These formulations enable a 10× reduction in the time required to achieve ordered nanopatterns with periods > 200 nm. Subsequent reactive ion etching demonstrates that these nanopatterns are readily transferrable to other materials. Exemplar applications such as structural colors made possible using these self-assembled patterns will be described.

References:

Research performed at the CFN and NSLS-II, U.S. DOE Office of Science Facilities at Brookhaven National Laboratory under Contract No. DE-SC0012704.
The history of coloration has been proceeded by trials and development of many technologies for selectively splitting the light. Structural coloration, among them, has grown up as a potential candidate alternating traditional pigments/dyes coloration since their great durability, sustainable production, and fine color tuning by controlling materials and dimension. As this property, structural color facilitates the creation of security features for anti-counterfeiting. However, conventionally, most of them have used metal/dielectric materials to make a resonating system at a specific wavelength and polarization condition which demands complex fabrication processes such as e-beam lithography or ion beam lithography technology. Even though this system can be suitable to an ultra-high definition structural color display, it is limited to only a few millimeter scales or less. To apply into a realistic application such as banknote, luxury products, or customer goods, it is necessary to make it over centimeter scale with a flexible medium.

In this work, to break through these significant flexibility/scalability limitations, we developed polarization distinguishable covert display with ultrathin porous nanocolumns (PNCs) on a metal film by glancing angle deposition (GLAD) method. Particularly, the unique property of this covert display showed powerful functions which provide a hurdle to the inadvertent viewing of stored optical information without compromising their aesthetic. This structure with lossy PNCs on a metal film makes a non-trivial phase shift at the interfaces causing short reflection path and finally shows strong resonance [1]. Furthermore, the PNCs fabricated with GLAD produce anisotropic media and has different effective complex refractive index causing different resonating condition depending on polarization direction [2]. Using this concept, we designed polarization distinguishable color filters with a variety of materials and dimensions with rigorous coupling wave analysis (RCWA) method. In this process, we obtained an enlarged color range occupying over 80% of standard RGB area. In this color response, some showed a small color difference ($\Delta E$), the other showed a large color difference following polarization angle. Additionally, we confirmed this result is originated from human eye’s spectral responses according to between tristimulus value and reflectance spectra having a single minimum. Using these results, we designed optical data label (i.e., QR code) which shows inadvertent viewing in the naked eye (under unpolarized light), on the other hand, this label can be selectively detected by polarized light. For practical application, we designed this label into daily consumer goods with the color matching between labels and products to avoid compromising aesthetics of products and successfully demonstrated onto wine bottleneck, food packaging with confirming the authentication process. As a multi-functional color display, we demonstrated a colorimetric detection. Due to the low complex refractive index of porous medium, PNCs are sensitive to subtle external environment change. Consequently, PNCs reveal a sensitive color change according to background refractive index or additional layer thickness change. Using this unique property, we presented colorimetric detection with external change for volatile organic compounds (VOCs) and humidity.


* Invited Paper
SESSION S.EL06.12: Live Keynote and Lightning/Flash: Nanophotonic Materials and Devices
Session Chairs: Marcelo Davanco, Abram Falk, Ning Li and Fengnian Xia
Sunday Afternoon, November 29, 2020
S.EL06

7:15 PM *S.EL06.04.01
2D Layered Semiconductors as Optical Gain Materials for On-Chip Photonic Applications Cun-Zheng Ning1,2, Zhen Wang1, Hao Sun1 and Qiyao Zhang1; 1Tsinghua University, China; 2Arizona State University, United States

One of very important requirements for nanolasers intended for future photonic chips is the energy consumption. The amount of total energy input to a laser required to a large extend is determined by the critical value of carrier density, at which optical gain occurs. In conventional semiconductors, optical gain is based on electron-hole plasma and it occurs at the so-called transparency density, which is near and above the Mott density, typically on the order of $10^{12}$ per square centimeter. In 2D materials, the orders of magnitude larger exciton binding energy make it possible to have optical gain based on various excitonic species such as excitons, trions, bi-excitons etc. Such optical gain can occur at density levels several orders of magnitude smaller, well below the Mott density. In this talk, we will discuss possibilities of such optical gain in 2D materials that could occur at extremely low injection levels. As an example, we will discuss our recent experimental results [1] on trion gain in a gated 2D MoTe2 structure that occurs at the density level ~5 orders of magnitude smaller than the Mott density.

References:

7:35 PM *S.EL06.04.03
Utilizing Geometry and Topology for Enabling Integrated Chiral Photonics Ritesh Agarwal; University of Pennsylvania, United States

With ever-increasing demand for faster speeds, copper interconnects that ferry vast amounts of data in computing devices are expected to significantly lag behind the requirements, thereby creating a bottleneck for moving data rapidly. Optical interconnects provide a promising alternative, allowing much faster speeds and larger bandwidths between different components, on or off chip. Three most critical interconnect components are light sources, waveguides and detectors. Currently, optical communication is performed by a combination of these devices where the information is encoded in photon number and frequency (intensity and bandwidth). However, no information is encoded in intrinsic properties of photons, i.e., photon spin and also possibly the orbital angular momentum modes of the light beam. Analogous to the idea of spintronics, where the spin degree of freedom of electrons are utilized to encode and transmit information, similar enhancements in the data processing capabilities of the optical interconnect systems can be obtained if information can be encoded in photon spin. Photons, have two fundamental spin polarizations reflected in their polarization state, i.e., right and left circular polarization. To fully utilize more degrees of freedom of light to enhance the data processing capabilities of network systems, it is required that new light sources, detectors and waveguides be designed and fabricated that can produce, transmit and detect light with complex polarizations. We will discuss some recent developments in our laboratory towards the development of topological waveguides that can route photonic signals based on photon spin and also photodetectors that are sensitive to circular polarization (photon spin). Either by protecting or breaking certain symmetries in (meta)materials, new photonic materials and devices will be discussed that can enable a new generation of photonic devices that can encode, transmit and sense information encoded in spin and angular momentum modes of light that are promising for the development of integrated chiral photonic systems with extremely large data processing capabilities.

7:55 PM *S.EL06.10.01
Diffractive Optical Neural Networks Designed by Deep Learning Aydogan Ozcan and Deniz Mengu; University of California, Los Angeles, United States

We introduce a physical mechanism to perform machine learning by demonstrating a Diffractive Deep Neural Network (D^3NN) architecture that can all-optically implement various functions following the deep learning-based design of passive layers that work collectively. We created 3D-printed diffractive networks that implement classification of handwritten digits and fashion products as well as the function of an imaging lens, spectral filters and wavelength demultiplexers at terahertz spectrum. This passive diffractive network can perform, at the speed of light, various complex
functions that computer-based neural networks can implement, and will find applications in all-optical image analysis, feature detection and object classification, also enabling new camera designs and optical components that perform unique tasks using diffractive neural networks designed by deep learning.

8:15 PM S.EL06.01.07
An Efficient Opto-Electronic III-V Nanowire Based Implementation of the Insect Brain Central Complex

David Winge¹, Heiner Linke¹, Magnus Borgström¹, Barbara Webb², Stanley Heinze¹ and Anders Mikkelsen¹; ¹Lund University, Sweden; ²University of Edinburgh, United Kingdom

Insects are capable of amazing tasks, such as traveling across hundreds of kilometers of unfamiliar terrain to pinpoint a specific breeding ground, with a brain that contains 100 000x fewer neurons than our own brains, using merely a few drops of nectar as energy supply. At each moment during navigation, the insect has to decide whether to turn right, left or go straight. Integrating sensory inputs, internal states, and previous experience, it computes its current and intended headings, compares the two, and initiates steering. A brain region called the central complex (CX) is essential for these tasks. Recently a biologically constrained computational model of the CX has been generated that can carry out these computations to generate homing behavior [1]. This computational model has been shown to carry out homing tasks using speed and heading information of limited precision, with considerable noise in the circuit. Containing less than 100 neurons, it can serve as a model system to understand the functionality and prove the efficiency of novel hardware solutions.

To realize this CX model we propose and theoretically model a network circuit based on existing III-V nanowire (NW) opto-electronic components that are optically connected through a shared waveguide structure. The neural weights of the mutual interconnections are achieved by controlling the far-field light emission patterns and by strategic placement of the nano-components. As a result, there is no need for physical connecting wires between the network nodes. Each node in this network is capable of both receiving, evaluating and sending optical signals, while power consumption is minimized by using high efficiency concepts from NW based photovoltaics and quantum dot emitters [2-6]. We show that the modeled coupling efficiencies and activation functions well suffice to facilitate excellent navigation in the insect neuron model [1]. As the efficiencies and electrical performance of the NW devices are known, we can estimate the energy consumption per operation and find that this should be at least as low as in biological processes [7] and beyond standard hardware implementations.

Our detailed simulations of the fundamental device component, which will act as a basic sigmoid neural node throughout the network, show how it performs the tasks of receiving light inputs, evaluating them and emitting a light output. We model it as an electrical circuit which is parametrized and solved by a standard SPICE solver (Ngspice). We describe the subcomponents using an Ebers-Moll model and the Shockley diode equation, respectively, where the relevant properties were calculated using a drift-diffusion model with thermionic boundary conditions in COMSOL. A NW phototransistor was optimized to give enough gain to broadcast the signal to the next layer using a realistic non-radiative Shockley-Read-Hall recombination lifetime for NWs of 1.34 ns [8] as well as Lorenz-Mie scattering theory. Extensive finite difference time domain (FDTD) simulations (Lumerical), were made for the central part of the CX model which consists of eight fully interconnected components. They were placed in a shared asymmetric waveguide which was optimized for the target wavelength. As the neurons of this layer are interconnected, input-output isolation is non-trivial, and the FDTD model was used to optimize the network in this respect. The gain of the fundamental device ensures both cascadeability and proper fan-out without the need of critical biasing [9], and the analog architecture carries a built-in robustness to noise [1].


8:19 PM S.EL06.10.03
Optical Signal Processing Using Dielectric Metasurfaces

Jinghui Yang, Wenqi Zhu, Lu Chen, Cheng Zhang, Henri J. Lezec and Amit Agrawal; National Institute of Standards and Technology, United States

Optical analog computing provide solutions with fast and power-efficient performance for big-data applications. Recently investigated metamaterials and metasurfaces demonstrate potentials in mathematical operations over wavelength-scale footprint. We extend the functionality of using nonlocal dielectric metasurface to perform spatial differentiation equation for
imaging processing. The study pave the way towards ultrathin devices for optical signal processing.

8:23 PM *S.EL06.09.01
SiGe/Si-Based Electro-Optic Platform for Microwave-Optical Transduction Jason S. Orcutt; IBM T. J. Watson Research Center, United States

Superconducting qubit quantum computers offer new capabilities for quantum information processing, but require < 50 mK environments and near complete isolation from outside noise sources. To enable quantum information to be exchanged with these systems outside of cryogenic conditions by means of higher energy photons, many approaches towards microwave-optical transduction are being explored by the research community. Three-wave mixing in linear electro-optic materials is a particularly appealing approach due to the inherent simplicity and elimination of excess noise sources that are introduced by intermediate states present in many alternative technologies. However, material microwave and optical loss rates have limited conversion efficiency below 50% in demonstrations to date. Here, I present IBM’s work towards integrating low loss SiGe/Si optical resonators with the low loss Nb-on-Si microwave resonators that have been developed for superconducting qubits. An effective linear electro-optic coefficient for coupling the microwave and optical fields by three wave mixing is induced by strongly biasing the microwave resonators to leverage the DC Kerr effect in Si and SiGe. For 1 MHz-rate transducers, the resulting microwave-optical coupling strength is calculated to be sufficient to reach the peak conversion efficiency condition. Demonstrating microwave-optical transduction in this platform is then dependent on achieving low defectivity fabrication of the proposed SiGe/Si optical waveguides. I will present a study of this materials problem and an analysis of the overall optimal transducer design.

This work was funded by LPS/ARO under CQTS program, contract number W911NF-18-1-0022.

8:43 PM *S.EL06.05.02
A New Paradigm for Scalable Quantum Optical Circuits—On-Chip Single Photon Source Arrays Integrated with Optically Resonant Metastructure Based Light Manipulating Units Anupam Madhukar1, Jiefei Zhang1, Swarnabha Chattaraj1 and Styuan Lu2; 1University of Southern California, United States; 2IBM T.J. Watson Research Center, United States

Manipulation of single photons generated deterministically from pre-specified sources on-chip to create multiphoton entangled states remains a major goal to be reached in photonic quantum information processing platforms. Notable advances have been made in single photon source performance and demonstrations of photon interference and entanglement based largely upon finding suitable single photon source from an otherwise random ensemble. The lack of scalable on-chip architectures stands as a major obstacle to realizing compact quantum information technologies.

In this talk I will present our proposition [1,2] and continuing efforts [3,4] to realize such a photonic chip built upon a unique class of spatially-ordered arrays of surface-curvature driven mesa-top single quantum dots (MTSQDs) [1,3]. These AlGaAs/InGaAs MTSQDs exhibit spectral uniformity as low as 1.8nm across 5×8 arrays, exhibit pairs of as-grown QDs having emission energy within 200μeV, and single photon purity > 99%. Following a planarization overlayer growth, these buried single photon sources (SPS) provide the essential platform for subsequent lithographic fabrication of emitted photon light manipulating units (LMUs). The LMUs exploit either the well-developed photonic 2D crystal approach or a new approach we introduced [1,2] based upon Mie-like resonances in interacting subwavelength-sized dielectric building block (DBB) based metastructures. The in-plane single Mie-like resonance of the metastructure (the LMU) provides all the needed basic photon manipulation functions to create controlled on-chip interference and entanglement [4]; enhancement of the SPS emission rate (Purcell enhancement), directional emission (local antenna), state-preserving propagation, path bifurcation (beam-splitting), and beam combining. Findings of our combined theoretical analysis, numerical simulations, and experimental studies of such SPS-LMU primitives — the essential building unit for quantum optical circuits — will be presented. The emphasis is on the holistic approach to proof-of-principle demonstration of the needed on-chip multifunctional system with its built-in trade-offs rather than the best of any individual light manipulation function.

The work is supported by the US Army Research Office (W911NF1910025) and the Air Force Office of Scientific Research (FA9550-17-1-0353).
In recent years, InAs quantum dot lasers have proven themselves resilient against crystalline defects that form during heteroepitaxial growth of III-Vs on silicon. The three-dimensional confinement and reduced in-plane diffusion lengths of carriers in quantum dots relative to quantum wells are the source of this resiliency, but alone these characteristics are not sufficient for demonstrating commercially reliable performance for lasers on silicon. Quantum dot active regions must be utilized together with highly optimized III-V/Si buffers to reduce the dislocation density to achieve acceptable device reliability.

In this talk, recent advances in GaAs/Si templates will be highlighted along with the resulting enhancements in laser reliability. Over the last three years, we have produced InAs quantum dot lasers on GaAs/Si templates with dislocation densities ranging from $3 \times 10^8$ cm$^{-2}$ down to $< 7 \times 10^6$ cm$^{-2}$ by optimizing thermal cycling procedures and strained filter layers. As the material has improved, the extrapolated mean-time-to-failure has increased several orders of magnitude to $>10,000,000$ h at 35°C and $>50,000$ h at 60°C.

In addition to improving laser reliability, the improvements in material quality have virtually closed the performance gap relative to native substrate lasers before aging. At dislocation densities of $7 \times 10^6$ cm$^{-2}$, low threshold, high power, and high efficiency lasers are readily achievable with continuous wave operation above 100°C. These improvements justified more advanced laser implementations and investigations into the dynamic performance of quantum dot lasers on silicon. The unique atom-like density of states of quantum dots has historically enabled unique properties such as an insensitivity to optical feedback, highly engineerable gain bandwidth, and ultrafast gain recovery; these properties unique to quantum dots have enabled Fabry-Perot lasers with complete insensitivity to optical feedback, high performance mode-locked lasers operating at 20 GHz with 64 channels capable of 4.1 Tbps transmission below the forward error correction (FEC) limit, and 100 GHz colliding pulse mode-locked lasers capable of 0.9 Tbps transmission below the FEC limit. Achieving each of these results required a high degree of optimization in the epi design and materials growth to obtain uniform distributions of high-quality quantum dots, which will be emphasized in the talk.

Further improving performance and, in particular, demonstrating commercially viable reliability at elevated temperatures $>60^\circ$C will require additional efforts to reduce the dislocation density in the laser active region. Our efforts to push the threading dislocation density $< 2 \times 10^6$ cm$^{-2}$ while also reducing the buffer thickness will be discussed in addition to efforts to address misfit dislocations that have been observed in the laser active region. Given the much larger cross-section of material that interacts with a misfit dislocation relative to a thread, it is believed that addressing these defects is critical to reaching the goal of native substrate level device reliability on a silicon substrate.

Mid-infrared light sources are key components for future chemical sensing, on-chip optical interconnect and LIDAR technologies. GeSn alloys can be synthesized under silicon CMOS compatible conditions. Therefore, GeSn can open pathways for miniaturization of mid-infrared devices such as on-chip molecular sensors, optical interconnects and thermal cloaking devices. Most importantly, direct band gap GeSn is a promising material for on chip integration of light emitters. Previous research on GeSn films has shown mid-infrared lasing at increasing temperatures, initially (in 2015) at less than 90K and, in more recent reports, at or near room temperature. It has also been shown that GeSn nanowires with high-Sn content exhibit strong direct-gap photoluminescence at room temperature. Compared to GeSn thin films, GeSn nanowires are less constrained to lattice match with misfitting (e.g. Ge, Si) substrates and therefore may achieve higher Sn contents without strain and defects that promote non-radiative recombination. Additionally, unlike in a planar GeSn film where the emission angle is limited to $< 13^\circ$ by its high refractive index (n=4), GeSn nanowires provide a platform to design the optical density of states for highly efficient light extraction directly from the light emitting material. GeSn nanowires may also constitute a superior medium for absorption and generation of photocarriers.

We demonstrate room temperature mid-infrared photodetection using resonantly absorbing GeSn/Ge core/shell nanowire photonic crystals. We have synthesized GeSn/Ge core/shell single crystal nanowires with 4% Sn that exhibit strong direct-
bandgap photoluminescence at room temperature. The vertical nanowire photodetection device consists of arrays of nanowires in-filled with PMMA insulating layer, an ITO top contact and an aluminum bottom contact. Using full wave FDTD simulations, we optimize Mie resonances of individual nanowires (300 nm in diameter) at the desired bandgap wavelength. We further engineer the absorption with nanowires arranged in photonic crystal arrays. To synthesize the nanowire device, gold catalysts were patterned on Ge [111] substrate and then two step VLS growth was performed to synthesize Ge core and GeSn shell. We performed photocurrent characterization with an FTIR spectrometer at room temperature. The photocurrent spectrum of Ge nanowire photonic crystals indicates a four-fold enhancement due to resonant absorption, with the photocurrent spectrum tunable by varying the photonic crystal geometry.

For emission, we designed, synthesized and characterized mid-infrared emission of GeSn/Ge core-shell nanowires with 9-12% Sn. Full wave FDTD simulations reveal that the geometry of GeSn/Ge nanowires can be tuned to be resonantly scattering at the direct band gap energy. To further enhance light extraction, we use FDTD simulations to optimize GeSn/Ge nanowires in photonic crystal arrays to maximize the density of photonic states above the light line within the emission spectrum. The light emitting device consists of a similar device structure to that which is useful for photodetection. Room temperature photoluminescence characterization reveals both direct- and indirect-gap emissions in the mid-infrared, while electroluminescence characterization at 200 mA/cm reveals direct bandgap emission at both 2000 nm and 2300 nm. Optimization of nanophotonic light extraction efficiency will be discussed.

SESSION S.EL06.13: Live Panel Discussion: Intelligent Photonics
Session Chair: Volker Sorger
Monday Afternoon, November 30, 2020
S.EL06

1:45 PM S.EL06.01.01
Information Processing with Silicon Photonics Bhavin J. Shastri1, Bicky A. Marquez1, Alexander N. Tait2, Thomas Ferreira de Lima2, Hsuan-Tung Peng2, Chaoran Huang2, Mario Miscuglio1, Volker J. Sorger1 and Paul R. Prucnal1; 1Queen's University, Canada; 2Princeton University, United States

Artificial Intelligence (AI) is transforming our lives in the same way as the advent of the Internet and cellular phones has done. AI is revolutionizing the healthcare industry with complex medical data analysis, actualizing self-driving cars, and beating humans at strategy games such as Go. However, it takes thousands of CPUs and GPUs, and many weeks to train the neural networks in AI hardware. Traditional CPUs, GPUs, and neuromorphic (i.e., brain-inspired) electronics such as the IBM TrueNorth and Google TPU, may find it a challenge to train the neural networks of the future.

Neuromorphic photonics has experienced a recent surge of interest over the last few years, promising orders of magnitude improvements in both speed and energy efficiency over digital electronics using: artificial neural networks, spiking neural networks, and reservoir computing. By combining the high bandwidth and efficiency of photonic devices with the adaptive, parallelism and complexity attained by methods similar to those seen in the brain, photonic processors have the potential to be at least ten thousand times faster than state-of-the-art electronic processors while consuming less energy/computation.

We will provide an overview of neuromorphic photonic systems and their application to optimization and machine learning problems. We will discuss the physical advantages of photonic processing systems and describe underlying device models that allow practical systems to be constructed. We also describe several real-world applications for control and deep learning inference. Lastly, we will discuss scalability in the context of designing a full-scale neuromorphic photonic processing system, considering aspects such as signal integrity, noise, and hardware fabrication platforms. This talk is intended for a wide audience and hopes to teach how theory, research, and device concepts from neuromorphic photonics could be applied in practical machine learning systems.

2:05 PM S.EL06.01.04
Ferroelectric Phase Shifters in Silicon Photonics for Novel Types of Optical Computing Jean Fompeyrine, Felix Eltes, Stefan Abel and Bert Offrein; IBM Research Zurich, Switzerland

Integrated photonic circuits efficiently combine multiple optical functions on a single physical platform, such as guiding, modulating, splitting, or detection of light. The integration of these functions removes barriers for designing and realizing large optical circuits, as present when using discrete components like bulky lenses or mirrors in tabletop optical networks.
With the rise of silicon photonics, integrated photonic circuits (PICs) are becoming increasingly large and highly functional, eventually allowing unprecedented concepts of photonic computing. Examples are integrated photonic quantum processors, microwave photonic filters and processors, and optical accelerators to train and execute neural networks.

An important building block in integrated optical circuits is an efficient link between the optical and electrical domain. Well-known examples of such links are integrated high-speed modulators to convert electrical signals into optical signals at very high-speed, and low-power tuning elements to compensate for variations in the device operation temperature and for device-to-device variations during fabrication. To enable such electro-optic links, the two most widely used physical effects are the plasma-dispersion effect and Joule heating. Although these effects are attractive to use due to their compatibility with standard photonic fabrication processes, their performance in integrated devices is intrinsically limited by high insertion losses and high-power dissipation.

Over the past decade, we established an alternative electro-optic switching technology by embedding a Pockels material into silicon-based photonic devices [1]. We reached this goal by developing a process to fabricate ferroelectric barium-titanate (BTO) thin films on silicon substrates using advanced epitaxial deposition techniques and by developing a BTO process technology [2]. We correlated the electro-optical properties of the thin films with their structural properties such as porosity and crystalline symmetry to show guidelines for improving the functional properties. By realizing integrated hybrid BTO/silicon devices, we demonstrated record-high, in-device Pockels coefficients of >900 pm/V. The Pockels effect in BTO-based photonic devices indeed enables extremely fast data modulation at rates beyond >40 Gbps and ultra-low-power electro-optic tuning of silicon and silicon-nitride waveguides. We also show ways of how to integrate and use BTO in plasmonic slot waveguide structures for very compact optical devices. With the development of a wafer-level integration scheme of single-crystalline BTO layers to a 200 mm process [3], we could demonstrate a viable path to combine the BTO-technology with existing fabrication routes.

With major breakthroughs in the past years, BTO has emerged as a strong candidate for a novel generation of electro-optic devices. Major achievements of the BTO technology will be covered in the presentation, ranging from important materials aspects, device development, integration concepts, and novel applications in the area of quantum computing, high-speed communication, and neuromorphic optical computing.


2:15 PM PANEL DISCUSSION

SESSION S.EL06.14: Live Keynote: Photonic Devices for Quantum Systems
Session Chairs: Kirsten Moselund and Noelia Vico Trivino
Monday Afternoon, November 30, 2020
S.EL06

2:45 PM *S.EL06.02.01
Manipulating Integrated Quantum Systems Using Classical Silicon Carbide Devices Christopher Anderson¹, Alexandre Bourassa¹, Kevin Miao¹ and David Awschalom¹,²; ¹University of Chicago, United States; ²Argonne National Laboratory, United States

The neutral divacancy (VV0) in silicon carbide (SiC) exhibits robust spin coherence and a high-quality near-infrared spin-photon interface in a material compatible with mature fabrication techniques. Here, we make use of this scalable semiconductor host and design electronic devices to manipulate embedded isolated quantum systems. Specifically, we create and isolate single spin defects in a commercial p-i-n diode [1]. This simple integration enables engineering of the defect’s charge environment and drastically reduces electric field noise. Surprisingly, the use of electrical gating mitigates spectral diffusion and achieves near-lifetime limited optical linewidths. Furthermore, by exploiting field confinement of the junction,
we show that the optical transitions can be gate-tuned by nearly a terahertz, revealing a spectral tuning range extending over 40,000 optical linewidths. This geometry may allow for spectral multiplexing of many quantum channels, and also provides a method for using electric fields combined with optical excitation for deterministic charge state control.

Applying gigahertz ac electric fields to SiC devices produces coherent interference in the form of Landau-Zener-Stückelberg fringes, arising from interactions between microwave and optical photons [2], even in the absence of a microwave resonator. We demonstrate lifetime-limited optical coherence and clock-like spin transitions with increased robustness against magnetic noise. Electrical driving of excited-state electron orbitals offers advantages over spin-based coupling and points towards new types of hybrid quantum systems. These results reveal new opportunities for electrical manipulation of spin-based quantum systems in scalable SiC electronic devices.

This work was done in collaboration with S. L. Bayliss, A. L. Crook, P. J. Mintun, S. J. Whiteley, G. Wolfowicz, H. Abe, A. Gali, V. Ivady, T. Ohshima, G. Thiering, P. Udvarhelyi.


3:05 PM *S.EL06.05.01
Novel Semiconductor Structures for Single Photon Emission and Detection Anna Fontcuberta i Morral; Ecole Polytechnique Federale de Lausanne, Switzerland

Semiconductor materials play a pivotal role in photonic technology. They can be used as tailored photon emitters and detectors. Combined with plasmonic structures and photonic design, their efficiency and functionality is further extended. In this talk we show how compound semiconductor nanostructures such as nanowires and nanoscale membranes (nanofins) can be used for both single photon emission and detection [[1],[2]]. We will explore what kind of heterostructures are optimal for these applications. We will also elucidate how photon detection can be optimized by the nanowire geometry and the combination with plasmonic structures [2,[3]]. Finally, we will also explore materials with a lower production and environmental cost and how to fabricate them at a similar functionality than compound semiconductors. We will show how GeSn thin films and nanostructures have the potential to become the leading material in mid-infrared photodetection.


3:25 PM *S.EL06.03.01
Quantum Neural Network—Connecting Quantum and Brain with Optics Yoshihisa Yamamoto1,2; 1Stanford University, United States; 2NTT Research, Inc., United States

Combinatorial optimization problems are ubiquitous in our modern life. Classical examples include lead optimization in drug and biocatalyst discovery, resource optimization in wireless communications, logistics and scheduling, sparse coding for compressed sensing, deep machine learning in artificial intelligence and fintech. These optimization problems can be mapped to either Ising model, XY model or k-SAT problem, which is a main reason why various Ising, XY and SAT solvers have been proposed and implemented in the recent years.

We have focused on the network of optical parametric oscillators to construct coherent Ising machines, XY machines and SAT solvers. An optical parametric oscillator (OPO) operates as a quantum analog device at below oscillation threshold and also functions as a classical digital device at above oscillation threshold. We need not only quantum computational resources, such as quantum correlation and quantum suppression of chaos, but also classical computational resources, such as spontaneous symmetry breaking and exponential amplitude amplification, to build an efficient optimizer. An OPO is almost a unique choice of device to realize such quantum and classical computational resources simultaneously at room temperatures.

A study on quantum state engineering in an OPO with measurement-feedback control was dated back to 1980s [1,2]. A
PPLN waveguide OPO device was identified as a stable and efficient generator for squeezed vacuum state pulses at communication wavelengths in 1990s [3]. An idea of using the pitchfork bifurcation and spontaneous symmetry breaking at OPO threshold as an irreversible decision making process was proposed in 2013 [4] and experimentally implemented [5,6]. A scalable architecture based on measurement-feedback coupling scheme was subsequently demonstrated [7,8]. Those devices already demonstrated competitive performance against modern heuristics [9] and quantum annealers [10]. In this talk, we will discuss the principles of quantum-classical crossover and future prospects of quantum neural network.


SESSION S.EL06.01: Intelligent Integrated Photonics
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL06

5:00 AM *S.EL06.01.01
Information Processing with Silicon Photonics Bhavin J. Shastri1, Bicky A. Marquez1, Alexander N. Tait2, Thomas Ferreira de Lima2, Hsuan-Tung Peng2, Chaoran Huang2, Mario Miscuglio3, Volker J. Sorger1 and Paul R. Prucnal2; 1Queen's University, Canada; 2Princeton University, United States; 3George Washington University, United States

Artificial Intelligence (AI) is transforming our lives in the same way as the advent of the Internet and cellular phones has done. AI is revolutionizing the healthcare industry with complex medical data analysis, actualizing self-driving cars, and beating humans at strategy games such as Go. However, it takes thousands of CPUs and GPUs, and many weeks to train the neural networks in AI hardware. Traditional CPUs, GPUs, and neuromorphic (i.e., brain-inspired) electronics such as the IBM TrueNorth and Google TPU, may find it a challenge to train the neural networks of the future.

Neuromorphic photonics has experienced a recent surge of interest over the last few years, promising orders of magnitude improvements in both speed and energy efficiency over digital electronics using: artificial neural networks, spiking neural networks, and reservoir computing. By combining the high bandwidth and efficiency of photonic devices with the adaptive, parallelism and complexity attained by methods similar to those seen in the brain, photonic processors have the potential to be at least ten thousand times faster than state-of-the-art electronic processors while consuming less energy/computation.

We will provide an overview of neuromorphic photonic systems and their application to optimization and machine learning problems. We will discuss the physical advantages of photonic processing systems and describe underlying device models that allow practical systems to be constructed. We also describe several real-world applications for control and deep learning inference. Lastly, we will discuss scalability in the context of designing a full-scale neuromorphic photonic processing system, considering aspects such as signal integrity, noise, and hardware fabrication platforms. This talk is intended for a wide audience and hopes to teach how theory, research, and device concepts from neuromorphic photonics could be applied in practical machine learning systems.

5:30 AM S.EL06.01.02
Intelligent Computing with Photonic Phase Change Material Memory Mario Miscuglio1, Juejun Hu2, Alexander V. Kildishev3 and Volker J. Sorger1; 1George Washington University, United States; 2Massachusetts Institute of Technology, United States; 3Purdue University, United States

Here we propose and emulate a photonic neural network whose neuron’s non-volatile weighting functionality is realized
through an engineered hybrid Ge$_2$Sb$_2$Se$_4$Te$_1$-silicon Mach Zehnder modulator photonic memory with thermoelectrical programmability. The network can effortlessly perform inference tasks with high accuracy at the speed-of-light.

Machine-learning tasks performed by neural networks demonstrated useful capabilities for producing reliable, and repeatable intelligent decisions. Integrated photonics, leveraging both component miniaturization and the wave-nature of the signals, can potentially outperform electronics architectures when performing inference tasks. However, the missing photon-photon force challenges non-volatile photonic device-functionality required for efficient neural networks. Here we present a novel concept and its optimization of multi-level non-volatile photonic memories based on an ultra-compact (<4µm) hybrid phase-change-material Ge$_2$Sb$_2$Se$_4$Te$_1$-silicon Mach Zehnder modulator, with low insertion losses (3dB), to serve as node in a photonic neural network (NN). An optimized electro-thermal switching mechanism is engineered, causing phase transitions in the GSST, induced by heating by tungsten contacts, which allows weight updating functionality of the network. We show that a 5 V pulse-train (<1µs, 20 pulses) applied to a serpentine contact produces crystallization and a single pulse of longer duration (2µs) amorphization, used to set the analog synaptic weights of a neuron. Emulating an opportunely trained 100 x 100 fully connected multilayered perceptron NN with these weighting functionalities embedded as photonic memory, shows a 92% inference accuracy and robustness towards noise when performing predictions of unseen data. Exploiting the low delay interconnectivity of photonic integrated chips and the non-volatile transitions of PCM, an all-optical (AO) trained NN, that effortlessly performs dot-product functionality can be achieved, enabling intelligent computing functionality at the time-of-flight of the photon.

The written portion of the material corresponds to discrete states of the weighting function, and assuming a stable writing resolution of about 500 nm, same achieved by optical writing, the total amount of available quantized resolution is given by 8 distinct states (3-bit), which can be further improved by extending the device length by multiple of $L_\pi$. Additionally, this is a reversible process, which allows to update the weights after many execution times. Interestingly, this solution is not hindered by insertion losses, which are negligible due to the rather low absorption coefficient of GSST at 1550 nm, and the total losses (~3dB) are mainly caused by the balancing mechanism (in this first analysis straightforwardly obtained achieved by placing a gold contact on the balancing arm). As an interim conclusion, this novel PCM MZM features by a micrometer-compact (<4µm) footprint and low insertion losses (3dB), enabling the implementation of a deep NN which comprises multiple nodes.

As preliminary study, we estimated the functionality of the proposed perceptron as main unit of the NN, by emulating its behavior in a 3-layer fully connected NN implemented in the Google Tensorflow tool and, as an initial example, for the MNIST data set. Nonlinear activation functions (here considered as electro-optic) are placed between two consecutive layers on each input connection. The network is trained both without and with noise of the weights and NLAF. Our hypothesis, confirmed by preliminary studies on the network is that, when we allow for a certain amount of noise during the training, the model during the inference stage, becomes more robust and the network can perform inference with up to 92% accuracy showing robustness towards noise.

5:45 AM S.EL06.01.03
Mie Resonant Dielectric Metastructure Based Optical Circuits Integrated with Quantum Dot Single Photon Source for on-Chip Scalable Quantum Information Processing Swarnabha Chattaraj1, Jiefei Zhang1, Siyuan Lu2 and Anupam Madhukar1; 1University of Southern California, United States; 2IBM Thomas J. Watson Research Center, United States

Realization of on-chip scalable optical quantum information processing (QIP) systems requires optical circuits built around arrays of single photon sources (SPSs) to manipulate the emitted photons and enable interference between photons from distinct SPSs resulting in entanglement. Towards such a goal we have reported a new class of on-chip quantum dot array - grown on lithographically fabricated mesas designed to exploit the attendant surface stress gradient driven adatom migration during MBE growth thus termed mesa-top single quantum dots (MTSQDs) [1]. These MTSQDs, we have demonstrated, are ~99% pure SPSs [2] that are readily integrable with on-chip light manipulating units (LMUs) that provide the needed multiple functions of enhancing the emission rate of the SPS and the directionality of the photon emission in the horizontal direction, on-chip propagation, splitting and recombining to enable on-chip interference towards entanglement. So far attempts towards creating such LMUs (mostly resonant cavity and waveguide) have been based on photonic crystal membrane structures and exploit departure from Bragg scattering to provide localized photon modes for individual cavity or waveguides thus facing the challenge of strict mode-matching between these components. In contrast, in this talk we present an approach to realizing all the required light manipulating functions based on metastructures made of subwavelength size dielectric building blocks (DBBs) where a common collective Mie resonance of the interacting DBBs is exploited to provide all the needed light manipulating functions simultaneously [3, 4, 5]. These Mie resonances are fundamentally different from
Bragg scattering as they are typically broad in spectrum, with a typical Q~100- that alleviates the strict requirements of spectral and spatial matching between the network components and with the SPS emission mode. Moreover, Mie resonances are less sensitive to effect of fabrication disorders that introduce aperiodicity in the array. Furthermore, the spectral broad nature of the Mie resonances allows controlled interference between the electric and magnetic modes resulting in directionality of photon emission and propagation without strong field localization—an effect that is unique to this class of LMUs. Importantly, providing all the needed light manipulating functions using the same collective Mie mode circumvents issue of mode mismatch between the components of the optical circuit including the SPS, and thus allows design and realization of large-scale circuits.

Aimed at the above noted objective of on-chip nanophotonic systems, in this talk we will present finite element method (FEM)-based design and simulation of the response of an MTSQD-DBB integrated optical circuit that exploits the dominant collective magnetic and electric dipole mode to provide the MTSQD emission rate enhancement (Purcell effect) ~5 as well as emission directionality (the nanoantenna effect), lossless on-chip propagation, beam-splitting, and beam-combining [4, 5]. We show that such structures enable on-chip interference of photons resulting in path entanglement between the two MTSQD SPSs at large distances. Finally, we will present FEM simulations of direct coupling of two SPSs via an intermediate lossless collective Mie mode over on-chip distances much longer than the wavelength. We show that such coupling can result in a super-radiant state involving on-chip SPSs at a distance resulting in a ~2 fold enhanced decay rate [5]. This emergent super-radiant state in such SPS-SPS coupled system is maximally entangled, and thus may act as a potential resource for on-chip QIP.

This work is funded by ARO W911NF-15-1-0025

6:00 AM *S.EL06.01.04
Ferroelectric Phase Shifters in Silicon Photonics for Novel Types of Optical Computing Jean Fompeyrine, Felix Eltes, Stefan Abel and Bert Offrein; IBM Research Zurich, Switzerland

Integrated photonic circuits efficiently combine multiple optical functions on a single physical platform, such as guiding, modulating, splitting, or detection of light. The integration of these functions removes barriers for designing and realizing large optical circuits, as present when using discrete components like bulky lenses or mirrors in tabletop optical networks. With the rise of silicon photonics, integrated photonic circuits (PICs) are becoming increasingly large and highly functional, eventually allowing unprecedented concepts of photonic computing. Examples are integrated photonic quantum processors, microwave photonic filters and processors, and optical accelerators to train and execute neural networks.

An important building block in integrated optical circuits is an efficient link between the optical and electrical domain. Well-known examples of such links are integrated high-speed modulators to convert electrical signals into optical signals at very high-speed, and low-power tuning elements to compensate for variations in the device operation temperature and for device-to-device variations during fabrication. To enable such electro-optic links, the two most widely used physical effects are the plasma-dispersion effect and Joule heating. Although these effects are attractive to use due to their compatibility with standard photonic fabrication processes, their performance in integrated devices is intrinsically limited by high insertion losses and high-power dissipation.

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With major breakthroughs in the past years, BTO has emerged as a strong candidate for a novel generation of electro-optic devices. Major achievements of the BTO technology will be covered in the presentation, ranging from important materials aspects, device development, integration concepts, and novel applications in the area of quantum computing, high-speed communication, and neuromorphic optical computing.


7:00 AM S.EL06.01.06
Data-Driven Design for Optical Analog Computing Wenjin Xue and Owen Miller; Yale University, United States

In this work, we find precision layered-material optical designs that can perform state-of-the-art edge detection among compact-form-factor approaches, offering high efficiency and large angular bandwidth / numerical aperture. We identify these designs by two approaches: first, adjoint-based “inverse design” of the layered structures, for rapid optimization of many parameters, and second, by training the structures on software-based edge-detection algorithms that can be “learned” into the hardware itself. Optical computing platforms based on such layered media offer simpler integration and more compact form factors than structured or free-space alternatives. We identify the benefits and tradeoffs of ideal material properties—metal/dielectric, lossy/lossless—within these optimal designs, and discuss its generalization beyond edge detection to more general optical analog computing.

7:15 AM S.EL06.01.07
An Efficient Opto-Electronic III-V Nanowire Based Implementation of the Insect Brain Central Complex David Winge1, Heiner Linke1, Magnus Borgstrom1, Barbara Webb2, Stanley Heinze1 and Anders Mikkelsen1; 1Lund University, Sweden; 2University of Edinburgh, United Kingdom

Insects are capable of amazing tasks, such as traveling across hundreds of kilometers of unfamiliar terrain to pinpoint a specific breeding ground, with a brain that contains 100 000x fewer neurons than our own brains, using merely a few drops of nectar as energy supply. At each moment during navigation, the insect has to decide whether to turn right, left or go straight. Integrating sensory inputs, internal states, and previous experience, it computes its current and intended headings, compares the two, and initiates steering. A brain region called the central complex (CX) is essential for these tasks. Recently a biologically constrained computational model of the CX has been generated that can carry out these computations to generate homing behavior [1]. This computational model has been shown to carry out homing tasks using speed and heading information of limited precision, with considerable noise in the circuit. Containing less than 100 neurons, it can serve as a model system to understand the functionality and prove the efficiency of novel hardware solutions.

To realize this CX model we propose and theoretically model a network circuit based on existing III-V nanowire (NW) opto-electronic components that are optically connected through a shared waveguide structure. The neural weights of the mutual interconnections are achieved by controlling the far-field light emission patterns and by strategic placement of the nano-components. As a result, there is no need for physical connecting wires between the network nodes. Each node in this network is capable of both receiving, evaluating and sending optical signals, while power consumption is minimized by using high efficiency concepts from NW based photovoltaics and quantum dot emitters [2-6]. We show that the modeled coupling efficiencies and activation functions work well together to facilitate excellent navigation in the insect neuron model [1]. As the efficiencies and electrical performance of the NW devices are known, we can estimate the energy consumption per operation and find that this should be at least as low as in biological processes [7] and beyond standard hardware implementations.

Our detailed simulations of the fundamental device component, which will act as a basic sigmoid neural node throughout the network, show how it performs the tasks of receiving light inputs, evaluating them and emitting a light output. We model it as an electrical circuit which is parametrized and solved by a standard SPICE solver (Ngspice). We describe the subcomponents using an Ebers-Moll model and the Shockley diode equation, respectively, where the relevant properties were calculated using a drift-diffusion model with thermionic boundary conditions in COMSOL. A NW phototransistor was optimized to give enough gain to broadcast the signal to the next layer using a realistic non-radiative Shockley-Read-Hall recombination lifetime for NWs of 1.34 ns [8] as well as Lorenz-Mie scattering theory. Extensive finite difference time domain (FDTD) simulations (Lumerical), were made for the central part of the CX model which consists of eight fully interconnected
components. They were placed in a shared asymmetric waveguide which was optimized for the target wavelength. As the neurons of this layer are interconnected, input-output isolation is non-trivial, and the FDTD model was used to optimize the network in this respect. The gain of the fundamental device ensures both cascadeability and proper fan-out without the need of critical biasing [9], and the analog architecture carries a built-in robustness to noise [1].


7:30 AM *S.EL06.01.08
Spectrally Controllable Lasers for Information Processing Based on Nanophotonic Networks Dhruv Saxena¹, Alexis Arnaudon¹, Oscar Cipolato¹, Michele Gaio¹, Sophia Yaliraki¹, Dario Pisignano², Andrea Camposeo², Mauricio Barahona¹ and Riccardo Sapienza¹; ¹Imperial College London, United Kingdom; ²NEST, Istituto Nanoscienze-CNR, Italy

Nanophotonic networks, where light flows in a mesh of interconnected optical waveguides, can serve as an unconventional lasing cavity, supporting resonant modes that are formed by light propagation and interference across many network links. In this talk, I will discuss our recent efforts to make spectrally controllable lasers with nanostructured sub-wavelength networks [1]. The networks are made from polymer nanofibers that are doped with a laser dye and can lase over a wide range of frequencies, corresponding to many network modes. Interestingly, we can exploit mode competition in the network laser for spectral control and signal processing. For example, we can experimentally single-out a lasing frequency out of the spectral haystack by selectively illuminating a very small subset of the network links. This result is also predicted by a graph description of Maxwell’s equations, and a steady-state ab initio laser theory (netSALT) which is used to model the network laser. In particular, netSALT enables the design of the network topology for lasing and identification of the most important edges in the network that are necessary for sustaining a particular mode.


SESSION S.EL06.02: Quantum Defects Engineering
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL06

5:00 AM *S.EL06.02.01
Manipulating Integrated Quantum Systems Using Classical Silicon Carbide Devices Christopher Anderson¹, Alexandre Bourassa¹, Kevin Miao¹ and David Awschalom¹,²; ¹University of Chicago, United States; ²Argonne National Laboratory, United States

The neutral divacancy (VV0) in silicon carbide (SiC) exhibits robust spin coherence and a high-quality near-infrared spin-photon interface in a material compatible with mature fabrication techniques. Here, we make use of this scalable semiconductor host and design electronic devices to manipulate embedded isolated quantum systems. Specifically, we create and isolate single spin defects in a commercial p-i-n diode [1]. This simple integration enables engineering of the defect’s charge environment and drastically reduces electric field noise. Surprisingly, the use of electrical gating mitigates spectral diffusion and achieves near-lifetime limited optical linewidths. Furthermore, by exploiting field confinement of the junction, we show that the optical transitions can be gate-tuned by nearly a terahertz, revealing a spectral tuning range extending over 40,000 optical linewidths. This geometry may allow for spectral multiplexing of many quantum channels, and also provides a method for using electric fields combined with optical excitation for deterministic charge state control.

Applying gigahertz ac electric fields to SiC devices produces coherent interference in the form of Landau-Zener-Stückelberg fringes, arising from interactions between microwave and optical photons [2], even in the absence of a microwave resonator.
We demonstrate lifetime-limited optical coherence and clock-like spin transitions with increased robustness against magnetic noise. Electrical driving of excited-state electron orbitals offers advantages over spin-based coupling and points towards new types of hybrid quantum systems. These results reveal new opportunities for electrical manipulation of spin-based quantum systems in scalable SiC electronic devices.

This work was done in collaboration with S. L. Bayliss, A. L. Crook, P. J. Mintun, S. J. Whiteley, G. Wolfowicz, H. Abe, A. Gali, V. Ivady, T. Ohshima, G. Thiering, P. Udvarhelyi.


5:30 AM S.EL06.02.02
Tailoring of Defect Centers in 3C-SiC for Potential Application in Quantum Information In Situ During Sublimation Epitaxial Growth
Peter J. Wellmann and Michael Schöler; University of Erlangen, Germany

In recent years, vacancy related defect centers in SiC have been identified as optically active, high potential candidates for the application in devices in the field of quantum information. Often such defect centers have been created by means of ion or electron beam implantation followed by subsequent annealing. As a result, these materials remain defective from a structural point of view with deteriorate electronic properties. In this work we present a process to generate and tailor vacancy defect centers in-situ during sublimation epitaxial growth of 3C-SiC with preserved electronic properties. (i) By adaption of the growth rate we were able to tailor the concentration of the carbon vacancy defect VcVsi, VcCsi and Vc at the discrete optical transition energies between 1.138 eV, 1.233 eV and 1.278 eV, respectively. (ii) Using extreme annealing conditions, we observed the generation of the nitrogen vacancy defect (NcVsi)- at an optical transition energy of 0.884 eV. In our presentation we will introduce the processing of the special 3C-SiC layers, identify their structural properties using Raman spectroscopy and discuss the optical active defect centers by means of low temperature photoluminescence measurements.

SESSION S.EL06.03: Exploratory Photonic Concept
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL06

5:00 AM S.EL06.03.01
Quantum Neural Network—Connecting Quantum and Brain with Optics
Yoshihisa Yamamoto1,2; 1Stanford University, United States; 2NTT Research, Inc., United States

Combinatorial optimization problems are ubiquitous in our modern life. Classical examples include lead optimization in drug and biocatalyst discovery, resource optimization in wireless communications, logistics and scheduling, sparse coding for compressed sensing, deep machine learning in artificial intelligence and fintech. These optimization problems can be mapped to either Ising model, XY model or k-SAT problem, which is a main reason why various Ising, XY and SAT solvers have been proposed and implemented in the recent years.

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A study on quantum state engineering in an OPO with measurement-feedback control was dated back to 1980s [1,2]. A PPLN waveguide OPO device was identified as a stable and efficient generator for squeezed vacuum state pulses at communication wavelengths in 1990s [3]. An idea of using the pitchfork bifurcation and spontaneous symmetry breaking at OPO threshold as an irreversible decision making process was proposed in 2013 [4] and experimentally implemented [5,6]. A scalable architecture based on measurement-feedback coupling scheme was subsequently demonstrated [7,8]. Those devices already demonstrated competitive performance against modern heuristics [9] and quantum annealers [10]. In this talk, we will discuss the principles of quantum-classical crossover and future prospects of quantum neural network.


5:30 AM S.EL06.03.03
Quantum Mechanical Simulation and Modelling of Semiconductor Nanowires Quantum-Dots for Quantum Cryptography Application
Vihar P. Georgiev, Hamilton Carrillo-Nunez, Amretashis Sengupta and Asen Asenov;
University of Glasgow, United Kingdom

Physical unclonable functions (PUF) are considered as one of the most promising methods for hardware authentication. PUFs are typically compact devices providing a response when challenged that is linked to uncontrollable stochastic processes and physics variability that occur during hardware manufacturing. As a result, it is practically impossible to produce two identical devices, which is highly desirable for applications in cybersecurity. For example, an important source of statistical variability in semiconductor nano-electronics, which has a huge impact on the electrical characteristics of each device, is the random dopant distribution (RDD) within the structure. The stochastic nature of the RDD profile for each device leads to a unique electrical output for each device. Indeed, this is the main idea and strength behind PUFs based on quantum dots that can be fabricated using standard CMOS technology and processes. In addition, as the dimensions of the modern transistors range from a few to tens of nanometers, there is a unique opportunity to use quantum mechanical effects, such as confinement and tunneling, as another layer of security based on quantum effects. One possible device structure that can be fabricated using the standard CMOS process and that can be implemented in current electrical circuits is a quantum-dot-in-wire device, which is considered in this work. The dot device relies on tunneling of electrons through a barrier and for this reason it can be considered a device that provides a quantum fingerprint.

Our work shows quantum mechanical simulations of quantum-dots (QDs) embedded within Si and III-V nanowires. To capture the effect of statistical sources of variability, we simulated more than 100 automatically unique nanowire devices with differing numbers and positions of dopants, not only in the quantum dot but also at the source and the drain regions also. Our results reveal that the specific number of dopants and their positions give rise to unique current-voltage characteristics, providing unique signatures for use as the basis of physical unclonable functions (PUFs). Hence, unique current-voltage characteristics can be defined as quantum fingerprints and applied to problems in cybersecurity, such as authentication and identification. Here we have also established a link between the RDD position, the transmission spectra, current spectrum and local density of states. Our work captures the complex nature of the quantum effects in such ultra-small-scaled devices and it can be used for investigating quantum mechanical effects in not only the dot but also in conventional transistors. Moreover, adoption of hardware security devices for authentication is on the rise. The technology proposed here delivers a practical means to extract fingerprints from quantum confined systems that could provide robust security to current electronics.

5:45 AM *S.EL06.03.04
Large-Scale Coherent Ising Machine for Solving Combinatorial Optimization Problems
Hiroki Takesue; NTT Basic Research Laboratories, Japan

In recent years, Ising model solvers based on artificial spin systems have been studied intensively. A coherent Ising machine (CIM) is one of such systems in which the binary phase state of degenerate optical parametric oscillators (DOPO) is used to
represent an Ising spin. By using long-distance (typically 1 km) fiber cavity that contains a phase sensitive amplifier based on the 2nd or 3rd order nonlinear optical effect, we can generate thousands of time-multiplexed DOPO pulses. The “spin-spin” interaction is implemented by using a measurement-feedback scheme, with which we can effectively realize all-to-all connection among thousands of DOPO pulses. The networked DOPO pulses are most likely to oscillate at a phase configuration that best stabilize the whole network, which gives the solution to the given Ising problems. In this talk, I will describe the large-scale CIM developed by NTT, which could find solution to maximum cut problem of 2000-node graphs faster than a conventional digital computer.

6:15 AM S.EL06.03.06
Quantum Electrodynamical Density Functional Theory for Light-Matter Coupling of Molecules in Lossy Cavities
Derek Wang¹, Tomas Neuman¹, Johannes Flick¹,² and Prineha Narang¹; ¹Harvard University, United States; ²Flatiron Institute, United States

Light-matter coupling can e.g. influence chemical reactivity of molecules or modify transfer of energy through matter via formation of hybrid light-matter polaritonic states [1]. To elucidate the microscopic nature of such effects, we extend quantum electrodynamical density functional theory (QEDFT)--a first-principles, non-perturbative methodology for describing interactions between quantized light and matter [2]--by fully accounting for photonic losses in realistic optical cavities. We demonstrate that our method successfully addresses situations where the photonic losses dominate the dynamics of the excitations and show that the first-principles approach correctly predicts spectral response of such weakly coupled systems. We further apply the method to describe the cavity-induced interaction among electronic excited states, opening up new pathways in strongly-coupled molecular systems.

This work was supported by the DOE ‘Photonics at Thermodynamic Limits’ Energy Frontier Research Center under grant DE-SC0019140. DW is an NSF Graduate Research Fellow.


6:30 AM S.EL06.03.07
Chromatic and Panchromatic Nonlinear Optoelectronic CMOSFETs for CMOS Image Sensors, Laser Multiplexing, Computing and Communication
James Pan¹,²; ¹Advanced Enterprise and License Company, United States; ²Northrop Grumman Corporation, United States

A Photonic CMOS Field Effect Transistor includes an ultra low-resistance, high quantum efficiency laser fabricated in the MOSFET drain region, and multiple photon sensors or Avalanche Photo Diodes (APD) in the channel / well regions. The MOSFET, laser, and APD's are fabricated as one integral transistor. When a voltage is applied to the gate and a voltage is applied to the drain, both MOSFET and laser are turned on. Light emitted from the laser is absorbed by the APD to cause an avalanche breakdown. The high breakdown current flows into the drain to be a high output current. When the MOSFET is off, both laser and APD are switched off. Very low resistance and forward voltage lasers (VF near 0V) have been reported. With modulation doped junctions, bandgap engineered tunneling mechanisms, and low temperature selective epitaxy process (III-V or II-VI direct bandgap semiconductors on Silicon), these very low resistance lasers or LEDs are suitable for being fabricated in the drain of the Photonic CMOSFETs.

The Photonic CMOSFETs not only generates an internal laser light, but also can be used as an external light sensor. The internal and external lights may be of the same or various different frequencies. In the former case, it is defined as Chromatic Photonic CMOS. In the latter case, it is defined as Panchromatic Photonic CMOS. The photon sensor, or avalanche photo diode in the Chromatic Photonic CMOSFETs is designed to absorb lights from a specified range of light spectrum. Narrow bandgap semiconductors, or wide bandgap semiconductors can be used to build photon sensors in the Photonic CMOSFETs for photon absorption from infrared to ultraviolet ranges.

Three light signals are processed by a Photonic MOSFET. The first signal comes from the drain voltage. The second signal comes from the gate voltage. The third signal comes from the external light. Light emitted from the built-in laser in the drain region is modulated by the gate and drain voltages, and absorbed by a specific photon sensor in the channel / well region. The external light is absorbed by another photon sensor in the well region, and generates a different light current. All these three light signals are processed and multiplexed by the Photonic CMOS transistor.

Nonlinear optical films can be fabricated in the well region of a Photonic MOSFET.

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The frequency or color of an input light signal is different from the output light due to multiple photon generations and absorptions in nonlinear optical films. The purpose of the nonlinear optical films is to increase the photon absorption rate and internal quantum efficiency of a Photonic MOSFET, and improve the laser multiplexing and communications. The nonlinear optical crystals can be fabricated on top of a total reflection layer (metal, or multiple refraction indices films), and below the CMOS channel region.

We will present information for device configurations of the Chromatic and Panchromatic Photonic CMOSFETs, and illustrate how light signals are modulated and multiplexed. We also include nonlinear optical crystals - and show the effects of such various nonlinear optics on the signal processing and light generation mechanisms. We will also provide evidence how the Chromatic Photonic CMOS technology may offer additional benefits for laser communication and more efficient signal processing systems.

Information regarding the Photonic CMOS output current (IDS) vs. input voltages (VGS and VDS) for various external and internal light spectrums will be presented. Techniques to optimize the internal quantum efficiency and photon absorption rate for various incident light frequencies will be illustrated. We will also present data for improved light sensitivity and changes in the output current due to the Photonic CMOS devices.

Finally, we will show the performance advantages of the Photonic CMOS for CMOS image sensor application - what are needed in the ROIC (Read Out Integrated Circuit) to process multiple multiplexed light signals.

SESSION S.EL06.04: Nanophotonics and Plasmonics
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL06

5:00 AM S.EL06.04.01
2D Layered Semiconductors as Optical Gain Materials for On-Chip Photonic Applications Cun-Zheng Ning1,2, Zhen Wang1, Hao Sun1 and Qiyao Zhang1; 1Tsinghua University, China; 2Arizona State University, United States

One of very important requirements for nanolasers intended for future photonic chips is the energy consumption. The amount of total energy input to a laser required to a large extend is determined by the critical value of carrier density, at which optical gain occurs. In conventional semiconductors, optical gain is based on electron-hole plasma and it occurs at the so-called transparency density, which is near and above the Mott density, typically on the order of $10^{12}$ per square centimeter. In 2D materials, the orders of magnitude larger exciton binding energy make it possible to have optical gain based on various excitonic species such as excitons, trions, bi-excitons etc. Such optical gain can occur at density levels several orders of magnitude smaller, well below the Mott density. In this talk, we will discuss possibilities of such optical gain in 2D materials that could occur at extremely low injection levels. As an example, we will discuss our recent experimental results [1] on trion gain in a gated 2D MoTe2 structure that occurs at the density level ~5 orders of magnitude smaller than the Mott density.

References:

5:30 AM S.EL06.04.02
Metal-Clad InP Cavities for Nanolasers on Si Preksha Tiwari1, Pengyan Wen1, Svenja Mauthe1, Noelia Vico Trivino1, Daniele Caimi1, Yannick Baumgartner1, Marilyne Sousa1, Markus Scherrer1, Chang-Won Lee2 and Kirsten Moselund1; 1IBM Research-Zurich (en dash), Switzerland; 2Hanbat National University, Korea (the Republic of)

Photonic integrated circuits offer high-speed data transmission and reduced energy per bit consumption. To meet the energy requirements for on-chip communication, a small form factor of the integrated III-V semiconductor emitters and detectors is crucial. Ding et al. suggest a laser volume of less than $\sim 2(2/\pi)^{3}$ to lower the energy to 10 fJ/bit.1 Scaling to these dimensions, however, is not possible for purely photonic devices, hence hybrid plasmonic-photonic cavities are being explored.2 Using template-assisted selective epitaxy (TASE), we can integrate high quality III-Vs epitaxially on Si, despite their lattice
and thermal mismatch. \cite{Schmid_2015} We have demonstrated InP microdisk lasers grown via TASE\cite{Mauthe_2019} and are currently integrating InGaAs quantum wells\cite{Baumgartner_2017} for emission above the Si absorption edge. Moreover, we have used intensity measurements of scattered photoluminescence (PL) in Au waveguides on InP to confirm that PL couples to surface plasmons and is guided in this materials system.\cite{Tiwari_2019}

In this work, we explore Au cladded III-V whispering gallery mode (WGM) cavities to further scale down the footprint of lasers. We design and fabricate InP cavities with resonances in the near-infrared using direct wafer bonding. InP is bonded on Si and (WGM) cavities with diameters from 100nm to 1000nm are dry etched subsequently. In a second step selected cavities are cladded with Au and the performance of purely photonic and metal-clad devices is compared. μ-PL spectroscopy is performed using a ps-pulsed supercontinuum laser at 750nm. A 100× objective is used to focus light on the sample from the top and collect the PL response. Measurements show evidence of lasing with resonant emission around 900 nm and a far field radiation pattern with fringes for cavities above 500 nm in diameter in both cases, with and without Au. For the Au cladded case, the threshold is higher. Indication of lasing is not observed for 400 nm wide purely photonic structures. However, for the cavities cladded with Au, a resonant peak emerges, indicating lasing at around 920 nm. Finite difference time domain simulations fit with our experimental observations and confirm a decrease in quality factor with decreasing diameter for the photonic cavities. Around 600 nm diameter, Q-factors become comparable to Au cladded cavities. When further reducing the cavity size, purely photonic cavities support no resonances anymore while cladded cavities do.

In summary, we observe evidence of lasing at room temperature for WGM cavities upon pulsed optical excitation. Preliminary results show that for smaller cavities one benefits from metal cladded designs and is able to scale down the emitter beyond the limit of purely photonic cavities. In a next step we will apply the same approach to InP cavities directly grown in silicon using TASE. This might further improve performance as the TASE growth results in atomically smooth sidewalls with reduced defect density.\cite{Ding_2015}

This work was supported by H2020 ERC project PLASMIC #678567 and by the Korea MSIT #2017R1A2B4007219.

SESSION S.EL06.05: Single Photon Emitters
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL06

5:00 AM *S.EL06.05.01
Novel Semiconductor Structures for Single Photon Emission and Detection  
Anna Fontcuberta i Morral; Ecole Polytechnique Federale de Lausanne, Switzerland

Semiconductor materials play a pivotal role in photonic technology. They can be used as tailored photon emitters and detectors. Combined with plasmonic structures and photonic design, their efficiency and functionality is further extended. In this talk we show how compound semiconductor nanostructures such as nanowires and nanoscale membranes (nanofins) can be used for both single photon emission and detection ([1],[2]). We will explore what kind of heterostructures are optimal for these applications. We will also elucidate how photon detection can be optimized by the nanowire geometry and the combination with plasmonic structures [2,[3]]. Finally, we will also explore materials with a lower production and environmental cost and how to fabricate them at a similar functionality than compound semiconductors. We will show how GeSn thin films and nanostructures have the potential to become the leading material in mid-infrared photodetection.


5:30 AM *S.EL06.05.02
A New Paradigm for Scalable Quantum Optical Circuits—On-Chip Single Photon Source Arrays Integrated with Optically Resonant Metastructure Based Light Manipulating Units  
Anupam Madhukar1, Jiefei Zhang1, Swarnabha Chattaraj1 and Siyuan Lu2; 1University of Southern California, United States; 2IBM T.J. Watson Research Center, United States

Manipulation of single photons generated deterministically from pre-specified sources on-chip to create multiphoton entangled states remains a major goal to be reached in photonic quantum information processing platforms. Notable advances have been made in single photon source performance and demonstrations of photon interference and entanglement based largely upon finding suitable single photon source from an otherwise random ensemble. The lack of scalable on-chip architectures stands as a major obstacle to realizing compact quantum information technologies.

In this talk I will present our proposition [1,2] and continuing efforts [3,4] to realize such a photonic chip built upon a unique class of spatially-ordered arrays of surface-curvature driven mesa-top single quantum dots (MTSQDs) [1,3]. These AlGaAs/InGaAs MTSQDs exhibit spectral uniformity as low as 1.8nm across 5×8 arrays, exhibit pairs of as-grown QDs having emission energy within 200μeV, and single photon purity > 99%. Following a planarization overlayer growth, these buried single photon sources (SPS) provide the essential platform for subsequent lithographic fabrication of emitted photon light manipulating units (LMUs). The LMUs exploit either the well-developed photonic 2D crystal approach or a new approach we introduced [1,2] based upon Mie-like resonances in interacting subwavelength-sized dielectric building block (DBB) based metastructures. The in-plane single Mie-like resonance of the metastructure (the LMU) provides all the needed basic photon manipulation functions to create controlled on-chip interference and entanglement [4]: enhancement of the SPS emission rate (Purcell enhancement), directional emission (local antenna), state-preserving propagation, path bifurcation (beam-splitting), and beam combining. Findings of our combined theoretical analysis, numerical simulations, and experimental studies of such SPS-LMU primitives — the essential building unit for quantum optical circuits — will be presented. The emphasis is on the holistic approach to proof-of-principle demonstration of the needed on-chip multifunctional system with its built-in trade-offs rather than the best of any individual light manipulation function.

The work is supported by the US Army Research Office (W911NF1910025) and the Air Force Office of Scientific Research (FA9550-17-1-0353).


2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
Advances in Quantum Dot Single Photon Sources

Yasuhiko Arakawa; The University of Tokyo, Japan

Since the first proposal of the semiconductor quantum dot in 1982[1], the quantum dots have been intensively investigated for both fundamental solid state physics and device applications. Advances of self-assembling crystal growth technology of quantum dots enabled realization of high performance semiconductor lasers[2] and quantum information devices such as single photon sources. Moreover, implementing a single quantum dot in an optical nanocavity provides a new platform for solid-state cavity quantum electrodynamics (cavity-QED)[3].

In this talk, we first discuss recent progress in growth and physics of GaN quantum dots for single photon sources (SPSs) at an ultraviolet wavelength, including a position controlled nanowire quantum dot with a giant biexciton binding energy over 60meV and high temperature operation up to 350 K[4,5]. Secondly, for implementation of SPSs onto silicon-based photonic integrated circuits, we also discuss a transfer printing method that integrates quantum dot SPSs into a silicon waveguide, demonstrating InAs/GaAs quantum dot SPSs with high waveguide coupling efficiencies, as well as the integration of two SPSs into a waveguide.[6]

References

Mid-infrared light sources are key components for future chemical sensing, on-chip optical interconnect and LIDAR technologies. GeSn alloys can be synthesized under silicon CMOS compatible conditions. Therefore, GeSn can open pathways for miniaturization of mid-infrared devices such as on-chip molecular sensors, optical interconnect and thermal cloaking devices. Most importantly, direct band gap GeSn is a promising material for on chip integration of light emitters. Previous research on GeSn films has shown mid-infrared lasing at increasing temperatures, initially (in 2015) at less than 90K and, in more recent reports, at or near room temperature. It has also been shown that GeSn nanowires with high-Sn content exhibit strong direct-gap photoluminescence at room temperature. Compared to GeSn thin films, GeSn nanowires are less constrained to lattice match with misfitting (e.g. Ge, Si) substrates and therefore may achieve higher Sn contents without strain and defects that promote non-radiative recombination. Additionally, unlike in a planar GeSn film where the emission angle is limited to < 13° by its high refractive index (n>4), GeSn nanowires provide a platform to design the optical density of states for highly efficient light extraction directly from the light emitting material. GeSn nanowires may also constitute a superior medium for absorption and generation of photocarriers.

We demonstrate room temperature mid-infrared photodetection using resonantly absorbing GeSn/Ge core/shell nanowire photonic crystals. We have synthesized GeSn/Ge core/shell single crystal nanowires with 4% Sn that exhibit strong direct-bandgap photoluminescence at room temperature. The vertical nanowire photodetection device consists of arrays of nanowires in-filled with PMMA insulating layer, an ITO top contact and an aluminum bottom contact. Using full wave FDTD simulations, we optimize Mie resonances of individual nanowires (300 nm in diameter) at the desired bandgap wavelength. We further engineer the absorption with nanowires arranged in photonic crystal arrays. To synthesize the nanowire device, gold catalysts were patterned on Ge [111] substrate and then two step VLS growth was performed to synthesize Ge core and GeSn shell. We performed photocurrent characterization with an FTIR spectrometer at room temperature. The photocurrent spectrum of Ge nanowire photonic crystals indicates a four-fold enhancement due to resonant absorption, with the photocurrent spectrum tunable by varying the photonic crystal geometry. For emission, we designed, synthesized and characterized mid-infrared emission of GeSn/Ge coreshell nanowires with 9-12% Sn. Full wave FDTD simulations reveal that the geometry of GeSn/Ge nanowires can be tuned to be resonantly scattering at the direct band gap energy. To further enhance light extraction, we use FDTD simulations to optimize GeSn/Ge nanowires in photonic crystal arrays to maximize the density of photonic states above the light line within the emission spectrum. The light emitting device consists of a similar device structure to that which is useful for photodetection. Room temperature photoluminescence characterization reveals both direct- and indirect-gap emissions in the mid-infrared, while electroluminescence characterization at 200 mA/cm reveals direct bandgap emission at both 2000 nm and 2300 nm. Optimization of nanophotonic light extraction efficiency will be discussed.

III-V compound semiconductor nanowires have been successfully used for a precise and simultaneous control of lattice parameters and bandgap structures bringing to existence a variety of functional nanoscale heterostructures and low-dimensional systems. Extending this paradigm to group IV semiconductors will be a true breakthrough that will pave the way to creating an entirely new class of silicon-compatible clean energy conversion, optoelectronic, and photonic devices. With this perspective, germanium-tin (GeSn) and silicon-germanium-tin (SiGeSn) alloys have recently been the subject of extensive investigations as new vertical systems to independently engineer lattice parameter and bandgap energy and directness.[1-5] The ability to incorporate Sn atoms into silicon and germanium at concentrations about one order of magnitude higher than the equilibrium solubility is at the core of these emerging potential technologies. In this presentation, we will address the epitaxial growth and stability of these metastable nanowires with focus on Ge/GeSn core/shell nanowires with a sub-30 nm core. The reduced dimension of the Ge core was found to facilitate the growth of GeSn shell at a Sn content of ~10at.%, about 10-fold higher than the equilibrium solubility. We will discuss the optical and electronic properties and present strategies to integrate these nanowires in fabrication of short wavelength infrared (SWIR) and mid-infrared (MIR) optoelectronic devices. Finally, by using a microfabricated strain engineering platform, we will show...
that tensile strain allows tuning of the optical properties of Ge/GeSn core/shell nanowires in the SWIR and MIR range, thus laying the groundwork to implement innovative optoelectronic devices.


SESSION S.EL06.08: III-V Photonic Materials and Devices
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL06

5:00 AM *S.EL06.08.01
Template-Assisted Selective Epitaxy for Integrated Photonics Svenja Mauthe, Preksha Tiwari, Markus Scherrer, Philipp Staudinger, Daniele Caimi, Marilyne Sousa, Yannick Baumgartner, Heinz Schmid, Kirsten Moselund and Noelia Vico Trivino; IBM Research-Zurich, Switzerland

High-density and high-efficiency small light sources will have a wide range of applications including sensing, spectroscopy, quantum computing, and optical communications. In this regard, the integration of III-V materials on silicon has been pursued for decades to combine the best of both semiconductor families: Silicon for electronics and photonics components such as passive waveguides, wavelength filters, modulators, and photodetectors along with III-V semiconductors as direct bandgap efficient light emitters. Several approaches have been investigated relying overall on either bonding III-Vs to a silicon wafer or direct growth.

The main challenge to be overcome in direct growth stems from the significant lattice and thermal mismatch between III-Vs and Si that leads to crystal defects. We have developed a novel growth method named template-assisted selective epitaxy (TASE) to cointegrate seamlessly different materials.1 The high crystal quality of TASE-grown III-Vs resulted in state-of-the-art electronic devices.2 TASE-grown materials fill and take the shape of a pre-defined hollow oxide template. Overall benefits of TASE include low defect density, absence of foreign catalyst (Au-free), and precise control of crystal composition, position, shape, and size.

For integrated photonics TASE offers several advantages that are not achievable with other integration schemes. As all the fabrication steps involve only Si – no III-V processing – the template can hence be fabricated in a Si photonic foundry on an SOI wafer. This way, based on the mature Si technology, we can create III-V nanostructures featuring arbitrary shapes, e.g., vertical or horizontal nanowires, rings, microdisks, or photonic crystals. It also enables in-plane co-integration with Si-based components. Dense co-integration of different III-Vs was implemented on the same chip by sequential growth runs.3 We have recently demonstrated microdisk lasers grown by TASE which compared favorably to similar structures fabricated by the mature wafer bonding approach.4 However, the true benefit of TASE comes from enabling a seamless integration with silicon. In this talk we shall focus on these aspects, and how this enables novel device architectures including hybrid III-V/silicon photonic crystal cavities and photodetectors.6

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References
5:30 AM S.EL06.08.02
Self-Assisted Epitaxial Growth of GaAsSb Nanowires on Monolayer Graphene Surya Nalamati1, Priyanka Ramaswamy1, Kendall Dawkins1, Jeffrey Kronz2, Robert Lavelle2, David Snyder2, C. Lewis Reynolds3, Matthew Cabral3 and Shanthish Iyer1; 1North Carolina A&T State University, United States; 2The Pennsylvania State University, United States; 3North Carolina State University, United States

We report the successful growth of high-quality GaAs1–xSbx nanowires on monolayer graphene/SiO2/p-Si (111) using molecular beam epitaxy (MBE) for the application of a flexible near-infrared photodetector. A systematic and detailed study of NW growth parameters, namely, growth temperature, V/III beam equivalent pressure (BEP) ratio, and Ga shutter opening duration, has been carried out. Growth of vertical <111> oriented nanowires on graphene with 4 K photoluminescence emission in the range 1.24–1.38 eV has been achieved. The presence of a weak D mode in Raman spectra of NWs grown on graphene suggests that NW growth did not alter the intrinsic properties of the monolayer graphene. High-resolution transmission electron microscopy and a selective area diffraction pattern confirmed the zinc-blende crystal structure of the NWs. This study suggests that Sb as a surfactant plays a critical role in the surface engineering of the substrate, leading to the superior optical quality of NWs exhibiting a higher 4 K photoluminescence intensity and lower full width at half maxima (fwhm) with significant improvement in optical responsivity compared to NWs grown on Si substrate of similar Sb composition. Novel growth conditions for improvement of NW density and device performance will be discussed.

5:45 AM S.EL06.08.03
Toward Scalable III-V Nanowire Networks for IR Photodetection Nicholas P. Morgan1, Martin Friedl1, Didem Dede1, Alexander Dorodnıy2, Sabbir Khan3, Lucas Gündiat1, Akshay Balgarkashi1, Wonjong Kim1, Jean-Baptiste Leran1, Peter Krostrup3,4, Juerg Leuthold2 and Anna Fontcuberta i Morral1; 1EPFL, Switzerland; 2ETH Zürich, Switzerland; 3University of Copenhagen, Denmark; 4Microsoft Quantum Materials Lab, Denmark

InGaAs is an ideal material for near-infrared (IR) photodetection at telecommunications wavelengths, but its devices typically require the use of bulk III-V substrates which are costly and largely incompatible with CMOS processing.1 Nanowire-based photodetectors are a promising route to the integration of III-V materials with Si electronics and even offer a number of performance advantages over bulk devices.2 For example, the anisotropic geometry of nanowires allows for the possibility of polarization-resolved photodetection as well as fast carrier collection, making them suitable for fast and efficient multiplexed applications.3 Recently, arrays and networks of high-quality horizontal InAs and InGaAs nanowires have been demonstrated using selective area epitaxy on III-V substrates by growing them on top of GaAs nanomembrane buffers.4,5 Extension of this technique through monolithic integration of GaAs nanomembranes on Si (001) offers the opportunity to create scalable, high-performance IR photodetectors at a fraction of the cost of current InGaAs-based devices. This, however, requires a reliable method to grow defect-free GaAs nanomembranes on Si. In this work, we investigate the growth of GaAs nanomembranes on Si by molecular beam epitaxy. Specifically, we combine various defect reduction techniques, including v-groove trenches, aspect ratio trapping and migration enhanced epitaxy, and characterize the resulting nanostructures. We demonstrate highly faceted nanomembranes several micrometers in length that exhibit large defect-free regions, which may be suitable as a template for future horizontal InGaAs nanowires. Furthermore, we introduce a novel architecture for photoconductive detectors based on these templated nanowires using plasmonic enhancement. Through frequency domain finite element simulations, we demonstrate polarization-sensitive absorption of up to 20% in the nanowire active material and the ability to tune the absorption response by changing the dimensions of the array. Finally, we present related work on the fabrication and characterization of photodetectors based on InAs1–xSbx and InSb nanowire crossovers and hashtags grown by the vapor-liquid-solid technique.6,7,8 These structures offer the possibility of polarization-resolved photodetection in the mid-IR. To the best of our knowledge, IR photodetectors based on nanowire crossovers and/or hashtags have not been previously reported.

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Epitaxial Quantum Dot Lasers on Silicon

Justin Norman1, Chen Shang1, Daehwan Jung2, Jennifer Selvidge1, Songtao Liu1, Yating Wan1, Zeyu Zhang1, Mario Dumont1, MJ Kennedy1, Robert Herrick3, Kunal Mukherjee1, Arthur Gossard1 and John Bowers1; 1University of California, Santa Barbara, United States; 2Korea Institute of Science and Technology, Korea (the Republic of); 3Intel Corporation, United States

In recent years, InAs quantum dot lasers have proven themselves resilient against crystalline defects that form during heteroepitaxial growth of III-Vs on silicon. The three-dimensional confinement and reduced in-plane diffusion lengths of carriers in quantum dots relative to quantum wells are the source of this resiliency, but alone these characteristics are not sufficient for demonstrating commercially reliable performance for lasers on silicon. Quantum dot active regions must be utilized together with highly optimized III-V/Si buffers to reduce the dislocation density to achieve acceptable device reliability.

In this talk, recent advances in GaAs/Si templates will be highlighted along with the resulting enhancements in laser reliability. Over the last three years, we have produced InAs quantum dot lasers on GaAs/Si templates with dislocation densities ranging from $3 \times 10^8 \text{ cm}^{-2}$ down to $7 \times 10^6 \text{ cm}^{-2}$ by optimizing thermal cycling procedures and strained filter layers. As the material has improved, the extrapolated mean-time-to-failure has increased several orders of magnitude to $>10,000,000 \text{ h}$ at $35^\circ \text{C}$ and $>50,000 \text{ h}$ at $60^\circ \text{C}$.

In addition to improving laser reliability, the improvements in material quality have virtually closed the performance gap relative to native substrate lasers before aging. At dislocation densities of $7 \times 10^6 \text{ cm}^{-2}$, low threshold, high power, and high efficiency lasers are readily achievable with continuous wave operation above $100^\circ \text{C}$. These improvements justified more advanced laser implementations and investigations into the dynamic performance of quantum dot lasers on silicon. The unique atom-like density of states of quantum dots has historically enabled unique properties such as an insensitivity to optical feedback, highly engineerable gain bandwidth, and ultrafast gain recovery; these properties unique to quantum dots have enabled Fabry-Perot lasers with complete insensitivity to optical feedback, high performance mode-locked lasers operating at 20 GHz with 64 channels capable of 4.1 Tbps transmission below the forward error correction (FEC) limit, and 100 GHz colliding pulse mode-locked lasers capable of 0.9 Tbps transmission below the FEC limit. Achieving each of these results required a high degree of optimization in the epi design and materials growth to obtain uniform distributions of high-quality quantum dots, which will be emphasized in the talk.

Further improving performance and, in particular, demonstrating commercially viable reliability at elevated temperatures $>60^\circ \text{C}$ will require additional efforts to reduce the dislocation density in the laser active region. Our efforts to push the threading dislocation density $< 2 \times 10^6 \text{ cm}^{-2}$ while also reducing the buffer thickness will be discussed in addition to efforts to address misfit dislocations that have been observed in the laser active region. Given the much larger cross-section of material that interacts with a misfit dislocation relative to a thread, it is believed that addressing these defects is critical to reaching the goal of native substrate level device reliability on a silicon substrate.

Optical Communication and Energy Conversion for Small-Footprint Edge Computing

Ning Li; IBM T.J. Watson Research Center, United States

Advancement in microelectronics technology enables autonomous edge computing platforms in the size of a dust mote, bringing efficient and low cost artificial intelligence computing close to end users. The key components of these edge computers include (i) communication devices to talk to nearby host computers and (ii) power sources to convert energy to on-chip electrical power. As RF communication and power converters suffer from low efficiency with reduced antenna size, optical devices can provide much higher efficiency in sub-centimeter footprint. As there is limited energy storage inside the small footprint of edge computers, we developed power-saving light-emitting-diodes (LEDs) with high efficiency at ultralow current and voltage[1], by improving the quantum well design and increasing the radiative radiation rate at low injection current. The device exhibits close to unity internal quantum efficiency at a current density orders of magnitude lower than that for conventional LEDs. Wireless communication is demonstrated at these low power conditions. We also investigated dust-sized III-V photovoltaic (PV) cells grown on silicon and Silicon-on-insulator substrate[2], considering surface passivation and crystallographic defects. We demonstrated highest power density micro-PVs on silicon substrate. These silicon substrates with integrated III-V devices can be used as the substrate carrier for heterogeneous integration of various silicon chiplets using wafer-level-packaging.

N. Li et al. Nat. Photonics 13, 588–592
Beyond Nanowire Size Constraints: New Epitaxy Strategies Towards Metastable III-V Layers
Philipp Staudinger¹, Svenja Mauthe¹, Nicolas Tappy², Anna Fontcuberta i Morral², Kirsten Moselund¹ and Heinz Schmid¹; ¹IBM Research Zurich, Switzerland; ²EPFL, Switzerland

Metastable crystal phases of conventional semiconductors comprise enormous potential for high-performance electro-optical devices, while at the same time benefitting from the chemical similarity to their stable counterparts which enables the reuse of established processing technology. AlAs, AlSb, AlP, GaP and Ge all possess indirect bandgaps in their thermodynamically stable cubic phase, whereas both theoretical calculations as well as first experimental reports suggest their band transition to be direct when their lattice periodicity is changed to the hexagonal wurtzite (WZ) or lonsdaleite (LD) symmetry [1, 2]. These findings recently triggered intense research interest for creating efficient light sources in the important amber-green wavelength regime of the visible spectrum where a lack of suitable emitting materials currently limits the performance of LEDs and semiconductor lasers [3]. Beyond that, direct bandgap Ge and SiGe compounds could even pave the way towards active group-IV optoelectronic devices. However, synthesizing these novel polytypes remains challenging and so far, has mainly been achieved in the form of thin nanowires, mostly by using Au catalysts and by compromising other important parameters such as crystal morphology or doping, hampering scientific and commercial exploitation.

In this work, we demonstrate new techniques to synthesize layers in their metastable WZ phase. InP is particularly suited for this task as both the stable cubic and the WZ phase exhibit a direct, but distinctive bandgap, which allows efficient optical analysis. We use MOCVD and selective area epitaxy to grow pure WZ nanowires and fins. We then show two extensions of this technique to obtain planar layers: The first one is based on confined epitaxy and enables growth on standard (001)-oriented substrates [4]. In a second, newly introduced approach we explore epitaxial layer overgrowth (ELO) on (111)A-oriented wafers. This allows to grow pure WZ layers on insulator exceeding areas of 100 µm², constituting a promising substrate for device fabrication. The material quality of the structures is determined by micro-photoluminescence (μ-PL), high-resolution scanning transmission electron microscopy (HR-STEM), atomic force microscopy (AFM), and cathodoluminescence (CL). We compare the investigated techniques, show their limitations and develop a general model to explain polymorphism in planar layers.

This work was supported by the EU H2020 program SiLAS (Grant Agreement No. 735008).

effective linear electro-optic coefficient for coupling the microwave and optical fields by three wave mixing is induced by strongly biasing the microwave resonators to leverage the DC Kerr effect in Si and SiGe. For 1 MHz-rate transducers, the resulting microwave-optical coupling strength is calculated to be sufficient to reach the peak conversion efficiency condition. Demonstrating microwave-optical transduction in this platform is then dependent on achieving low defectivity fabrication of the proposed SiGe/Si optical waveguides. I will present a study of this materials problem and an analysis of the overall optimal transducer design.

This work was funded by LPS/ARO under CQTS program, contract number W911NF-18-1-0022.

5:30 AM *S.EL06.09.02
Quantum Photonics with InAs Quantum Dots Marcelo Davanco; National Institute of Standards and Technology, United States

Photonic quantum technologies rely on the fact that photons can be endowed with long coherence times, can travel long distances at light-speed, and interact only weakly with the environment, thereby constituting near-ideal carriers of quantum information. Single-photon qubits are a core resource for many quantum technologies currently being developed for systems that, based on quantum mechanical effects, have great potential to perform communication, signal processing, computation and measurements with significantly superior security, efficiency and sensitivity [1–3]. In such applications, an ideal quantum light source would emit a pure, high-rate stream of highly indistinguishable single-photons produced on-demand. Single-photon sources based on single quantum emitters – such as quantum dots, organic molecules, point-defects in solids, etc. - have a great potential to fulfill all such requirements. Among the various types of single quantum emitters available in the solid-state, self-assembled InAs/GaAs quantum dots constitute the most promising material system to date [4], having been used to demonstrate triggered single-photon emission with indistinguishability close to that of spontaneous pair sources, and orders or magnitude higher generation rates [5, 6]. Such quantum dots consist of nanometer-scale islands of InAs that are grown epitaxially in a GaAs host, and are operated at cryogenic temperatures. Importantly, the ability to produce quantum dots within high index contrast GaAs nanophotonic geometries enables strong control of crucial quantum dot emission characteristics, such as the excited state decay rate and outcoupling into select spatial modes [5–7]. The former characteristic translates into control of the single-photon emission rate and, to some degree, coherence. The latter translates into efficient funneling of the single-photons into a useful, output optical spatial mode – e.g., a low-divergence Gaussian beam [7, 8] or a single optical fiber mode [9] -, which has a strong impact on the overall source efficiency. This talk will describe our progress in developing high efficiency single-photon sources based on self-assembled InAs/GaAs quantum dots in nanophotonic structures. In particular, because the availability of mature chip-scale photonic integration techniques provides compelling advantages towards scalable photonic quantum systems, our recent results on deterministic fabrication of heterogeneous integrated photonic devices with single quantum dot based sources of on-chip waveguide-coupled single-photons [10, 11] will be covered.

References

6:00 AM *S.EL06.09.03
Superconducting Single Photon Detectors and Their Applications in Quantum/neuro Networks Sae Woo Nam; National Institute of Standards and Technology, United States

Single-photon detectors are increasingly becoming an essential tool for a wide range of applications in physics, chemistry, biology, communications, medicine, and remote sensing. In the area of computing, efficient single photon detection is important for quantum information processing with photons as well as recently proposed work for large-scale superconducting optoelectronic networks for neuromorphic computing. Ideally, a single photon detector generates a
measurable signal only when a single photon is absorbed. Furthermore, the ideal detector would have 100% detection efficiency, no false positive (dark counts), and transform-limited timing resolution. Recently, there has been tremendous progress in the development of superconducting nanowire single-photon detectors (SNSPDs or SSPDs) towards nearly ideal performance. The SNSPD is an alternative to conventional semiconductor avalanche photodiodes (APDs) especially for wavelengths in the near-infrared region of the spectrum. Since the first demonstration of single photon detection with a superconducting nanowire, there has been significant effort to package nanowire detectors into systems that could be used in real-world applications. I will review a few technological breakthroughs in SNSPD designs and performance, will briefly describe where advances in materials and material science could have immediate impact on the use of these detectors for computing.

6:30 AM S.EL06.09.04
Chromium Ions as High Fidelity Optically Addressable Spin Qubits in Commercial Silicon Carbide Berk Diler1, Samuel J. Whiteley1,1, Christopher Anderson1,1, Gary Wulfowicz1,2, Marie E. Wesson1, Edward Bielejec2, F. Joseph P. Heremans1,2 and David Awschalom1,1,2; 1The University of Chicago, United States; 2Argonne National Laboratory, United States

Optically active spin defects in wide bandgap semiconductors continue to attract attention as qubits in the solid state. The ground state spin sublevels of these defects can store and process information while the atom-like optical transitions can initialize and read out the spin. Introducing these defect centers reliably into the host material is critical for future device integration. To this end, we explore chromium ion creation through implantation and annealing in silicon carbide (SiC) [1], a technologically mature and CMOS compatible wafer scale host crystal. Chromium in the 4+ charge state (Cr4+) has an S = 1 ground state and an S = 0 excited state with a near-infrared (1070 nm) strain insensitive optical transition that has a high Debye-Waller factor of 75%, making it interesting for quantum communication through fiber optic networks. We find that the created Cr4+ ensemble has an order of magnitude narrower linewidth of the optical hole (31 MHz) compared to as grown samples. We use the Λ-like level structure as a spin-photon interface and study the transition rates to optimize for high fidelity spin initialization and readout of 79%. At cryogenic temperatures (15 K), we measure long ensemble spin coherence times of $T_2^* = 317$ ns and a $T_2 = 81 \mu$s limited by the ensemble density and $T_1$ greater than 1 s. These results demonstrate Cr4+ in SiC as an attractive optically active spin-qubit for integration within quantum devices.

Funding Agencies: DOE
The success of deep learning has recently stimulated broad interest in optical neural networks due to their key advantages: (1) ease of parallelization and scalability, (2) low power and (3) high data processing speed. Merging wave optics with deep learning methods, Diffractive Deep Neural Networks (D3NN) have been introduced as an optical neural network framework, which is based on the engineering of light-matter interaction occurring at successive diffractive layers that connect an input (e.g., an object to be classified) to an output plane through optical diffraction. During the design of a D3NN, which is performed in a computer using deep learning methods, including e.g., error backpropagation and stochastic gradient descent, the phase and/or amplitude patterns of each diffractive layer of a network are jointly-optimized to solve a given computational task such as image classification. After its design, the resulting diffractive optical network is physically fabricated to perform all-optical inference at its output plane. Successful demonstrations of diffractive neural networks include all-optical object classification and ultra-compact imaging systems, involving 3D-printed diffractive layers that compute through the diffraction of terahertz (THz) radiation. In these previous works, the diffractive networks processed spatially and temporally coherent radiation, involving a monochromatic plane-wave illumination. Here we expand our D3NN framework to simultaneously process a continuum of wavelengths, making it applicable to all-optical computing settings where broadband illumination is essential and/or advantageous. Using the native and/or engineered dispersion of materials, broadband diffractive optical neural networks simultaneously process all the target wavelengths within a desired band to compute a statistical or deterministic task that it is trained for. We experimentally confirmed the success of this framework by designing, 3D-printing and testing seven different diffractive networks that process an input THz pulse to perform a series of tunable, single passband and dual passband spectral filters, as well as spatially-controlled wavelength de-multiplexing. Using a THz Time-Domain Spectroscopy (TDS) system, we demonstrated a very good match between our experimental results and the corresponding numerical design for each fabricated broadband diffractive network. Leveraging deep learning-based optimization tools and material dispersion properties, this broadband diffractive network framework provides a powerful method to engineer light-matter interaction in 3D, opening up new avenues to design non-intuitive, task-specific optical components as well as all-optical classifiers and processors. The presented method is broadly applicable to various parts of the electromagnetic spectrum, including the visible band, and can be further strengthened by the additional degrees of freedom provided by engineered material systems including e.g., metamaterials. We believe broadband diffractive networks provide a unique framework to perform all-optical statistical inference for machine learning tasks as well as to design deterministic and task-specific optical components, broadly covering a non-intuitive and yet powerful design space.

5:45 AM S.EL06.10.03
Optical Signal Processing Using Dielectric Metasurfaces Jinghui Yang, Wenqi Zhu, Lu Chen, Cheng Zhang, Henri J. Lezec and Amit Agrawal; National Institute of Standards and Technology, United States

Optical analog computing provide solutions with fast and power-efficient performance for big-data applications. Recently investigated metamaterials and metasurfaces demonstrate potentials in mathematical operations over wavelength-scale footprint. We extend the functionality of using nonlocal dielectric metasurface to perform spatial differentiation equation for imaging processing. The study pave the way towards ultrathin devices for optical signal processing.

6:00 AM *S.EL06.10.04
Flat Optics for Image Differentiation You Zhou1, Hanyu Zheng1, Ivan Kravchenko2 and Jason G. Valentine1; 1Vanderbilt University, United States; 2Oak Ridge National Laboratory, United States

Image processing has become a critical technology in a variety of science and engineering disciplines. While most image processing is performed digitally, optical analog processing has the advantages of being low-power and high-speed though it requires a large volume. Here, we demonstrate optical analog imaging processing using a flat optic for direct image differentiation allowing one to significantly shrink the required optical system size. We first demonstrate how the image differentiator can be combined with traditional imaging systems such as a commercial optical microscope and camera sensor for edge detection at a numerical aperture up to 0.32. Second, we demonstrate how the entire processing system can be realized as a monolithic compound flat optic by integrating the differentiator with a metalens. The compound nanophotonic system manifests the advantage of thin form factor optics as well as the ability to implement complex transfer functions and could open new opportunities in applications such as biological imaging and machine vision.

The differentiator consists of carefully designed silicon nanorods that can transform an image into its second-order derivative, taking the Laplacian of the incident field. The optical response is based on interference between direct transmission and a low-Q guided resonance allowing for transmission at large incident angles but none at normal incidence. Fourier imaging was carried out showing th required quadratic transfer function for an NA up to 0.32, which allows resolving edges at the scale of 4 microns. To showcase its practical application, we first demonstrate the device at a wavelength of 740 nm by integrating the differentiator with a commercial microscope. This allowed us to reveal high-contrast edge information.
when imaging biological cells, akin to phase contrast microscopy though with a considerably simpler system. Using scalable manufacturing techniques, not involving lithography, we also fabricated the nanoarray over a centimeter-scale wafer and demonstrate edge detection when placing the filter directly in front of an imaging sensor. Lastly, we have demonstrated the creation of a monolithic flat optic combining both a metalens and the differentiator for realizing a compact image processing system.

SESSION S.EL06.11: Poster Session: Photonic Materials for Information Processing and Computing
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
5:00 AM - 8:00 AM
S-EL06

S.EL06.11.01
(Si)GeSn Semiconductors for Integrated MIR Opto-Electronics Simone Assali1, Alain Dijkstra2, Anis Attiaoui1, Mahmoud Atalla1, Aashish Kumar1, Samik Mukherjee1 and Oussama Moutanabbir1; 1Ecole Polytechnique de Montreal, Canada; 2Technische Universiteit Eindhoven, Netherlands

Sn-containing group IV semiconductors (Si)GeSn represent a versatile platform to implement a variety of Si-compatible photonic, optoelectronic, and photovoltaic devices. This class of semiconductors provides two degrees of freedom, strain and composition, to tailor the band structure and lattice parameter thus enabling a variety of heterostructures and low-dimensional systems on a Si substrate. In this presentation, we will discuss the recent progress in controlling and understanding the opto-electronic properties of metastable (Si)GeSn semiconductors. The relevance of these semiconductors for Si-compatible mid-infrared optoelectronics will be discussed form both materials and device perspectives. The growth of the (Si)GeSn multi-layer heterostructure with Sn contents up to ~20at.% is currently performed using a chemical vapor deposition (CVD) reactor on a Silicon wafer. By reducing the growth temperature, the Sn content in the alloy is increased, while preserving a high degree of crystal purity for the heterostructure in the topmost Sn-rich layer.[2,3] Atom probe tomography (APT) measurements will be discussed to address the abruptness of the interfaces in the GeSn multi-layer heterostructure and the uniform composition in the 18 at.% GeSn layer grown on top.[2] Positron annihilation lifetime spectroscopy (PAS) and depth-profiled Doppler broadening measurements will be discussed to enrich the understanding of point defects in these semiconductors. Based on these analyses, we found that divacancies are the predominant type of point defects in GeSn with composition in the 6.5-13 at.% range.[4]

Photoluminescence (PL) emission studies will be presented and discussed. In a GeSn layer with a Sn content of 18 at.% the room temperature PL emission was found to be centered at 0.36 eV (i.e. 3.5 μm wavelength).[2] However, the compressive in-plane strain (-1.3 %) in these GeSn layers reduces the directness of the alloy, leading to a higher energy gap value. By releasing the strain down to -0.2% in the 18 at.% Sn layer using a fully-underetched micro-disk geometry, a 50 meV red-shift of the PL emission energy down to 0.31 eV (i.e. 4.0 μm wavelength) is obtained. Moreover, the strained and relaxed PL emission and absorption measurements ranging from 300K down to 4K will be shown.[5] These observations will be discussed in the light of photocurrent measurements and photodetectors operating at MIR wavelengths.


S.EL06.11.02
Epitaxial Growth of Atomically-Sharp GeSn/Ge/GeSn Tensile Strained (≥1.5 %) Quantum Well on Si Simone Assali, Aashish Kumar, Jérôme Nicolas, Samik Mukherjee, Anis Attiaoui, Patrick Del Vecchio and Oussama Moutanabbir; Ecole Polytechnique de Montreal, Canada

In a full-group IV integrated semiconductor platform for tensile-strained Ge the direct-band gap can be obtained when the Ge is grown on a lattice-mismatched Ge0.87Sn0.13 substrate. With this approach the main challenge is to increase the incorporation of Sn in Ge above the ~1 at.% equilibrium composition. Major developments were recently achieved in the epitaxial growth
of random GeSn alloys with composition above 16 at.%. A biaxial tensile strain in a Ge layer up to ~1.5% was demonstrated when growing on a Ge$_{0.88}$Sn$_{0.12}$ substrate.[2-3] However, despite the large amount of tensile strain in Ge, no information is available on the abruptness of the Ge-GeSn interface and on the possibility of the subsequent GeSn growth on top.

Here, we discuss the epitaxial growth of a tensile-strained GeSn/Ge/GeSn (s-Ge) QW heterostructure with sharp interfaces and in-plane biaxial strain above 1.5% grown on lattice-mismatched Ge$_{0.86}$Sn$_{0.14}$.[4] The sharpness of the Ge/GeSn heterostructure interfaces will be addressed using TEM-EELS and atom probe tomography (APT) measurements. A coherent s-Ge epitaxy with a tunable layer thickness in the sub-20 nm range is achieved. The pseudomorphic nature of the s-Ge layer will be discussed by combining cross-sectional STEM measurements and XRD-RSM measurements performed at a synchrotron radiation facility.

The s-Ge QW platform is a new versatile platform to investigate light-hole (LH) spin-based qubits and 2D high hole mobility electronics. Under tensile in-plane biaxial strain, LH occupies the top of the valence band and the LH-HH splitting can exceed 100s meV. Moreover, when the tensile in-plane biaxial strain approaches 2% only LH are confined in the QW, thus minimizing LH-HH interactions.


S.E.L06.11.04
Homogeneous Cooling Dynamics in Laser Enhanced-Direct Print Additive Manufacturing of Circular Optical Fiber Interconnects
Roger B. Tipton1, Dianhao Hou1, Thomas Weller2 and Venkat Bhethanabotla1; 1University of South Florida, United States; 2Oregon State University, United States

Integrated photonics have many compelling advantages for computing and communication applications, including high-speed and extremely wide bandwidth operations. When fused deposition printing (FDM) a PMMA plastic optical fiber on a surface the bottom of the fiber is flat due to non-uniform cooling and the force of gravity on the fiber during solidification. Here we show that by embedding the fiber in a urethane optical cladding material, the fiber cools homogeneously and retains its round ship which is optimum for light transmission. This homogeneous cooling allows the use of a flexible, low cost additive and subtractive assembly method called laser enhanced-direct print additive manufacturing (LE-DPAM) to produce plastic optical fiber interconnects for photonic systems we have enabled higher transmission rates, lower power requirements, improve signal integrity and timing, less heat generation, and improve security of communication signals.

S.E.L06.11.05
Eldred Lee1,2, Zhehui Wang2, Michael James2, Eric Fossum1, Kaitlin Anagnost1 and Jifeng Liu1; 1Dartmouth College, United States; 2Los Alamos National Laboratory, United States

Since the discovery of X-rays, the continuous expansion of X-ray technology has transformed our society. However, the capability gap for hard X-ray detectors in the 10-100 keV range is problematic. Even though scintillator-based methods are widely used, they are limited by their decay time response, light yield, and spatial resolution, which may prevent them from being effective in the next generation of light source facilities, the generic platform of imaging sensor technology, and quantum image computing.

One class of X-ray detection primarily focuses structured photocathode designs that rely on external photoemission and collecting electrons converted from photons using an external electric field. This research only demonstrated up to 5% photon-to-electron conversion efficiency (electron generation) at 7.5keV incident photon energy, which is still commendable as this value has been roaming around the 1-1.5% area for external photoemission for a few decades [1, 2]. However, we believe that there is a potential to significantly increase this 5% electron generation even beyond 7.5keV incident photon energy via X-ray photon emission from high-Z materials.

Here, we present the Monte Carlo simulation results and analyses via Monte Carlo N-Particle Software (MCNP) that demonstrate a tremendous potential of revolutionizing the advancement of X-ray imaging with a two-layer design that consists of a high-Z semiconductor material on top of a Si layer. The high-Z layer is called photon attenuation layer (PAL), and the Si layer the electron detection layer (EDL). PAL-EDL latticed multi-pixel X-ray detector can also lead to low inter-pixel scattering with significant electron and photoelectron generation. The underlying principle of this design is photon energy down conversion, where the top high-Z PAL leads to an effective X-ray photon energy attenuation down to a few keV.
and allows Si to absorb them with a much higher absorption coefficient. This approach is distinct from scintillators in that the attenuated photons remain in X-ray spectral regime instead of visible regime. For instance, with PbTe, CdTe or CZT PAL and the Si EDL, we have observed >22% electron generation at 10keV X-ray photon energy and >2.8% electron generation at 40 keV incident photon energy with minimum inter-pixel scattering effects. The average electron energy lies between a few hundred eV and a couple keV.

At 30-40keV, we observed that adding a high-Z PAL on top of Si EDL can lead up to 13x higher electron generation than the typical Si direct-detection method seen in commercial products such as photomultipliers. Furthermore, because MCNP does not include the “avalanche gain” process in Si, the observed efficiencies may be underestimated. The MCNP results will be coupled with models that take the avalanche gain process into consideration (e.g. TCAD). In addition, this high-Z PAL-Si EDL configuration can be integrated to regular backside illumination (BSI) CMOS image sensor or quanta image sensor-based devices, paving the way towards a billion-pixel X-ray camera design for wide field-of-view applications in light sources [3].


S.E.L06.11.07
Study of Space Charge Limited Conduction Mechanism and Effect of In Situ Annealing on the Trap Distribution in GaAsSb Nanowires Mehul K. Parakh, Sean Johnson, Rabin Pokharel, Priyanka Ramaswamy, Surya Nalamati, Jia Li and Shanthi Iyer; North Carolina A&T State University, United States

This work presents the first observation of space charge limited conduction (SCLC) mechanism in intrinsic GaAsSb nanowires (NWs) grown by Ga-assisted molecular beam epitaxy and the effect of post-growth in-situ annealing in an ultra-high vacuum on trap concentration and its energy distribution in the NWs. Current-voltage (I-V) measurements on single NW (using conductive atomic force microscopy) and ensemble NWs (using two probe method) exhibited linear behavior at lower bias transitioning to a power-law behavior at higher bias, where the dominance of injected carriers over thermally generated charge carriers was observed. Temperature-dependent I-V analysis (I-V-T) on as-grown ensemble NW device in SCLC region yielded a trap concentration of $10^{16}$ cm$^{-3}$ distributed over a wide energy distribution in the bandgap as opposed to the reduced trap concentration of $7 \times 10^{14}$ cm$^{-3}$ in in-situ annealed NW ensemble confined to a narrower energy distribution of 0.12 eV located below the band edge, suggesting that annealing in ultra-high vacuum is an effective approach for the annihilation of the traps. The trap energy level in in-situ annealed NWs is speculated to be originating from Ga vacancy, and Ga$_{As}$ Sb anti-site defect level during growth. Observations of increased PL intensity with reduced full-width half maxima at 4K and lower LO mode in corresponding Raman spectra for in-situ annealed NWs compared to as-grown NWs further attest to the annihilation of traps on in-situ annealing. Further, AFM current mapping also exhibited a considerable increase in several conducting NWs in in-situ compared to as-grown NWs. Hence, I-V-T analysis of the SCLC mechanism has been demonstrated to be a simple approach to obtain information on growth induced traps in the NWs.

S.E.L06.11.08
Photonic CMOS Field Effect Transistor Fabricated with an Ultra-Low Resistance Built-in Laser, Nonlinear Optical Films, and Multiple Photon Sensors for Very High Resolution, Low Dark Current CCD and CMOS Imaging Applications James Pan1,2; 1Advanced Enterprise and License Company, United States; 2Northrop Grumman Electronic Systems, United States

Photon-generated carriers may substantially improve the output current, and reduce series resistance of CMOSFETs. Photonic devices, such as Multiple Quantum Well Lasers, Quantum Dots Lasers, Vertical Cavity Surface-Emitting Lasers (VCSEL), Light Emitting Diodes (LEDs) have been reported for various applications. With modulation doped laser junctions, and bandgap engineered tunneling mechanisms, ultra-low resistivity and laser diode forward voltage can be achieved. These laser diodes can be fabricated in the drain region of a MOSFET. A photon sensor, such as avalanche photo diode (APD), can be included in the channel / well regions. The laser, APD, and MOSFET are fabricated as one integral
transistor. When the MOSFET is turned off, the laser is also turned off. The laser is switched on only when a gate voltage and a drain voltage are applied to the MOSFET. Light emitted from the laser is absorbed by the APD. Light current produced by the built-in photon sensors or APD reduces series resistance and may substantially improve the output current and switching speed.

Indium Tin Oxide (ITO) is commonly used in Charge Coupled Devices (CCD) receiving front illumination. The gate electrode material can be replaced with ITO, which is transparent for specific light spectrums. The new Photonic CMOS transistor, including nonlinear optical films and multiple photon sensors (for various light spectrums) can be used for CCD (with ITO) or CMOS image products (without ITO) for front or back illumination.

When external light is absorbed in the depleted channel and well regions (where the multiple photon sensors or APDs are located) of a Photonic MOSFET, light electrons are generated. These light electrons produce a drain current, which turns on the built-in laser in the drain region. The result is not only a light current, but also a new beam of a laser light are generated. Much higher resolution may be achieved with multiplexing of the light signals and specially designed ROIC (Read Out Integrated Circuit), which may also include Photonic CMOSFETs.

Nonlinear Optics have been reported for various products and applications. The nonlinear crystal films change the input light signal and produces an output light signal of a different frequency or color. In the new Photonic CMOS transistor, in addition to the built-in laser in the drain, there are multiple avalanche photo diodes in the channel / well regions, nonlinear crystal films below the APDs, and a reflector (metal or multiple indices total reflection film stack) in the bottom of the device. The APDs are designed to absorb lights from various bands of spectrums. When light passes through the Photonic CMOS Transistor, some APD films absorb lights of specific frequencies, and other APD films absorb the reflected light of different frequencies through the nonlinear crystal layers. This feature enhances the absorption rate and external quantum efficiency of the Photonic MOSFET, and may significantly improves the quality and resolution of the images from the CCD or CMOS imaging devices.

In this paper we will discuss Photonic MOSFET drain current (IDS) vs. spectral characteristics of nonlinear optical films. With the nonlinear optical films, it is possible to substantially improve the CMOS performance according to these data. Dark current density and resolution using a Photonic CMOS image sensor vs. traditional CMOS image sensor are analyzed. The advantages of a Photonic CMOS image sensor are lower dark current, and higher light sensitivity, due to the built-in lasing device and multiple photon sensing films, and nonlinear optical features.

Information regarding incident light spectrums vs. Ion / Ioff ratio for a Photonic CMOS image sensor will presented. Comparison of the speeds of CMOS image sensors with and without the built-in nonlinear optics films will be discussed.

We will also introduce various types of crystals of nonlinear optics suitable for the Photonic CMOS image sensing applications.

* Invited Paper

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**SYMPOSIUM S.EL.07**

Fundamental Mechanisms and Materials Discovery for Brain-Inspired Computing—Theory and Experiment
November 21 - November 28, 2020

**Symposium Organizers**
Sarbajit Banerjee, Texas A&M University
Sanjini Nanayakkara, National Renewable Energy Laboratory
Huaxiang Wu, Tsinghua University
J. Joshua Yang, University of Southern California

* Invited Paper
SESSION Tutorial S.EL07: New Approaches for Computing from Brain-Inspired Dynamics
Session Chair: Sanjini Nanayakkara
Saturday Morning, November 28, 2020
S.EL07

8:00 AM *
New Approaches for Computing from Brain-Inspired Dynamics R. Stanley Williams; Texas A&M University, United States

With the saturation of Moore’s scaling of transistors, there has been an explosion in activity and creativity to find new modes of computation that will continue to scale exponentially with time even though transistor circuits only improve modestly. Much of the inspiration for new ways of computing comes from what little we understand about the brain. We actually don’t know how the brain computes, but many different possibilities have been proposed, e.g. multinary logic (ternary and higher), Neural Networks of all kinds, extensions of Hebbian learning via spike-timing dependent plasticity, Boltzmann/Ising machines, Hopfield networks, Bayesian inference and Markov Chains, to name a few. Actually, these possibilities are not necessarily mutually exclusive – the brain may use some combination of them or even use a higher order generalization that contains several of them, since many share mathematical similarities. How to express these computational modes in hardware is a significant challenge. Since the brain itself is a highly nonlinear dynamical system, an appropriate focus for research is nonlinear dynamical circuit theory. This is the realm of the Principle of Local Activity, which provides a basis for understanding and building new generations of neuron-like amplifiers and chaotic oscillators, and designing circuits that are biased at the Edge of Chaos, where complexity and emergent behavior are found. What new types of devices will be used to construct these circuits? Can we emulate or even surpass neural data processing and computation using new types of dynamical electronic-ionic-thermal devices that express similar behavior? Finally, what materials will we use to build these new devices and incorporate them into the existing commercial integrated circuit foundries? I will present a brief historical survey of brain-inspired computation that begins with research in neurophysiology and psychology in the 1920’s. I will show what constitutes the present state of the art, and actually how primitive that is compared to the human brain despite the hype surrounding present machine learning. I will describe some major opportunities that exist for new computing paradigms based on emerging hardware and electronic devices such as memristors, which have the potential for many orders of magnitude improvement in time to solution and energy consumption compared to purely digital systems. I will also highlight some of the most exciting research and the groups performing it in labs around the world.

SESSION S.EL07.01: Session I
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL07

5:00 AM S.EL07.01.02
Electronic Structure, Defect Chemistry and Element Doping in Phase-Change Vanadium Dioxide Baiyu Zhang and Xiaofeng Qian; Texas A&M University, United States

Vanadium dioxide, a strongly correlated electronic material, is known for its metal-insulator transition (MIT) accompanied by a structural phase transition. While the controversy in the phase transition mechanism makes VO₂ one of the most challenging subjects, recent years have witnessed a great effort in studying the MIT mechanism and modulation, and the potential of VO₂ in device applications, owing to the MIT temperature close to room temperature. Element doping is an effective approach to regulate MIT in VO₂. For example, W and Mo doping reduce MIT temperature of VO₂, while Ge doping has opposite effect. Here we present our first-principles study of VO₂ upon element doping. We will reveal the effect of the doping on atomistic and electronic structure of VO₂ as well as the corresponding defect chemistry in both insulating monoclinic phase and metallic tetragonal phase. Finally, we will discuss the implications of first-principles simulation results on the phase transition and future improvement of VO₂ based neuromorphic materials.
Atomistic Models of Switching Mechanisms in ReRAM Devices Alexander Shluger¹, Jonathon Cottom¹, Jack Strand¹ and Kamal Patel¹,²; ¹Univ College London, United Kingdom; ²A*STAR, Singapore

The mechanistic origins of memristive behaviour strongly depend on the chemical composition and morphology of materials comprising memristive devices and their interfaces. We use symmetric TiN/SiO₂/TiN and asymmetric Au/Ti/a-SiO₁.₉₅/Mo stacks described in [1] and HfO₂ based stacks [2] as model systems to discuss the mechanisms of electroforming and reset in resistive random access memory devices (ReRAM) using density functional theory (DFT) and atomistic modelling. The bulk system (far from the interface) is approximated as stoichiometric polycrystalline HfO₂ or amorphous (a)-SiO₂ and HfO₂, whereas the oxide/TiN interface is considered explicitly and constructed using DFT simulations assuming different degrees of hydroxylation of oxide surface. Grain boundaries in polycrystalline HfO₂ are shown to attract O vacancies and facilitate electroforming [2]. Structural degradation of amorphous oxide films is facilitated by electron injection and bias application. In particular, trapping of two extra electrons at intrinsic sites inside a-SiO₂ film results in weakening of Si-O bonds and emergence of efficient bond breaking pathways for producing neutral O vacancies and interstitial O₂⁻ ions with low activation barriers (≈ 0.2 eV) [3]. These barriers are further reduced at the TiN/SiO₂ interface and by the electric field, facilitating diffusion of O₂⁻ from the bulk towards the interface coupled to a lowering of the formation energies for the O₂⁻ as a function of the distance from the interface. The charge transition level for the O (0/2-) moves towards that of the TiN Fermi level as the O₂⁻ approaches the interface resulting in a transfer of the electrons to the TiN electrode at the interface. Once the interstitials arrive at the interface, there is an initial ‘oxidation’ of the interface via the formation of a TiO layer, preferably at Ti-interface sites [4]. The Ti-O bonds are strong with high barriers (> 1.2 eV) for dissociation and O migration along the surface. Once the interface Ti-sites are occupied, O₂⁻ are incorporated at or in the layers directly below the interface or diffuse inside TiN via grain boundaries. A significant amount of oxygen is emitted into gas [1,4]. Reset happens as a result of O trapped at the interface and inside the grain boundaries diffusing back into the oxide and recombining with O vacancies. Retention is facilitated by the high barrier to Ti-O bonds dissociation at the interface, which is reduced as the reset bias is applied. We discuss the role of interface structure in the mechanisms of oxygen trapping and release at the metal/oxide interfaces in resistive switching/reset processes.


Surveying Metastable Phase Space for ‘Transformers’—Tuning Electron Correlation in MₓV₂O₅ Materials to Realize Neuromorphic Functionality Justin L. Andrews, Abhishek Parija, Joseph Handy and Sarbajit Banerjee; Texas A&M University, United States

Solid-state materials that exhibit electronic instabilities can be leveraged to emulate the spiking behavior characteristic of neuronal function; however, beyond VO₂ and NbO₂, the palette of materials that exhibit sharp electronic phase transitions above room temperature is sparse. The rational design of such materials is complicated by the complexity of neuronal dynamics which further requires independent control over the onset threshold and the conductance switching magnitude of their electronic transitions. Thereby, synthetic approaches that enable precise control over the extent and strength of electron correlation within a given system are greatly desirable. Given the complexity of the problem, the chosen chemical system should exhibit electronic behavior spanning extremes between highly-correlated and itinerant domains. Ternary vanadium oxides (MₓV₂O₅) represent such a system due to the availability of multiple accessible redox states and a variety of low-dimensional structural motifs that can accommodate the intercalation of a variety of ions spanning the breadth of the periodic table, offering vast compositional tunability. We have reported a number of electronic phase transitions in this mixed-valence (xd²/dₙ²) MₓV₂O₅ system, including voltage-driven lone pair-mediated metal-insulator transitions in the quasi-1D β-Pb₀.₅₃V₂O₅, temperature-driven metal-insulator transitions in the layered δ-K₀.₅V₂O₅, and pronounced semiconductor-semiconductor transitions in δ-A₀.₅V₂O₅. More recently, we have observed colossal (six orders of magnitude) metal-
insulator transitions in $\beta'$-Cu$_3$V$_2$O$_5$ and have shown these electronic transitions to be driven by polaron oscillations that are mediated by copper diffusion between two adjacent crystallographic sites. However, moving beyond elucidation of the mechanisms underpinning these observed transitions into two adjacent crystallographic sites. However, moving beyond elucidation of the mechanisms underpinning these observed transitions is intuitive materials design requires a robust and modular synthetic approach. We have recently pioneered the use of topochemistry to synthesize metastable polymorphs of V$_2$O$_5$. These polymorphs exhibit distinctive vanadium-oxygen bonding motifs that in turn give rise to varying extents of d-band dispersion. We have used these metastable V$_2$O$_5$ materials as inorganic equivalents of ‘synthons’ in subsequent intercalation reactions to independently control the intercalated ion (‘M’), its stoichiometry (‘x’), and how it is situated within the desired V$_2$O$_5$ framework (layered or quasi-1D tunnel structure). Using this approach we have targeted and synthesized metastable binary and ternary vanadium oxide materials that have found use as photocatalysts, multivalent ion cathode materials, and as materials for neuromorphic computing. Ultimately, we have demonstrated a chemical system, denoted as $[\text{M(H}_2\text{O)}_x]_n\text{V}_2\text{O}_5$,

where M, its degree of hydration, its stoichiometry, and the vanadium-oxygen connectivity are each independently tunable, establishing ternary vanadium oxides a promising system for the rational engineering of electronic instabilities.

5:45 AM S.EL07.02.03
Indirect Observation of Domain-by-Domain Transition through Electrical Characterization of BVO2 Adelaide
Bradieich, Aliya J. Yano, Heidi Clarke, Erick Braham, Sarbajit Banerjee and Patrick Shamberger; Texas A&M University, United States

Exploration of new computing architectures is underway in order to meet the challenge of advancing computing past the limitation of the impending end to the further downsizing of transistors. Neuromorphic computing architectures are being developed in order to push the constraints of conventional computing by mimicking certain behaviors of the brain. However, using conventional materials, many different elements are needed in order to simulate the most basic of functions. Consequently, the development of novel functional materials to replace materials used in conventional networks is necessary to enable efficiency. Vanadium dioxide is of interest for neuromorphic applications due to its temperature-controlled metal-insulator transition (MIT) from an insulating monoclinic phase to a metallic rutile phase. It has been shown that vanadium dioxide devices are well-suited to applications in neuromorphic computing because of their ability to mimic neuronal behavior. In order to control various aspects of the phase transition, such as transition temperature, hysteresis, and change in resistivity, it is common practice to dope the VO$_2$. However, this also can introduce intrinsic defects into the material that can result in a length-scale dependent variability in properties. Consequently, a comprehensive study of the behavior of doped VO$_2$ on a device level is critical for moving forward in the development of neuromorphic devices. In this study, it is demonstrated that doping VO$_2$ with interstitial boron results in the formation of multiple domains. Temperature-controlled optical microscopy confirms their presence, which causes the MIT in a single particle to occur in discrete steps over a small range of temperatures. Within that temperature range, there exist stable phase fractions of fully transitioned material. This behavior is not immediately evident through the characterization of a B-VO$_2$ device, in which the phase transition is triggered by Joule heating due to application of current or voltage across the material. When the device is switched by application of a voltage sweep, the decreasing resistance from M1 to R results in sudden, self-propagating heating to above the T$_{MIT}$, accelerating the transition of the material. In this case, the phase transition appears to occur suddenly and abruptly as in undoped VO$_2$. However, when the MIT is triggered by application of a current sweep, the decreasing resistance results in a self-limiting heating. This slows down heating of the device, allowing an indirect observation of the more gradual transition of the material as seen in optical microscopy. Analysis of the current sweeps shows small discrete changes in the measured resistance, corresponding to the discrete transition of a domain. This study provides insight into the number of domains present in the material, as well as information on the relationship between the dopant concentration and the number of domains formed. Through the different electrical characterization methods, it illustrates a history-dependent coexistence of the two phases of B-VO$_2$.

6:00 AM BREAK

6:30 AM *S.EL07.02.04
Finding and Understanding Materials that Compute R. Stanley Williams; Texas A&M University, United States

With the near saturation of Moore’s scaling of transistors, there has been a recent explosion in activity and creativity to find new modes of computation that will continue to advance exponentially with time even though transistor circuits only improve modestly. Much of the inspiration for new ways of computing comes from what little we understand about the brain. We actually don’t know how the brain computes, but many different possibilities have been proposed, e.g. multinary logic, Neural Networks of all kinds, extensions of Hebbian learning via spike-timing dependent plasticity, Boltzmann/Ising machines, Hopfield networks, Bayesian inference and Markov chains, to name a few. These possibilities are not necessarily mutually exclusive – the brain may use some combination of several of them or even use a higher order generalization that
contains all of them, since many share mathematical similarities. How to express these computational approaches in an
electronic circuit is a significant challenge. Since the brain itself is a highly nonlinear dynamical system, an appropriate area
to investigate is nonlinear dynamical circuit theory. This is the realm of the Principle of Local Activity, which provides a
basis for inventing and building new generations of two-terminal oscillators and amplifiers that emulate the integrate and fire
dynamics of neurons to produce action potentials for signal processing and axon-like active transmission lines. Combining
such devices will enable the design of circuits that are biased at the Edge of Chaos, where the emergence of complex patterns
and behavior in a homogeneous medium are found. What new types of devices will be used to construct these circuits? Can
we emulate neural computation using new electronic-ionic-thermal devices that exhibit dynamical behavior? These could be
based on properties such as negative differential resistance and/or capacitance that arise from thermally activated transport,
Mott transitions, molecular redox chemistry, electro-mechanical response in soft matter, and/or multi-ferroelectric
characteristics. Finally, how do we find the materials that we will use to build these new devices and measure their
properties? There are known materials that have the right type of electronic properties, but they often have disadvantages
such requiring exotic elements or a phase transition temperature that is too low or too high compared to normal operating
conditions. Can we intentionally design materials that will operate in the Goldilocks zone for a brain-inspired computing
machine – or must we test everything that we can fabricate combinatorially? What properties should we try to optimize, e.g.
transition temperatures, hysteresis loop widths, conductance and capacitance changes, or magnitude of negative differential
resistance? What are the ways of using the properties we do understand to invent the new materials we need? This is a rapidly
growing research field that requires coordinated efforts across a broad range of materials expertise from fundamental
chemistry to circuit design and fabrication.

7:00 AM S.EL07.02.05
Efficient Parallel Training of a Crossbar Array Using Organic Redox Transistors Yiyang Li1,2, T. Patrick Xiao1,
Armantas Melianas3, Erik Isele1, Christofer Bennet1, Sapan Agarwal1, Alberto Salleo3, Elliot J. Fuller1 and A. Alec
Talin1; 1Sandia National Laboratories, United States; 2University of Michigan, United States; 3Stanford University, United
States

In-memory computing using crossbar arrays of non-volatile memory has the potential to significantly decrease the energy
consumption of both inference and training. While crossbar arrays for inference, or dot-product engines, using two-terminal
memristors and three-terminal flash memory have been demonstrated to be more efficient than their digital counterparts,
crossbar arrays for training have been much more challenging due to difficulties in matching materials properties with
training algorithms. In particular, energy-efficient training arrays necessitate the ability to conduct an outer product update,
where all the synaptic weights are simultaneously updated, a feat which has not been accomplished in two-terminal devices.
We recently developed the three-terminal organic redox transistor based on PEDOT:PSS which is able to conduct binary
outer product updates between neighboring conductance states, a crucial step towards energy-efficient training [1]. However,
no training algorithm has been implemented.

In this work, we demonstrate for the first time how three-terminal redox transistors are able to train a perceptron network that
is adapted to multiple tasks in parallel. We use a small crossbar array of nine synapses to simultaneously train an AND gate,
an OR gate, and a NAND gate. We conduct nonbinary and continuous analogue weight updates by controlling the
programming time along a given row and column, at micro-second time scales. We use crossbar simulation software
(CrossSim) to replicate this training in simulation, and show strong agreement between simulation and experiment.
Simulations further show that the ability to train small perceptron networks is enabled by linear and predictable weight
updates as well as the low device-to-device variation of the redox transistors, and that two-terminal TaOx memristors will not
be able to train this small network to complete accuracy. By showing experimental evidence of training, this work further
validates the ability of CrossSim to predict how accurately and quickly analogue non-volatile memory are able to train an
artificial neural network.

Reference:
[1] Fuller, et al. Parallel programming of an ionic floating gate memory array for scalable neuromorphic
5:00 AM *S.EL07.03.01
First Order Reversal Curve Distributions for Ferroelectric Materials as a Function of Temperature and Imprint
Susan E. Trolier-McKinstry, Kathleen Coleman and Betul Akkopru-Akgun; The Pennsylvania State University, United States

The Preisach model describes the hysteresis response of a ferroelectric material as being a composite of an ensemble of hysterons. The irreversible hystereron distribution can thus be used to estimate the stability of various states as a function of prior field history. This paper will describe the first order reversal curve distributions for lead zirconate titanate thin films as a function of a number of variables, including the levels of donor and acceptor doping, the level of imprint, and temperature from 10 – 300 K. Ultimately, data of this type are required to fully describe the number of discriminable states in a neuromorphic computing system.

5:30 AM S.EL07.03.02
Dynamically Evolving Metastability in an Atomic Hourglass—Temporal Control of the Metal-Insulator Transition of VO₂ by a Mobile Dopant
Erick Braham, Diane Sellers, Ruben Villarreal, Timothy Brown, Theodore Alivio, Heidi Clarke, Luis De Jesus, Raymundo Arroyave, Patrick Shamberger and Sarbajit Banerjee; Texas A&M University, United States

Solid-solid phase transitions are often accompanied by massive changes in fundamental materials properties such as resistivity and optical transmittance. The relative stabilities of the phases involved in these transitions can be modulated through several means one of which being through doping or alloying which has been shown to create an immutable alteration of the transformation barriers. Reversible post synthetic modulation of a phase transition continues to be a challenge that, if allowed, would enable distinct potential for useful for neuromorphic computing, chronometry, and sensing. Metal—insulator transition materials are excellent candidates for neuromorphic computing of which VO₂ is a canonical example. We demonstrate in VO₂ mobile dopants that are weakly coupled to the lattice provide a means of imbuing an entirely reversible and dynamical modulation of the metal-insulator transition of VO₂. Specifically, we demonstrate the remarkable time-dependent evolution of the relative phase stabilities of insulating monoclinic (M₁) and metallic rutile (R) phases of VO₂ in a completely reversible “hourglass” fashion as interstitial boron species relax from high-energy sites where they are situated upon a thermally induced phase transition. The relaxation process corresponds to a 50°C range of the transition temperature achieved within the same sample as a function of residence time and temperature. The diffusive boron dopant atoms provide a means of attaining a reconfigurable and readable time- and thermal history dependent response that derives from intrinsic material properties.

6:00 AM *S.EL07.03.04
Atomistic Understanding of Memory Effect in Monolayer Memristors and Emerging Applications
Saban Hus¹, Ruijing Ge¹, Po-An Chen¹, Xiaohan Wu¹, Jack Lee¹, Meng-Hsueh Chiang² and Deji Akinwande¹; ¹The University of Texas at Austin, United States; ²National Cheng Kung University, Taiwan

This talk will present the latest research progress on the atomic-level details of non-volatile resistance switching (NVRS) in 2D memory devices. In particular, we will focus on our scanning tunneling microscopy (STM) based imaging and transport studies, together with the first principle calculations on the common point defects of 2D materials. For this investigation, we employ the STM tip as the top electrode of vertical metal-insulator-metal (MIM) memory device and examine the defect sites in atomic resolution before and after resistive switching events. These studies provide one to one correlation between the structural and electronic properties of the heterogeneities and their role in the resistance switching mechanism. Through these studies, we seek to deduce which particular defect structures are most desirable for NVRS and utilize this information for emerging applications.

6:30 AM BREAK

7:00 AM S.EL07.03.05
Control of Metal-Insulator Transition Character in VO₂ through Chemical Doping
Patrick Shamberger, Heidi Clarke, Adelaide Bradicich, Aliya Yano, Diane Sellers, Erick Braham and Sarbajit Banerjee; Texas A&M University, United States

Chemical control of the coupled electronic-structural transformation in correlated oxide systems is a vigorously investigated area, due to fundamental interest in the role chemical dopants play in stabilizing different crystal structures and altering
electronic band structure, as well as practical interest in being able to tune the critical transformation temperature and the degree of volatility of the transformation. Such an approach holds promise for tuning the properties of adaptive oxide phases to demonstrate novel functionality and emulate neuromorphic behaviors. While chemical doping has shown dramatic effects in changing the thermodynamic stability of different doped VO$_2$ phases, including increasing or depressing phase transformations by up to ~20°C, and stabilizing phases that are not typically observed in undoped VO$_2$ upon simple heating and cooling, very little is known regarding the impact of chemical doping on transformation behavior in this system. Doping could potentially modify the behavior of the electronic-structural phase transformation by at least three mechanisms: 1) by altering the energy landscape of the system, including the magnitude of energy barriers limiting forward and reverse transformation, 2) by stabilizing intermediate phases, which may introduce alternative transformation paths, or 3) by introducing localized regions of strain surrounding chemical dopants, which could affect local thermodynamic equilibria heterogeneously throughout a sample. Importantly, all three of these effects could potentially impact either the energy barriers limiting incipient nucleation of a new daughter phase within a parent phase, or the mobility of heterophase boundaries, impacting the rate of growth of domains of a daughter phase. Clarifying changes in phase transformation mechanisms requires microscopic investigation of domain nucleation and growth in both undoped and doped systems. Resolving these questions can expose important underlying clues in understanding transformation mechanisms in both undoped and chemically doped systems, and can reveal new approaches to engineering metal-insulator transitions (MIT) with desired transformation behavior.

Here, we present representative illustrations of the effect of chemical dopants on altering phase transformation mechanisms and progression, drawn from select interstitial and substitutional doping schemes. We will illustrate 1) the use of dopants to simultaneously alter transformation equilibrium temperature and hysteresis, 2) the use of dopants to extend the width of the phase transformation, introducing extended regions of phase coexistence, as well as 3) the use of dopants to introduce relaxation effects, which can be used to dynamically tune the equilibrium transformation temperature of the system.

7:15 AM *S.EL07.03.07
Strategies to Precisely Control Synaptic Weights for Neuromorphic Computing Arrays Jeehwan Kim; Massachusetts Institute of Technology, United States

Neuromorphic computing has recently emerged as a non-Von Neuman computing method. Because its analog switching ability to represent multiple synaptic weights by varying conductance in the vertical filaments formed in the switching medium, a resistive memory has been considered as an artificial synapse for suitable neuromorphic hardware platform. Conventional resistive memories typically utilize a defective amorphous solid as a switching medium for defect-mediated formation of conducting filaments. However, the imperfection of the switching medium also causes stochastic filament formation leading to spatial and temporal variation of the devices. Such variation of artificial synapses prevented community from obtaining large-scale artificial neural networks. In this talk, I will present new type of resistive memory that can more precisely confine the conducting paths so that uniform artificial synapses have been obtained leading to 100% yield 32x32 arrays with a great programmability. In this talk, I will discuss about our strategies to control the ionic conduction paths: one is to utilize threading dislocations as confinement paths of ionic conduction in SiGe epitaxially grown on a Si wafer and another is to alloy Ag active metal with silicidable metals to have additional controls in conduction channels. These result in low temporal/spatial variation, linear synaptic weight update, great endurance, and long retention time. Actual crossbar arrays were fabricated and I will present properties and programmability of our ANN arrays.

5:00 AM *S.EL07.04.01
Advanced Materials and Nanodevices for Brain-Inspired Computing Francis Balestra; CNRS, France

The brain-inspired computing schemes are expected to reduce the time, energy and area required to propose solutions for a number of Artificial Intelligence-related applications. Brain-inspired computing architectures can be implemented by analog or digital circuits using innovative materials and CMOS or beyond CMOS nanodevices, such as small slope switches, to potentially improve energy efficiency thanks to their
steep subthreshold slope and low operating voltage. The exploitation of the subthreshold FET characteristics, which naturally exhibit exponential relationships in their transfer functions, also allow to directly emulate the biophysics of neural systems. On the other hand, the ability to alter the conductance levels in a controllable way makes Phase Change Memory devices particularly well-suited for synaptic realizations. The two key synaptic attributes of efficacy and plasticity can be efficiently realized using a unit comprising PCM devices and FETs. In this presentation, we will show the disruptive properties of advanced NanoFETs for ultimate integration, reduction of energy consumption and enhanced performance, such as Nanowire FETs, Carbon NanoTube FETs, Tunnel FETs, Negative capacitance FETs, Hybrid Devices, combined with novel materials such as III-V, Ge, 2D/TMDs, Heterostructures, Phase Change, Nanofilament, Ferroelectric, Semimetal.

These innovative materials could be used for boosting NanoFETs electrical properties and/or developing new generation of memory devices, for instance Storage Class Memories, for near-memory computing where FET processing units are placed in close proximity to the memory unit for increased system performance. They can also be used for In-Memory Computing, for which the computation is performed in place by exploiting the physical attributes of memory devices organized as a computational memory unit [1-5].


5:45 AM BREAK

SESSION S.EL07.05: Poster Session: Fundamental Mechanisms and Materials Discovery for Brain-Inspired Computing—Theory and Experiment
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
5:00 AM - 8:00 AM
S-EL07

S.EL07.05.01
Polaron Oscillation and Cation Shuttling Underpin the Metal-Insulator Transition of β'-Cu₃V₂O₅ Joseph Handy, Justin L. Andrews and Abhishek Parija; Texas A&M University, United States

Silicon circuitry has been the mainstay of the semiconductor industry for several decades but is fundamentally constrained by the Fermi-Dirac electron distribution of electron energies, which establishes an immutable limit to the steepness of switching characteristics that can be achieved within a device. As such, electrostatically-modulated transistors inevitably give rise to much wasteful power consumption, requiring large swathes of logic circuitry on a chip to be left inoperative at any given time. Much attention has therefore focused on the design of materials exhibiting a pronounced switching of electrical conductance with minimal energy dissipation in response to small external stimuli. Electron-correlated transition metal oxides exhibiting pronounced metal-to-insulator transitions are excellent candidates for energy efficient computation and further provide a means of emulating the spiking behavior of biological neural circuitry. Amongst the rare palette of materials exhibiting pronounced metal—insulator transitions, β’-Cu₃V₂O₅ stands out for its tunability of the transformation temperature and, as we demonstrate here, a pronounced nonlinear response to applied temperature, voltage, and current in relation to Cu stoichiometry. We have shown that polaron oscillation, underpinned by the real-space shuttling of Cu-ions between two adjoining split-site positions within a 1D tunnel defined by VO₅ square pyramids and VO₆ octahedra underpins the metal-insulator transition of this material. Our work combines high-resolution structure refinement from variable-temperature single-crystal and powder X-ray diffraction; variable-temperature extended X-ray absorption fine structure spectroscopy (EXAFS) studies of local structure; angle-integrated photoemission spectroscopy, resonant inelastic X-ray scattering (RIXS), and hard X-ray photoemission spectroscopy (HAXPES) studies of electronic structure; density functional theory (DFT)
modeling of electronic structure; and single-nanowire measurements of transport phenomena. The results provide unprecedented mechanistic insight into the close interplay between crystal structure distortions and emergence of electron correlation which gives rise to the metal—insulator transition of a strongly correlated system. The utilization of cation diffusion and polaron shuttling demonstrates a means of using ionic vectors in conjunction with subtle structural distortions to obtain highly nonlinear and memristive conductance switching as required for neuromorphic computing and sensing.

**SYMPOSIUM S.EL09**

Phase-Change Materials for Electronic and Photonic Nonvolatile Memory and Neuro-Inspired Computing
November 21 - November 30, 2020

**Symposium Organizers**
Paolo Fantini, Micron Technology Inc.
Juejun Hu, Massachusetts Institute of Technology
Wei Zhang, Xi'an Jiaotong University
Paola Zuliani, STMicroelectronics

* Invited Paper

**SESSION Tutorial S.EL09: Phase-Change Memory—Materials Fundamentals and Advanced Applications**
Session Chairs: Juejun Hu, Riccardo Mazzarello, Wolfram Pernice and Matthias Wuttig
Saturday Morning, November 28, 2020

S.EL09

8:00 AM *
**Phase-Change Materials—Empowered by an Unconventional Bonding Mechanism** Matthias Wuttig; RWTH Aachen University, Germany

Phase-change materials (PCMs) have demonstrated a wide range of potential applications ranging from electronic memories to photonic devices. These applications are enabled by the unconventional portfolio of properties that characterizes crystalline PCMs. Here, I address the origin of these unusual properties and how they are related to the application potential of these materials. Evidence will be presented that the properties are related to an unconventional bonding mechanism. Employing a novel map, which separates solids according to the number of electrons transferred and shared between adjacent atoms, it is shown that PCMs occupy a well-defined region. Depicting physical properties such as the optical dielectric constant as the third dimension in the map reveals systematic property trends. Such trends can be utilized to unravel the origins of the unconventional materials properties or alternatively, as a means to optimize them.

9:30 AM *
**Atomistic Simulations of Phase-Change Materials** Riccardo Mazzarello; RWTH Aachen University, Germany

Phase-change materials (PCMs) are used in optical devices and electronic non-volatile memories, and are promising candidates for neuro-inspired computing applications. These technologies exploit the ability of PCMs to switch rapidly between amorphous and crystalline states with pronounced optical and electrical contrast. In this tutorial an overview is given of recent computational work on PCMs based on density functional theory and machine-learning potentials. It will be shown that simulations have enabled the elucidation of fundamental links between structure and dynamics. Such links have shed light on technologically relevant properties of PCMs, including the ultrafast crystallization at high temperature, the behaviour of the liquid phase in the deep undercooling regime and the relaxation of the amorphous state.

11:00 AM *
Integrated Phase-Change Photonic Devices and Systems Wolfram Pernice; University of Münster, Germany

Driven by the rapid rise of silicon photonics, optical signaling is moving from the realm of long-distance communications to chip-to-chip, and even on-chip domains. If on-chip signaling becomes optical, we should consider what more we might do with light than just communicate. We might, for example, set goals for the storing and processing of information directly in the optical domain. Doing this might enable us to supplement, or even surpass, the performance of electronic processors, by exploiting the ultrahigh bandwidth and wavelength division multiplexing capabilities offered by optics. Here, I show how, by using an integrated photonics platform that embeds chalcogenide phase-change materials into standard silicon photonics circuits, we can achieve some of these goals. Specifically, I show that a phase-change integrated photonics platform can deliver binary and multilevel memory, arithmetic and logic processing, as well as synaptic and neuronal mimics for use in neuromorphic, or brain-like, computing -- all working directly in the optical domain.

SESSION S.EL09.08: Live Keynote I: Phase-Change Materials for Electronic and Photonic Nonvolatile Memory and Neuro-Inspired Computing

Session Chairs: Matthias Wuttig and Wei Zhang
Sunday Afternoon, November 29, 2020
S.EL09

5:00 PM *S.EL09.05.13
Electronic Properties of Phase Change Compounds in the Liquid State—Effective Charges for Electromigration and Semiconductor-Metal Transition from First Principles Matteo Cobelli1, Mario Galante2, Daniele Dragoni1, Stefano Sanvito2 and Marco Bernasconi1; 1Università di Milano-Bicocca, Italy; 2Trinity College, Ireland

In the reset process of phase change memories, the active material is brought rapidly above the melting temperature by Joule heating. Atomic migration in the liquid state due to the high electric field can lead to alloy demixing and eventually to device failure. The electromigration force $F$ responsible for ionic migration is proportional to the electric field via the effective charge $Z^*$ ($F = Z^* E$). Information on the effective charges is thus of great relevance for the electrothermal modeling of the device. However, experimental estimates of the effective charges in the liquid state suffer from large uncertainties. A possible route to estimate $Z^*$ relies, in fact, on the modeling of the concentration profile of the different species in highly cycled memory cells which, however, depends on several mostly unknown parameters that have to be plug into phenomenological transport equations [1].

In this work, we show that a direct first principles calculation of the effective charges in metallic liquids is possible by computing the atomic forces in the presence of both an electric field and an electronic current within the Non-Equilibrium Green Function scheme implemented in the code Smeagol [2]. We will present results on the calculation of the effective charges, including the wind force, for the GeTe and Sb$_2$Te$_3$ phase change compounds in the liquid state.

Another feature of the liquid state that affects device operations is the opening of an electronic gap upon cooling from the melting point to the glass transition temperature during reset. The temperature at which the metallic liquid turns into a semiconductor is another important parameter for the electrothermal modeling of the device. By means of density functional molecular dynamics and the use of a hybrid exchange and correlation functional, we have estimated the temperature of gap opening in the supercooled liquid phase of GeTe and Ge$_2$Sb$_2$Te$_5$ compounds.


5:15 PM S.EL09.02.02
Phase Change Materials by Design—The Power and Potential of Maps Matthias Wuttig; RWTH Aachen University, Germany

It has been a long-time dream of mankind to design materials with tailored properties. In recent years, the focus of our work has been the design of phase change materials for applications in data storage. In this application, the remarkable property portfolio of phase change materials (PCMs) is employed, which includes the ability to rapidly switch between the amorphous and crystalline state. Surprisingly, in PCMs both states differ significantly in their properties. This material combination
makes them very attractive for data storage applications in rewriteable optical data storage, where the pronounced difference of optical properties between the amorphous and crystalline state is employed. This unconventional class of materials is also the basis of a storage concept to replace flash memory. Today’s talk will discuss the unique material properties, which characterize phase change materials. In particular, it will be shown that only a well-defined group of materials utilizes a unique bonding mechanism (‘Bond No. 6’), which can explain many of the characteristic features of crystalline phase change materials. Different pieces of evidence for the existence of this novel bonding mechanism, which we have coined metavalent bonding, will be presented. In particular, we will present a novel map, which separates the known strong bonding mechanisms of metallic, ionic and covalent bonding, which provides further evidence that metavalent bonding is a novel and fundamental bonding mechanism. This insight is subsequently employed to design phase change materials as well as thermoelectric materials.

5:25 PM S.EL09.05.14

In Situ Study of Vacancy Disordering in Crystalline Phase-Change Materials under Electron Beam Irradiation

Xudong Wang¹, Tingting Jiang¹, Jiangjing Wang¹ and Wei Zhang¹,²; ¹Center for Advancing Materials Performance from the Nanoscale, State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, China; ²Xi’an Jiaotong University Suzhou Institute, China

Fast and reversible phase transitions in chalcogenide phase-change materials (PCMs) play a key role in next-generation memory and computing chips. The Ge-Sb-Te compounds, such as Ge2Sb2Te5 and GeSb2Te4, are under active investigations, not only because they serve as the key element in commercial products, but also because they provide a rich platform for fundamental research in materials science.

Disorder-driven metal insulator transition has been reported in crystalline Ge-Sb-Te phase-change materials (PCMs), where the high concentration and statistical distribution of atomic vacancies were identified as the key factor in shaping the localization properties of electrons and, thus, the electrical transport. Vacancy ordering has been consistently observed in crystalline Ge-Sb-Te thin films upon thermal annealing, triggering a structural transition from a cubic rocksalt structure to a layered hexagonal structure and an insulating to metallic transition.

In this work, we demonstrate an opposite vacancy disordering process upon extensive electron beam irradiation, which drives the reverse transition from the stable hexagonal phase to the metastable cubic phase. The combined in situ transmission electron microscopy experiments and density functional theory nudged elastic band calculations reveal three transition stages, including (I) the vacancy diffusion in the hexagonal phase, (II) the change in atomic stacking, and (III) the vanishing of vacancy-rich planes. The driving force of the vacancy disordering process is attributed to the kinetic knock-on collision effects of the high-energy focused electron beams, which prevail over the heating effects.

Our electron irradiation experiment not only provides an alternative approach to tune the vacancy distribution that is crucial for the disorder-driven metal-insulator transition of GST crystals, but also makes an instruction for the TEM measurement of structural details of a particular solid-state phase of PCMs that the three critical TEM parameters, namely, accelerating voltage, beam intensity and recording time, should be reduced as much as possible to avoid structural transitions during the measurement.

5:35 PM *S.EL09.06.01

Reconfigurable Infrared Flat Optics with Novel Phase Change Materials

Christopher M. Roberts¹, Yifei Zhang², Mikhail Shalaginov², Paul Robinson¹, Paul Miller¹, Kevin Tibbetts¹, Sean Gorsky¹, Vladimir Liberman¹, Carlos A. Rios Ocampo², Tian Gu², Myungkoo Kang³, Anupama Yadav³, Kathleen Richardson³, Juejun Hu³ and Jeffrey Chou¹; ¹MIT Lincoln Laboratory, United States; ²Massachusetts Institute of Technology, United States; ³University of Central Florida, United States

Previously, we have reported on a novel class of chalcogenide phase change materials, based on Ge-Sb-Se-Te (GSST) alloys, with excellent infrared transparency from 1.5 to > 15 micron wavelengths. Increasing Se substitution leads to a progressive lowering of extinction coefficient. A material in this family with a particular useful stoichiometry, Ge2Sb2Se5Te (GSS4T1), possesses broadband transparency through the infrared range while maintaining a large index contrast between its amorphous and crystalline phases. Defining a figure of merit as Δn/k (where n,k are the real, imaginary parts of the refractive index), our materials shows >100x figure of merit (FOM) improvement over conventional GST throughout the infrared range.

In this talk, we describe novel applications enabled by reversible switching of low loss GSS4T1 material. In the first application, we exploit the exceptional FOM of the Se-doped PCM to realize a nonvolatile photonic switch with
unprecedented high performance. Our device, based on a racetrack SiN resonator with a PCM gate, exhibits a large switching contrast ratio of 42 dB and a low insertion loss of < 0.5 dB, far outperforming previous nonvolatile switches as well as devices based on the classical GST-225 material with a similar configuration.

Additional novel applications are enabled by our development of wafer-scale pixelated electrical switchable PCM devices. The pixelated devices are fabricated in a CMOS-compatible clean room on 8 inch wafers utilizing a full Si-based fabrication tool set. Devices of various pixel sizes, from 1 to 30 micron have been fabricated. Additionally, fabrication of more complicated sub-pixel metasurfaces was demonstrated. Electrical switching measurement is obtained by applying electrical pulse trains through a programmable voltage generator into the gate of a high powered transistor. Microsecond switching of 30-micron and 1-micron pixels in a wafer-scale device has been demonstrated. Current devices have demonstrated over 1,000 switching cycles and further durability improvements are underway.

As an application of pixelated electrical device, we have demonstrated a concept of compact infrared reflection spectrometer with no moving parts. Here, we leverage the ability to obtain gradually changing reflection signature of the pixel with voltage between fully-converted crystalline and amorphous phases. This wavelength shift is essentially a nonlinear filter which can be used to reconstruct an input spectrum. Since the reflection response of the pixel states is pre-determined, a spectral response of the scene can be extracted once the pixel spectrum is fully characterized with a known calibrated spectral source. We have carried out such characterization utilizing a supercontinuum laser in the short-wave infrared part of the spectrum and the results of spectral signature extraction for three different incident spectral scenarios.

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5:50 PM *S.EL09.06.02
Effects of Spatial Confinement on Phase-Change Materials Ann-Katrin U. Michel and David J. Norris; ETH Zürich, Switzerland

Phase-change materials (PCMs) allow for an ultrafast and reversible transition between their amorphous (a) and crystalline (c) state. This structural transition results in a pronounced change in their optical and electrical properties. The strong resistivity contrast of several orders of magnitude has been employed in electronic and neuromorphic memories, while the unity-scale refractive index change $\Delta n = |n_a - n_c|$ has been applied in rewriteable optical-data-storage memories. Additionally, $\Delta n$ is the subject of research in various photonic applications.\textsuperscript{[1]}

For tunable photonics, PCMs are very desirable, but expensive and laborious to produce. Thus, colloidal PCMs that can be easily synthesized could provide broader access to this material class and allow for deposition on a variety of substrates, including prepatterned holes and vertical interconnect accesses. However, due to the size reduction from GeTe thin films to small nanoparticles (NPs), new effects can arise. Examples are the occurrence of localized surface plasmon resonances in c-GeTe NPs,\textsuperscript{[2]} and size dependence of the crystallization temperature $T_c$.\textsuperscript{[3]} Thickness dependent temperature scaling was also reported for very thin sputtered PCM films, and related to their bonding characteristics.\textsuperscript{[4]} Recent results indicate that the spatial confinement of PCMs into small NPs results in an increase of the optical band gap $E_g$, while maintaining the pronounced contrast between the band gaps for a- and c-PCMs $E_{g,a}$ and $E_{g,c}$ respectively.\textsuperscript{[5]}

Insights into small-size PCM NPs can promote the application of these materials in different fields, and add value to fundamental scientific questions, especially regarding the current debate on the unique chemical bonding in PCMs.\textsuperscript{[6]} Despite the bottom-up synthesis of PCM NPs, structural confinement can be realized by sub-wavelength patterning. While laser pulses do not allow for switching on such small length scales, tip-induced crystallization can lead to features below 100 nm. The resulting so-called metasurfaces feature extremely strong field confinement and nearly $2\pi$ phase shift.\textsuperscript{[7]}


\textsuperscript{[7]}
6:05 PM S.EL09.04.02
Crystallization Properties of Nano Amorphized Areas in Epitaxial Epitaxial GST on Si (111) by TEM In Situ Characterizations

Antonio M. Mio\textsuperscript{1}, Giuseppe D'Arrigo\textsuperscript{1}, Jos Boschker\textsuperscript{2}, Alessandro Meli\textsuperscript{1}, Stefano Cecchi\textsuperscript{2}, Eugenio Zallo\textsuperscript{2}, Antonella Sciuto\textsuperscript{2}, Marzia Buscema\textsuperscript{2}, Elena Bruno\textsuperscript{2}, Raffaella Calarco\textsuperscript{2} and Emanuele Rimini\textsuperscript{1}; \textsuperscript{1}CNR-IMM, Italy; \textsuperscript{2}Paul-Drude-Institut fur Festkorperelektronik, Germany; \textsuperscript{3}Dipartimento di Fisica e Astronomia Ettore Majorana, Università degli Studi di Catania, Italy

The crystallization behavior of amorphous nano-regions (20-100 nm in diameter) embedded in a textured epitaxial Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} 25 nm thick film grown on Si (111) substrate has been investigated in situ by TEM analysis. The amorphous regions were obtained by irradiation with 30 keV Ge\textsuperscript{+} at a fluence of 1.5x10\textsuperscript{14} ions/cm\textsuperscript{2} of masked samples. The adopted configuration simulates the GST structure of a device in the RESET state, it is then of relevance for understanding their data retention characteristics. The \textit{in situ} TEM analysis indicates that the amorphous to crystal transition is characterized by an initial growth velocity of 3.6 pm/s at 75°C, probably related to the external partially damaged area. For the previous annealed sample, a velocity of about 2.6 pm/s was observed at 90°C and a growth speed of 170 pm/s at 110°C for the 50nm and 100nm diameter amorphous spots. The 20 nm diameter amorphous spots recrystallize after the annealing at 90°C. The transition is governed only by crystallization (nucleation is absent) of the atoms located at the boundary of the amorphous dot with the surrounding crystalline regions. In some case a preferential growth along surfaces normal to the [110] and to the [121] directions has been found. The crystallographic characterization of the regrowth crystal indicates a good matching with the zone axis of the surrounding material although the crystalline seed Si (111) at the bottom interface is missing for the damage.

6:05 PM S.EL09.04.02
Pulsed Laser Deposited Sb\textsubscript{2}Te\textsubscript{3}, GaSb and Ge –Rich GST Thin Films and Heterostructures for Memory Devices

Daniel T. Yimam, Jamo Momand and Bart J. Kooi; Zernike Institute for Advanced Materials, University of Groningen, Netherlands

Future Electronic Smart Systems (ESS) require energy efficient storage and fast processing of large amount of data. Phase-Change Materials, exhibiting large electrical and optical contrast between two phases also allowing multiple intermediate states, are highly desired for this application, because in principle they also have the ability to store and process data at the same physical place\cite{Wuttig2007}. Despite progresses which have been made to achieve the full potential of Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} based PCM devices, several reliability issues still hinder the realization of ultimate performance. Void formation due to density change upon switching, low crystallization temperature for automotive applications, and resistance drift over time are among the few. GaSb is considered as a promising candidate for future phase change random access memory (PCRAM) devices because of its fast crystallization, high crystallization temperature, and lack of density change upon switching at a specific composition of Ga\textsubscript{30}Sb\textsubscript{70}\cite{Putero2013}. Pulsed Laser Deposition (PLD) has become one of the most popular thin film deposition technique. Some of the reasons for this popularity are the flexibility, processing speed, and the wide range of materials that can be deposited. In this work we discuss PLD of single and alternating layers of Sb\textsubscript{2}Te\textsubscript{3}, GaSb, and Ge-rich GST thin films on various substrates. Amorphous, polycrystalline, and textured heterostructures of Sb\textsubscript{2}Te\textsubscript{3}/GaSb and Sb\textsubscript{2}Te\textsubscript{3}/Ge-rich GST are deposited. Reflection high-energy electron diffraction (RHEED) is used as in-situ growth monitoring tool during deposition to achieve desired film quality. Moreover, deposited films are characterized by Scanning Transmission Electron Microscope (S/TEM) for composition and quality analysis before producing single cell vehicles for electrical device testing.

6:15 PM S.EL09.03.02
Phase Change Memory from Fundamental Research to Industrial Development

Zhitang Song; Chinese Academy of Sciences, China

Phase change random access memory (PCRAM) has been successfully applied in the computer storage architecture, as storage class memory, to bridge the performance gap between DRAM and Flash-based solid-state drive due to its good scalability, 3D-integration ability, fast operation speed and compatible with CMOS technology. A good understanding of phase change mechanism is of great help to design new phase change materials with fast operation speed, low power consumption and long-lifetime. In this presentation, we firstly review the development of PCRAM and different understandings on phase change mechanisms in recent years, and then propose a new view on the mechanism, which is based on the octahedral structure motifs and vacancies. Octahedral structure motifs are the based units during phase transition. Robust octahedra and plenty of vacancies in both amorphous and crystalline phase, respectively avoiding large atomic
rearrangement and providing necessary space, are of crucial to achieve the nanosecond or even sub-nanosecond operation of PCRAM. Based on this mechanism, we introduce Sc-based robust octahedra in Sb$_2$Te$_3$ phase change materials, called Sc-Sb-Te, and achieve 700 ps operation speed. Recently, the concentration of dopants has also been optimized by correlative atom probe tomography and transmission electron microscopy investigations. Focusing on phase change materials and PCRAM for decades, we have successfully developed 128Mb embedded PCRAM chips, which can meet the requirements of most embedded systems.

6:40 PM S.EL09.04.06
Effect of Optical Illumination on Resistance Drift in Ge$_2$Sb$_2$Te$_5$ Line Cells
Raihan Sayeed Khan, Helena Silva and Ali Gokirmak; University of Connecticut, United States

The large resistivity contrast between the highly resistive amorphous phase and low resistive crystalline phase of phase change memory (PCM) provides opportunities for multi bit per cell memory and neuromorphic applications. However, the drift of resistance of amorphous phase limits the potential of PCM as multiple intermediate states can overlap over time. Although resistance drift is generally attributed to structural relaxation [1], we have observed significant resistance drift in Ge$_2$Sb$_2$Te$_5$ line cells at cryogenic temperatures and also being affected by optical illumination, indicating charge trapping [2]. A detailed understanding of the mechanisms behind resistance drift may allow for mitigating techniques. In this work, we study the effect of optical illumination between 125 K and 300 K and also the effect of different optical illumination conditions on the drift coefficient.

References:

6:50 PM S.EL09.05.03
Thermal Properties of Carbon Nitride Toward Use as an Electrode in Phase Change Memory Devices
Kiumars Aryana$^1$, John Gaskins$^1$, Joyeeta Nag$^2$, John Read$^2$, David Olson$^1$, Michael Grobis$^2$ and Patrick E. Hopkins$^1$; $^1$University of Virginia, United States; $^2$Western Digital Corporation, United States

In phase change memory cells, the majority of heat is lost through the electrodes during the programming process that leads to significant drops in the performance of the memory device. In this investigation, we report on the thermal properties of thin film carbon nitride with modest electrical resistivity of 5-10 mW cm, low thermal conductivity of 1.47W/m/K, and low interfacial thermal conductance between carbon nitride and phase change material for length scales below 40 nm. The thermally insulating property of carbon nitride makes it a suitable thermal barrier, allowing for less heat loss during Joule heating within the memory unit. We compare carbon nitride thermal properties against commonly used electrodes and insulators such as tungsten and silicon nitride, respectively, to demonstrate the promise of carbon nitride as a potential material candidate for electrode applications in phase change memory devices.

SESSION S.EL09.09: Live Keynote II: Phase-Change Materials for Electronic and Photonic Nonvolatile Memory and Neuro-Inspired Computing
Session Chairs: Juejun Hu and Andriy Lotnyk
Monday Morning, November 30, 2020
S.EL09

11:30 AM *S.EL09.02.01
Density Functional Simulations of the Atomic Structure and Dynamics of Phase Change Materials
Jaakko Akola$^{1,2}$, Janne Kalikka$^3$ and Robert Jones$^3$; $^1$Norwegian University of Science and Technology, Norway; $^2$Tampere University, Finland; $^3$Forschungszentrum Juelich, Germany

Crystallization of phase change materials has been studied by extensive density functional/molecular dynamics simulations (DF/MD). Four crystallization simulations of amorphous Ge$_2$Sb$_2$Te$_5$(460 atoms) have been completed at 600 K with simulation times up to 8.2 ns.$^{1,2}$ A sample with a history of order crystallizes completely in 1.2 ns, but ordering in others takes...
more time and is less complete. The amorphous starting structures without memory display phases (<1 ns) with subcritical nuclei (10–50 atoms) ranging from nearly cubical blocks to string-like configurations of ABAB squares and AB bonds extending across the cell. Percolation initiates the rapid phase of crystallization and is coupled to the directional p-type bonding. The results emphasize the stochastic nature of crystallization and the importance of sufficiently large samples. This is particularly evident in describing the role of crystallites that can merge to form larger units or hinder complete crystallization by the formation of grain boundaries.

Amorphous Sb is known to crystallize extremely rapidly already at room temperature. Crystallization of Sb has been studied at 600 K using six DF/MD simulations with up to 882 atoms. Crystallization proceeded layer-by-layer in most cases and was extremely rapid (~36 m/s). As shown in Fig. 1, diffusion plays a minor role in the process as the crystallization proceeds from the crystalline rim, and the evolution of bond lengths and ring statistics supports the bond-interchange model of Sb-rich phase change materials.

We have also carried out extensive DF/MD simulations (over 500 atoms, up to 100 ps) of liquid bismuth at four temperatures between 573 - 1023 K. These simulations provided details of the dynamical structure factors, the dispersion of longitudinal and transverse collective modes, and related properties (power spectrum, viscosity, and sound velocity). Agreement with available inelastic x-ray and neutron scattering data and with previous simulations is generally very good. The results show that DF/MD dynamics simulations can give dynamical information of good quality without the use of fitting functions, even at long wavelengths.

References:

11:45 AM S.EL09.02.03
Accurate and Efficient Deep Neural Network for High-Throughput-Simulation-Based Optimization of Chalcogenide Phase Change Materials Jie Liu1,2; 1Hunan University, China; 2University of Washington, United States

Chalcogenide phase change materials (PCM) are widely-used in optical data storage technologies. Also, they are promising to become the next-generation mainstream electronic non-volatile memory technology. These have been discussed and simulated in our prior work [1-4]. The operation of PCM-based devices hinge on the repeated rupture and formation of atomistic-scale chemical bonds to reversibly switch between crystalline and amorphous phases, which require atomistic-scale simulation methodology to achieve in-depth optimization. Nowadays, there are two categories of such methodologies — density functional theory (DFT) and artificial neural network (ANN). DFT-based molecular dynamics (MD) is accurate but inefficient -- it is practically applicable to only hundreds of atoms. ANN-based MD is efficient but inaccurate -- its maximum error of atomic force prediction can be over 10 eV/Angstrom.

In our recent work [5], we present a method based on deep neural network (DNN) to model PCM, which is both accurate and efficient. The DNN-based MD has a computational complexity of O(N), where N is the number of atoms. So, DNN-based MD is orders of magnitude faster than DFT, whose computational complexity is around O(N³). Furthermore, the maximum error of atomic force prediction of DNN-based MD is around 0.1 to 1 eV/Angstrom, which is much more accurate than ANN in the existing literature. In our another recent work [6], we present a transfer learning (TL) method, to handle the needs to simulate multiple combinations (different PCM stoichiometry, doping, etc.). Compared to the state-of-art methods in PCM literature, the proposed TL method can significantly reduce the amount of DFT data used to train the neural network, which is beneficial to enable high-throughput simulations.

Combining the accuracy and efficiency [5], and the trasferrability between different materials [6], we aim at establishing a general-purpose PCM optimization method based on high-throughput simulations.

The working principle of conventional phase change memory device is based on ultrafast reversible phase changes between crystalline and amorphous phases of Ge-Sb-Te (GST) materials. For information storage, phase change memory device uses a large contrast either in electrical resistance between the amorphous phase (high-resistance state) and crystalline phase (low-resistance state) or in optical reflectivity between the amorphous phase (low reflectivity state) and crystalline phase (high reflectivity phase). The erase of GST-based memory cell is achieved by applying a high intensity either electrical or laser pulses. These processes lead to the amorphization via melting and subsequent fast quenching of the phase change alloy. However, GST alloys are poor glass formers. Thus, rapid cooling rates are required to suppress the recrystallization of the alloys during the erase process. On another hand, the write process is accomplished by applying either electrical or optical pulses with low intensity. This results in an amorphous-to-crystalline phase transition. Due to intrinsic feature of GST alloys, a main challenge in material science is the optimization of memory writing times, which are limited by the crystallization kinetics of the alloys. In order to speed up the crystallisation rates, several strategies were proposed, including doping of GST materials, precrystallization of an amorphous matrix or using GST based superlattices. Being a nucleation-dominant material, the crystallization of GST alloy in a nanosized phase-change memory cell might however proceed at the crystalline interfaces. This contribution focuses on determination of crystallization dynamics in epitaxial Ge2Sb2Te5 (GST225) thin films on application relevant (nanosized) length and (nanosecond) time scales. We irradiate the thin films by a single UV laser pulse with a 20 ns pulse duration and with different laser fluences. First, we study the structural transitions in epitaxial GST225 thin films starting from the layered trigonal GST225 structures [1]. We compare the obtained results with the behaviour of GeTe-Sb2Te3 based superlattices (SLs) after the laser irradiation. In both cases, the results reveal the phase transition to the cubic GST225 structure. The cubic phase forms from a transient molten phase at the melt-crystalline interface upon cooling process and crystallizes with epitaxial relationship to the parent phase. Second, by introducing a method based on combination of high temporal and spatial resolution, we determine the crystallization rates of the cubic GST225 phase [2]. The rates are ranging from 0.4 m/s to 1.7 m/s. The values are well in agreement with the published experimental and theoretical data. Moreover, a variation of the laser fluence leads to different cooling rates, which result in different solidification rates and freezing of an amorphous state. Irradiation of amorphous GST225 phase by laser pulse with lower fluence leads to the re-crystallization of the phase and epitaxial formation of the cubic GST225 structure. Overall, our work shows an approach for the investigation of crystallisation kinetics in wide range of phase change materials on application relevant length and time scales. In addition, we demonstrate amorphization and crystallization of GST225 material by using UV laser with single pulse duration and wavelength only, where in the conventional amorphous-to-crystalline phase transitions the lasers with different pulse durations, number and wavelengths are usually applied.


**12:10 PM S.EL09.04.03**

**Nanoscale Probing of Phase Transition Properties in Chalcogenides Using Embedded Heater-Thermometer**

Nicolas Wainstein, Guy Ankonina, Shahar Kvatinisky and Eilam Yalon; Technion - Israel Institute of Technology, Israel

Phase-change materials (PCM) are technologically attractive materials for non-volatile memory, neuromorphic computing, optoelectronics, and recently, radiofrequency (RF) applications. Chalcogenide PCMs present a dissimilar resistance between the crystalline (low-resistivity) and amorphous phase (high-resistivity). The phase transition is thermally activated, and its kinetics can span orders of magnitude in time, down to sub-nanosecond timescales. Hence, proper probing of the thermal actuation is required to understand the fundamental material properties of PCMs, particularly the physics of melt-quench processes in nanoscale devices, interface vs. bulk effects, drift, and threshold voltage phenomena. Research efforts have been made to characterize PCM using a microthermal stage (MTS) [1]. The MTS structure used either a top Pt heater for the thermal actuation of a lateral Ge2Sb2Te5 (GST) device or a Pt heater surrounding the GST. Thus, the MTS allowed for probing with thermal time scales on the order of microseconds or longer.

Four-terminal, in-line, indirectly heated phase-change switches (IPCS) have been proposed for high-performance RF
applications, thanks to their state-of-the-art figure-of-merit (FOM)=1/(2πRONCOFF) [2, 3]. A typical IPCS consists of two RF ports in-line with the PCM (i.e., the RF path), separated by a small gap, and two terminals for thermal actuation using an embedded heater. The heater runs transversely to the direction of the RF path, under the PCM. The heater and the RF path are separated by a thin electrically isolating film (e.g., Si3N4). GeTe has been so far the material of choice for RF applications due to its low resistivity in the crystalline phase and relatively large resistivity contrast with the amorphous state, but recently an Sb-Te1 IPCS was demonstrated with similar FOM and improved energy efficiency [3].

In this study, we report on the use of IPCS device structure as a platform for electro-thermal characterization of phase transition properties of PCM in nanoscale films at nanosecond temporal resolution. The isolation between the heater and the PCM layer electrically decouples the heating pulse and PCM probing. Thus, the phase transition, as well as temperature-dependent properties up to temperatures of ~100 K, can be measured during heating pulse application with ns resolution. Furthermore, since the heater is buried underneath the PCM, our setup allows for 1) steady-state PCM temperature validation using scanning thermal microscopy (SThM) from the top surface, 2) separation between contribution of contact (interface) and bulk effects by varying overlap and underlap between the heater and the PCM contacts, and 3) test different materials of interest without significant change in the fabrication process. We use GeTe as a prototype material with known melting temperature, crystallization kinetics, and surface treatment for low ohmic contacts [4]. Measurements are carried out using RF probes for the heater and the PCM to reduce the overshoot and ringing of short-pulses and produce clean waveforms for nanosecond probing. The experimental results are compared to a detailed finite element electro-thermal model to extract key material properties. Overall, our platform can be used to uncover the intriguing kinetics of crystallization and amorphization in chalcogenides and other amorphous semiconductors.


12:20 PM S.EL09.05.08

Combinatorial Exploration of Phase Change Memory Materials with Enhanced Properties Heshan Yu1, Changming Wu2, Xiaohang Zhang4, Apurva Mehta4, Ritesh Agarwal4, Mo Li2, Gilad Kuson4 and Ichiro Takeuchi1; 1University of Maryland, United States; 2University of Washington, United States; 3Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, United States; 4University of Pennsylvania, United States; 5National Institute of Standards and Technology, United States

As one of the most promising candidates for developing new neuromorphic architectures for non-von Neumann computing and information storage, Ge2Sb2Te5(GST225) in photonic devices shows non-volatile, fast, and multi-step changes between the amorphous state and the meta-stable states. In order to search for other composition ratios with desired properties, e.g. large figure of merit, lower switching energy, etc., we have systematically investigated a broad composition range of the Ge-Sb-Te (GST) system. The GST combinatorial spread was fabricated by co-sputtering Ge, Sb and Te targets and was confirmed by wavelength dispersive spectroscopy that the composition variation across the Si wafer covers most part of the GST phase diagram. X-ray diffraction measurements (synchrotron radiation), Raman spectroscopy and resistance mapping clearly show evolution of the structure and phase-change temperature in the GST system. Refractive index and extinction coefficient were calculated at each composition spot using a scanning ellipsometer: some composition ratios were found to have a small extinction coefficient in the amorphous state, a high phase-change temperature, and a large figure of merit. Then, the nano-size photonic devices fabricated by these ratios were measured and showed good reversibility (more than 40000 cycles) and multi-level symmetric switching (at least 15 levels), suggesting that such compositions can be promising for photonic devices for neuromorphic control. Further, we confirm that compositions with promising properties are near the boundary between the Sb-Te and the Ge-Sb-Te phases, indicating that co-existence of the phases at microstructural level may be playing a role in giving rise to their properties. This work is funded by an ONR MURI (Award No. N00014-17-1-2661).

12:30 PM *S.EL09.05.02

Amorphization and Crystallization of Ge Rich GeSbTe Thin Films for Embedded Memory Applications Stefania M. Privitera1, Corrado Bongiorno1, Veronique Sousa2, Gabriele Navarro2, Chiara Sabbione2, Marie Claire Cyrille2, Egidio Carria3 and Emanuele Rimini1; 1IMM-CNR, Italy; 2CEA-LETI, France; 3STMicroelectronics, Italy

GeSbTe alloys, widely employed for phase change non volatile memory, are usually not suitable in embedded and automotive applications, because of the low crystallization temperature. Doping, in particular with Ge, has been shown to be a viable way to extend the thermal stability of GeSbTe alloys [1,2]. However, once an optimised composition has been selected, during device operation, the material stoichiometry may change, due to the atomic migration induced by the high temperature and/or by the electric field [3]. These variations may lead to programming and retention performance.
degradation or even to device failure. It is therefore crucial to understand the extent of the atomic migration and its impact on the stoichiometry, as well as on the crystallization properties. In order to decouple the effect of the atomic diffusion at high temperature from that of the field induced electromigration, we have irradiated crystalline Ge rich GeSbTe thin films by laser. The films were prepared by sputter deposition in the amorphous phase, and then converted into the crystalline structure by annealing at 400°C. The irradiation has been performed by using a Yb-YAG laser (515 nm) with 600 ns pulse, operating at different energy densities. By changing the energy density, complete or partial melting and quenching, with amorphization of the film, can be achieved. In this way we are able to study the thermal diffusion processes decoupled from the field induced electromigration. After melting and quenching, the atomic elements distribution has been studied by Transmission Electron Microscopy (TEM) and Electron Energy Loss Spectroscopy (EELS). We find that, even without the electric field, the melting gives rise to a prominent diffusion of Ge atoms. By employing finite elements computational analysis, a diffusion coefficient of Ge on the order of $5 \times 10^{-5}$ cm$^2$ s$^{-1}$ in the molten phase has been estimated.

After amorphization under different irradiation conditions, we have followed the crystallization upon thermal annealing by in-situ time resolved reflectivity measurement. Such a crystallization process, after the first melting and quenching, is expected to be different from the crystallization of the as deposited amorphous film, since the melting produces not only sub-critical crystalline nuclei, but also a modification of the stoichiometry. The study of the crystallization in such a “primed” material is very similar to the situation occurring in a real memory device after the first erasing step and therefore it is relevant for reliability evaluations.


12:45 PM S.ELO9.05.09
Cw Laser Annealing Induces Stress Field During Phases Transition in Ge$_2$Sb$_2$Te$_5$ Layer
Giuseppe D’Arrigo$^1$, Mario Scuderi$^1$, Antonio M. Mio$^1$, Gregory Favaro$^2$, Antonella Scuoto$^1$, Marzia Buscema$^1$, Alessandro Meli$^1$, Giovanni Li Destri$^3$, Egidio Carria$^4$, Domenico Mello$^4$, Michele Calabretta$^4$, Alessandro Sitta$^4$, Julian Pries$^5$, Matthias Wuttig$^5$ and Emanuele Rimini$^5$; $^1$CNR-IMM, Italy; $^2$Anton Paar USA Inc., Switzerland; $^3$Università di Catania, Italy; $^4$STMicroelectronics, Italy; $^5$RWTH Aachen University, Germany

The mechanical properties, Hardness and Young module, of crystalline micrometer stripes of Ge$_2$Sb$_2$Te$_5$ and of the surrounding 2.2 $\mu$m thick amorphous film have been measured simultaneously. Crystallization was performed by a Continuous Wave laser irradiation process in the range 1.25-3.2 mW. The density changes between the amorphous and the crystalline phase cause a relevant stress in the processed material. Usually the stress is measured by the wafer curvature. This methodology doesn’t allow a detailed investigation of the local mechanical modifications when the two phases amorphous and crystalline are contiguous, as in an optical or electrical storage device. The use of micrometer patterned structures and nano-indentation measurements allow us to determine the mechanical behavior of the two contiguous GST phases. The measured values of the mechanical property are more dispersed for the crystallized material than those for the contiguous amorphous phase. The Young module and the hardness are 51±8 GPa and 2880±450 MPa for the crystallized and 33±4 GPa and 1989±300 MPa for the amorphous phase respectively. Microcracks are also seen, together with fracture lines. The occurrence of delamination at laser power densities above 1.70 mW indicates that for these crystallized thicknesses the maximum tensile strength in the amorphous and crystalline phases was reached and exceeded. The phase transition has also been investigated by several analytical tools (TEM, SEM, Raman and XRD diffraction). A simulation code was adopted to compute the temperature-time-space profile as a function of the laser power. These results were used to compare the measured crystallized thickness to that calculated.

12:55 PM S.ELO9.04.04
Uncovering $\beta$-Relaxations in Amorphous Phase-Change Materials
Shuai Wei$^1$, Si-Xu Peng$^2$, Yudong Cheng$^1$, Julian Pries$^1$, Hai-Bin Yu$^1$ and Matthias Wuttig$^1$; $^1$RWTH Aachen University, Germany; $^2$Huazhong University of Science and Technology, China

Relaxation processes are decisive for many relevant physical properties of amorphous materials. For amorphous phase-change materials (PCMs) employed in non-volatile memories, relaxation processes are, however, difficult to characterize due to the lack of bulk samples. Here, instead of bulk samples, we use powder mechanical spectroscopy for powder samples to detect the prominent excess wings – a characteristic feature of $\beta$-relaxations – in a series of amorphous PCMs at temperatures...
below the glass transition. By contrast, β-relaxations are vanishingly small in amorphous chalcogenides of similar composition, which lack the characteristic features of phase-change materials. This conclusion is corroborated upon crossing the border from PCMs to non-PCMs, where β-relaxations drop significantly. Such a distinction implies that amorphous PCMs belong to a special kind of covalent glasses whose locally fast atomic motions are preserved even below the glass transitions. These findings also suggest a correlation between β-relaxation and crystallization kinetics of PCMs, which may have technological implications for phase-change memory functionalities.

1:05 PM S.EL09.05.05
Modeling Charge and Electro-Thermal Heat Transport in Phase Change Memory Cells Md Tashfiq Bin Kashem, Jake Scoggin, Ali Gokirmak and Helena Silva; University of Connecticut, United States

In order to model phase change memory (PCM) cells, dynamic materials models have to be coupled with charge and heat transport models [1]-[7]. Since PCM cells experience high temperatures, very large thermal gradients (~ 50 K/nm) and high current densities during their normal reset and set operations, thermoelectric contributions are significant for both charge and heat transport in these cells. Furthermore, some of the assumptions made for large scale thermoelectric devices do not hold under these extreme conditions.

Charge transport in PCM cells can be modeled using a drift-diffusion approximation. However, electronic material properties such as carrier concentrations, mobilities and diffusivities are not well characterized for phase change materials. In this study, we construct (i) a drift-diffusion model using thermoelectric characteristics of the material, measured in a large temperature range, and (ii) an electrothermal heat transport model that does not assume mild temperature gradients only. Our simulation results show that both Thomson heat (thermoelectric effects in the bulk materials) and Peltier heat (thermoelectric effects at the contact regions) play a significant role, and give rise to significantly asymmetric thermal profiles in symmetric PCM cells.

Acknowledgments: This work is partially supported by NSF under award DMR-1710468.

References:

1:15 PM S.EL09.02.06
Reversible Electrochemical Phase Change in Monolayer to Bulk-Like MoTe2 by Ionic Liquid Gating Dante Zakhidov\(^1\), Daniel A. Rehn\(^1\)\(^2\), Evan J. Reed\(^1\) and Alberto Salleo\(^1\); \(^1\)Stanford University, United States; \(^2\)Los Alamos National Laboratory, United States

Transition metal dichalcogenides (TMDs) exist in various crystal structures with semiconducting, semi-metallic, and metallic properties. The dynamic control of these phases is of immediate interest for next generation electronics such as phase change memories and TMDs have the potential to outperform current phase-change materials such as GeSbTe on energy efficiency while also being fundamentally more scalable. Of the binary Mo and W-based TMDs, MoTe\(_2\) is attractive for electronic applications because it has the lowest energy difference (40 meV) between the semiconducting (2H) and semi-metallic (1T') phases, allowing for MoTe\(_2\) phase change by electrostatic doping.

Here we report phase change between the 2H and 1T' polymorphs of MoTe\(_2\) in thicknesses ranging from the monolayer case to effective bulk (73nm) using an ionic liquid electrolyte at room temperature and in air. We find consistent evidence of a partially reversible 2H-1T' transition using in-situ Raman spectroscopy where the phase change occurs in the top-most layers of the MoTe\(_2\) flake. We empirically find that the transition voltage of the phase change increases with thickness which provides a direct avenue to transition-voltage control for phase change devices. We also show evidence of electrochemical activity during the gating process by observation of Te metal deposition. This finding suggests the formation of Te vacancies which have been reported to lower the energy difference between the 2H and 1T' phase, potentially aiding the phase change process. This provides another avenue for transition-voltage control through defect engineering but also emphasizes the need for better understanding of electrolyte gating and chalcogenide vacancy formation. Our discovery that the phase change can be achieved on the surface layer of bulk materials reveals that this electrochemical mechanism does not require isolation of a
single layer and the phase change effect may be more broadly applicable than previously thought. We will also discuss recent work on implementation of a solid state device with the use of ionic gels and porous dielectrics.

SESSION S.EL09.01: Memory and Computing

On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

5:00 AM *S.EL09.01.01

Beyond von–Neumann Computing—Engineering Artificial Synapses for In–Memory Computing

Valeria Bragaglia, Benedikt Kersting, Prasad Jonnalagadda, Antonio La Porta, Daniel Jubin, Diana Dávila, Jason Giannopoulos, Manuel Le Gallo, Ghazi Syed, Folkert Horst, Jean Fompeyrine, Bert Offrein and Abu Sebastian; IBM Research-Zurich, Switzerland

The processing of an input dataset by a deep neural network, e.g. for classification tasks, is a series of vector-matrix multiplications (input data * synapse weight). The size and number of matrices that need to be processed are too large to be stored in a Static Random Access Memory (SRAM) unit. For this reason, data need to be shuffled constantly between memory and processing unit in a classical computing architecture, leading to inefficiency and performance mitigation. Dedicated neuromorphic computing hardware may help to overcome these issues and is a promising technology for the post-von Neumann computing era. Especially memristive devices are suitable for this dedicated hardware. A crossbar of memristive devices stores the synaptic weights in a physical matrix. The weight can be read non-destructively and updated e.g. during training. The matrix vector multiplication can be performed in-memory by coding the synaptic weight to the device conductance and the input data to the read voltage amplitude.

Several memristive technologies are under study for the implementation of neuromorphic hardware, and they rely on diverse physical mechanisms and materials [1]. However, improvements in the device characteristics are required for optimal hardware acceleration in both performance precision and energy consumption. Examples of challenges are the minimization of inter and intra device asymmetricity, non-linearity and stochasticity, and the increase of the dynamic range.

In this talk I will present Phase Change Memories (PCM) and filamentary-based Oxide Resistive Ram (OxReRAM), the two most promising candidates to represent artificial synapses in neuromorphic hardware [2,3]. In PCM-based memristors, the conductance change relies on a phase transition in the material, while for filamentary-based OxReRAM, the synaptic weight depends on the rupture/formation of oxygen vacancies based conductive paths. Strength and challenges of the two classes of memristors will be discussed. For each technology, an innovative design and material stack concepts will be presented, demonstrating enhanced operational characteristics. The material-stack characterization by means of X-ray reflectivity and diffraction, Hall-measurements as well as the electrical characterization of the devices will be covered. A discussion on the ideal class of applications for a more efficient use of PCM- or OxReRAM-based synapses will follow.


5:30 AM S.EL09.01.02

Optical Properties and Photonic Applications of Monatomic Phase-Change Materials

Zengguang Cheng, Samuel Humphrey, James Y. Tan, Tara Milne, Nikolaos Farmakidis, Eugene Soh, Seongdong Lim, Robert Taylor and Harish Bhaskaran; University of Oxford, United Kingdom

With the increasing demand of high-density storage and neuromorphic hardware driven by the rapidly growing of artificial intelligence, miniaturized phase-change memory device has been developed for energy-efficient data storage and computing[1]. Typical phase-change memory devices are based on complex compounds with precisely controlled stoichiometry. Therefore, monatomic phase-change materials using single element of antimony has been proposed as a promising candidate in ultra-small phase-change device without the need of compositional optimization[2]. On the other hand, the integration of phase-change materials with photonics has provided considerable opportunities of data storage[3], computing[4] and machine learning[5] in photonics, benefited from the fast speed, large bandwidth and low cross talking in optical domain[6] as well as the exceptional properties of phase-change materials[7]. Herein, we systematically studied the material properties, especially the optical properties, of thin-layer antimony films during the phase-changing process. With a huge contrast of optical constants between the amorphous and crystalline states, we demonstrated integrated non-volatile
photonic memories using monatomic phase-change materials, resulting in a unique platform for phase-change photonic applications.

References

5:45 AM S.E.L09.01.03
Phase Change Material Volatile and Non-Volatile Memory in Photonic Neural Networks Mario Miscuglio1, Robert E. Simpson2, Simon Wall3 and Volker J. Sorger1; 1George Washington University, United States; 2Singapore University of Technology and Design, Singapore; 3ICFO–The Institute of Photonic Sciences, Spain

Here we demonstrate heterogeneous integration of phase-change materials GST and GSST for memory functionality in silicon photonic circuits. Using these materials we show a) an electro-optic WRITE and optical READ as a dot-product multiplier that can be used as a a non-volatile 'weight in photonic neural networks (NN), and b) an all-optical WRITE and optical READ performing the nonlinear activation function ‘thresholding’ of the NN. An all-optical (AO) nonlinear (NL) material forms the ultimate basis for a new generation of photonic NNs. Here we show the response and integrate such material-based nonlinearity into a photonic perceptron. Besides passive weighting functionalities, which saves static power with respect to an implementation with EOMs, we will use a nonlinear activation function (NL AF, ‘threshold of NN) based on temporary optical response of GST when optically pumped. For the implementation of the optical nonlinearity, instead of an electro-optic mediated nonlinearity, as proposed by our group and others, we propose to integrate a thin film of GST in an all-optical thresholder in a pump-probe configuration. In this configuration there is no conversion between light and electronics until read out, that could be pushed at the very end of the network. Thus, the inference delay of this network is ps-short. This GST film acts as an optical intensity modulator of the weighted-addition on a second probe source. The optical transitions which modulates the nonlinear function are corroboration by a recent break-through in GST mediated optical nonlinearity which allows for optical modulation of light without requiring the material to recrystallize. This physical modulation mechanism relies on a femtosecond-short excitation, which directly detaches electrons from resonantly bonded states resulting in a non-equilibrium, immediate decrease in the dielectric function and the saturation of the imaginary part of the dielectric function at the same value as the amorphous-state. This femtosecond pulse induced change in the optical properties is not the same as those dictated by thermal process, used for the weighting functions, and hence does not result in the change in crystallinity. Without the complete depopulation of the resonantly bonded state, we can achieve up to 13% reversible modulation of the dielectric function, more than 10x larger than that observed in silicon photo-switches. This allows for a response time of about 10 fs of these all-optical NLaF (thresholds) for pure optical NNs. The neuron is then interconnected to others in a feedforward fully connected NN of L layers (multi-layered perceptron). The input signal is encoded in the laser intensity. Each layer consists of a logic block which performs pointwise matrix multiplication (i) and element-wise NLaF (ii). The weighed addition is performed using a similar approach seen in. In this case, the weights are not fixed thermally which requires a great expense of power budget and insulation strategies, but it is fixed using phase change materials, which have been optically written (in a similar fashion as a rewritable DVD) and kept at their respective state without any dissipation of static power. The NLaF is also performed using GST films in a pump-probe configuration; the optical pump, from free space, induces the temporary phase transition and the material alters its complex refractive index in a volatile way. The effective mode index of the waveguide, in which the probe signal travels, is altered as nonlinear function of the available power after the weighted addition.
SESSION S.EL09.02: Structures, Characterization and Design
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL09

5:00 AM *S.EL09.02.01
Density Functional Simulations of the Atomic Structure and Dynamics of Phase Change Materials Jaakko Akola, Janne Kalikka, Robert Jones; 1Norwegian University of Science and Technology, Norway; 2Tampere University, Finland; 3Forschungszentrum Juelich, Germany

Crystallization of phase change materials has been studied by extensive density functional/molecular dynamics simulations (DF/MD). Four crystallization simulations of amorphous Ge2Sb2Te5 (460 atoms) have been completed at 600 K with simulation times up to 8.2 ns. A sample with a history of order crystallizes completely in 1.2 ns, but ordering in others takes more time and is less complete. The amorphous starting structures without memory display phases (<1 ns) with subcritical nuclei (10–50 atoms) ranging from nearly cubical blocks to string-like configurations of ABAB squares and AB bonds extending across the cell. Percolation initiates the rapid phase of crystallization and is coupled to the directional p-type bonding. The results emphasize the stochastic nature of crystallization and the importance of sufficiently large samples. This is particularly evident in describing the role of crystallites that can merge to form larger units or hinder complete crystallization by the formation of grain boundaries.

Amorphous Sb is known to crystallize extremely rapidly already at room temperature. Crystallization of Sb has been studied at 600 K using six DF/MD simulations with up to 882 atoms. Crystallization proceeded layer-by-layer in most cases and was extremely rapid (~36 m/s). As shown in Fig. 1, diffusion plays a minor role in the process as the crystallization proceeds from the crystalline rim, and the evolution of bond lengths and ring statistics supports the bond-interchange model of Sb-rich phase change materials.

We have also carried out extensive DF/MD simulations (over 500 atoms, up to 100 ps) of liquid bismuth at four temperatures between 573 - 1023 K. These simulations provided details of the dynamical structure factors, the dispersion of longitudinal and transverse collective modes, and related properties (power spectrum, viscosity, and sound velocity). Agreement with available inelastic x-ray and neutron scattering data and with previous simulations is generally very good. The results show that DF/MD dynamics simulations can give dynamical information of good quality without the use of fitting functions, even at long wavelengths.

References:

5:30 AM S.EL09.02.02
Phase Change Materials by Design—The Power and Potential of Maps Matthias Wuttig; RWTH Aachen University, Germany

It has been a long-time dream of mankind to design materials with tailored properties. In recent years, the focus of our work has been the design of phase change materials for applications in data storage. In this application, the remarkable property portfolio of phase change materials (PCMs) is employed, which includes the ability to rapidly switch between the amorphous and crystalline state. Surprisingly, in PCMs both states differ significantly in their properties. This material combination makes them very attractive for data storage applications in rewriteable optical data storage, where the pronounced difference of optical properties between the amorphous and crystalline state is employed. This unconventional class of materials is also the basis of a storage concept to replace flash memory. Today’s talk will discuss the unique material properties, which characterize phase change materials. In particular, it will be shown that only a well-defined group of materials utilizes a unique bonding mechanism (‘Bond No. 6’), which can explain many of the characteristic features of crystalline phase change materials. Different pieces of evidence for the existence of this novel bonding mechanism, which we have coined metavalent bonding, will be presented. In particular, we will present a novel map, which separates the known strong bonding mechanisms of metallic, ionic and covalent bonding, which provides further evidence that metavalent bonding is a novel and fundamental bonding mechanism. This insight is subsequently employed to design phase change materials as well as thermoelectric materials.
Chalcogenide phase change materials (PCM) are widely-used in optical data storage technologies. Also, they are promising to become the next-generation mainstream electronic non-volatile memory technology. These have been discussed and simulated in our prior work [1-4]. The operation of PCM-based devices hinge on the repeated rupture and formation of atomistic-scale chemical bonds to reversibly switch between crystalline and amorphous phases, which require atomistic-scale simulation methodology to achieve in-depth optimization. Nowadays, there are two categories of such methodologies -- density functional theory (DFT) and artificial neural network (ANN). DFT-based molecular dynamics (MD) is accurate but inefficient -- it is practically applicable to only hundreds of atoms. ANN-based MD is efficient but inaccurate -- its maximum error of atomic force prediction can be over 10 eV/Angstrom.

In our recent work [5], we present a method based on deep neural network (DNN) to model PCM, which is both accurate and efficient. The DNN-based MD has a computational complexity of $O(N)$, where $N$ is the number of atoms. So, DNN-based MD is orders of magnitude faster than DFT, whose computational complexity is around $O(N^3)$. Furthermore, the maximum error of atomic force prediction of DNN-based MD is around 0.1 to 1 eV/Angstrom, which is much more accurate than ANN in the existing literature. In our another recent work [6], we present a transfer learning (TL) method, to handle the needs to simulate multiple combinations (different PCM stoichiometry, doping, etc.). Compared to the state-of-art methods in PCM literature, the proposed TL method can significantly reduce the amount of DFT data used to train the neural network, which is beneficial to enable high-throughput simulations.

Combining the accuracy and efficiency [5], and the transferrability between different materials [6], we aim at establishing a general-purpose PCM optimization method based on high-throughput simulations.

An optical laser pulse was employed to melt the PCM, whose structure was probed at different time delays after the excitation, i.e., during the quenching process. The resulting data show that the increase of kinetic activation energy coincides with the onset of a Peierls distortion in the PCMs Ag$_4$In$_3$Sb$_6$Te$_{26}$ (AIST) and Ge$_{15}$Sb$_{85}$. Based on the weak dependence of this onset temperature on the cooling-rate, we attribute this onset to a liquid-liquid phase transition. Ab-initio computer simulations confirm this trend in the atomic structure and provide further insight into the underlying mechanism: The distortion breaks the local symmetry, opens an electronic band gap and localizes charges, giving the bonds more covalent character, which is commonly associated with a decrease in the flexibility of bond angles. This insight reveals a relation between the structure and kinetics of PCMs. In this contribution, we will also discuss similar measurements on the most common PCM Ge$_2$Sb$_2$Te$_5$ and contrast its behavior to a similar but distinct transition mechanism observed in supercooled liquid Ge.


6:30 AM S.ELO9.02.05
Liquid State Behavior of Favored PCM Formulations—The Role of the Metallicity C. Austen Angell1, Pierre Lucas2 and Shuai Wei3; 1Arizona State University, United States; 2University of Arizona, United States; 3RWTH Aachen University, Germany

The functioning of PCM materials in the context of involatile digital memory technology involves a complex interplay of liquid, glass and crystal phase behaviors. Here we focus attention on the peculiarities of the liquid state as judged by the temperatures at which transitions from metallic to semiconducting states occur, relative to melting points. In some cases like As$_2$Se$_3$ and As$_2$Te$_3$, this transition occurs far above the melting point. In others, like pure Te, it is observed to occur quite deep in the supercooled liquid state. Data are sparse for elements and binary compounds, but we can include other compositions by introduction of a metallicity parameter, MP, which is the inverse of the composition-averaged Pauling electronegativity, \( \chi \), thus \( MP = \frac{1}{\chi_1 + \chi_2 + \chi_3} \). When we plot the temperatures of at which the M-SC transition occurs (scaled by the melting points), against MP, we find, by extrapolation, that all of the preferred PCM compositions have their M-SC transitions at similar depth in the supercooled liquid state, where the crystallization rate is exceptionally high. The implications, and applications, of this finding will be discussed.

7:00 AM S.ELO9.02.06
Reversible Electrochemical Phase Change in Monolayer to Bulk-Like MoTe$_2$ by Ionic Liquid Gating Dante Zakhidov1, Daniel A. Rehn1,2, Evan J. Reed1 and Alberto Salleo1; 1Stanford University, United States; 2Los Alamos National Laboratory, United States

Transition metal dichalcogenides (TMDs) exist in various crystal structures with semiconducting, semi-metallic, and metallic properties. The dynamic control of these phases is of immediate interest for next generation electronics such as phase change memories and TMDs have the potential to outperform current phase-change materials such as GeSbTe on energy efficiency while also being fundamentally more scalable. Of the binary Mo and W-based TMDs, MoTe$_2$ is attractive for electronic applications because it has the lowest energy difference (40 meV) between the semiconducting (2H) and semi-metallic (1T') phases, allowing for MoTe$_2$ phase change by electrostatic doping.

Here we report phase change between the 2H and 1T’ polymorphs of MoTe$_2$ in thicknesses ranging from the monolayer case to effective bulk (73nm) using an ionic liquid electrolyte at room temperature and in air. We find consistent evidence of a partially reversible 2H-1T’ transition using in-situ Raman spectroscopy where the phase change occurs in the top-most layers of the MoTe$_2$ flake. We empirically find that the transition voltage of the phase change increases with thickness which provides a direct avenue to transition-voltage control for phase change devices. We also show evidence of electrochemical activity during the gating process by observation of Te metal deposition. This finding suggests the formation of Te vacancies which have been reported to lower the energy difference between the 2H and 1T’ phase, potentially aiding the phase change process. This provides another avenue for transition-voltage control through defect engineering but also emphasizes the need for better understanding of electrolyte gating and chalcogenide vacancy formation. Our discovery that the phase change can be achieved on the surface layer of bulk materials reveals that this electrochemical mechanism does not require isolation of a single layer and the phase change effect may be more broadly applicable than previously thought. We will also discuss recent work on implementation of a solid state device with the use of ionic gels and porous dielectrics.
Towards the Investigation of Electronic Properties of Epitaxial Phase Change Materials

Fabrizio Arciprete1,2, Valeria Bragaglia3, Stefano Cecchi2, Eugenio Zallo2, Ernesto Placidi4,1, Daniele Dragoni5, Marco Bernasconi5, Jos Boschker2 and Raffaella Calarco6,2; 1University of Rome Tor Vergata, Italy; 2Paul-Drude-Institut für Festkörperlektronik, Germany; 3IBM Research-Zurich, Switzerland; 4Sapienza University of Rome, Italy; 5University of Milano-Bicocca, Italy; 6CNR-IMM, Italy

Phase Change Materials (PCMs) represent an important materials class from both a fundamental and technological point of view. Although much effort is still required to determine all the physical mechanisms underlying their complex physical properties, memory devices based on PCMs, which exploit the resistance contrast between the amorphous and crystalline phases, are already at the production stage. The ternary (GeTe)m(Sb2Te3)n alloys are the prototypical phase change materials commonly used for optical and memory devices in the composition Ge2Sb2Te5 (GST225). Among other fabrication methods, such as pulsed laser deposition and sputtering, which is the main technique used in industry, Molecular Beam Epitaxy (MBE) has recently gained in importance because of the advantage to obtain epitaxial quasi single-crystalline PCM layers. This achievement has made it possible the investigation of material properties for which structural perfection is of crucial importance. For example, we have been able to demonstrate that highly ordered crystalline phases can be deposited by van der Waals (vdW) epitaxy, where adjacent building blocks are weakly bonded among them and to the substrate. Furthermore, epitaxial quasi single-crystalline GST, with ordered stacking of intrinsic vacancies, exhibits a large resistivity range that is promising for the realization of memory cells with large programming windows [1].

In this presentation we will first review our advances in the growth of epitaxial GST alloys by MBE on both Si and InAs substrates. We have carried out a growth engineering of single-crystalline GST to achieve unprecedented control over structural order, phase, and composition. The combined use of X-ray diffraction and Raman spectroscopy allowed us to draw a growth phase diagram for GST [2].

The capability to retain the stored information during the memory lifetime is a fundamental property of PCM, and any spontaneous evolution of the amorphous phase toward the more stable crystalline one is undesired. This is especially true when the device working temperature may be higher than the crystallization temperature, as in automotive applications. In this regards we will present our first results in the search of suitable PCM alloys with improved physical properties in terms of crystallization temperature and crystallization speed. In particular we will show our first crystallization study of Ge-rich GST, aiming to identify thermally stable PCMs with high crystallization temperature, and our first results on the investigation, by X-ray Photoemission Spectroscopy (XPS), of the electronic properties of both epitaxial GST and Ge-rich GST. XPS data will be correlated with X-ray diffraction and Raman characterization.

become one of the most popular thin film deposition technique. Some of the reasons for this popularity are the flexibility, processing speed, and the wide range of materials that can be deposited. In this work we discuss PLD of single and alternating layers of Sb$_2$Te$_3$, GaSb, and Ge-rich GST thin films on various substrates. Amorphous, polycrystalline, and textured heterostructures of Sb$_2$Te$_3$/GaSb and Sb$_2$Te$_3$/Ge-rich GST are deposited. Reflection high-energy electron diffraction (RHEED) is used as in-situ growth monitoring tool during deposition to achieve desired film quality. Moreover, deposited films are characterized by Scanning Transmission Electron Microscope (S/TEM) for composition and quality analysis before producing single cell vehicles for electrical device testing.

5:00 AM *S.EL09.04.02
Crystallization Properties of Nano Amorphized Areas in Epitaxial Epitaxial GST on Si (111) by TEM In Situ Characterizations  
Antonio M. Mio$^1$, Giuseppe D'Arrigo$^1$, Jos Boschker$^2$, Alessandro Meli$^1$, Stefano Cecchi$^2$, Eugenio Zallo$^2$, Antonella Sciuto$^1$, Marzia Buscema$^1$, Elena Bruno$^3$, Raffaella Calarco$^2$ and Emanuele Rimini$^1$; $^1$CNR-IMM,
The crystallization behavior of amorphous nano-regions (20-100 nm in diameter) embedded in a textured epitaxial \( \text{Ge}_2\text{Sb}_2\text{Te}_5 \) 25 nm thick film grown on Si (111) substrate has been investigated in situ by TEM analysis. The amorphous regions were obtained by irradiation with 30 keV Ge\(^+\) at a fluence of \( 1.5 \times 10^{14} \) ions/cm\(^2\) of masked samples. The adopted configuration simulates the GST structure of a device in the RESET state, it is then of relevance for understanding their data retention characteristics. The in situ TEM analysis indicates that the amorphous to crystal transition is characterized by an initial growth velocity of 3.6 pm/s at 75°C, probably related to the external partially damaged area. For the previous annealed sample, a velocity of about 2.6 pm/s was observed at 90°C and a growth speed of 170 pm/s at 110°C for the 50nm and 100nm diameter amorphous spots. The 20 nm diameter amorphous spots recrystallize after the annealing at 90°C. The transition is governed only by crystallization (nucleation is absent) of the atoms located at the boundary of the amorphous dot with the surrounding crystalline regions. In some case a preferential growth along surfaces normal to the [110] and to the [121] directions has been found. The crystallographic characterization of the regrowth crystal indicates a good matching with the zone axis of the surrounding material although the crystalline seed Si (111) at the bottom interface is missing for the damage.

5:45 AM S.EL09.04.03

Nanosecond Probing of Phase Transition Properties in Chalcogenides Using Embedded Heater-Thermometer Nicolas Wainstein, Guy Ankonina, Shahar Kvatinsky and Eilam Yalon; Technion - Israel Institute of Technology, Israel

Phase-change materials (PCM) are technologically attractive materials for non-volatile memory, neuromorphic computing, optoelectronics, and recently, radiofrequency (RF) applications. Chalcogenide PCMs present a dissimilar resistance between the crystalline (low-resistivity) and amorphous phase (high-resistivity). The phase transition is thermally activated, and its kinetics can span orders of magnitude in time, down to sub-nanosecond timescale. Hence, proper probing of the thermal actuation is required to understand the fundamental material properties of PCMs, particularly the physics of melt-quench processes in nanoscale devices, interface vs. bulk effects, drift, and threshold voltage phenomena. Research efforts have been made to characterize PCM using a microthermal stage (MTS) [1]. The MTS structure used either a top Pt heater for the thermal actuation of a lateral Ge\(_2\)Sb\(_2\)Te\(_5\) (GST) device or a Pt heater surrounding the GST. Thus, the MTS allows for probing with thermal time scales on the order of microseconds or longer.

Four-terminal, in-line, indirectly heated phase-change switches (IPCS) have been proposed for high-performance RF applications, thanks to their state-of-the-art figure-of-merit (FOM)=1/(2\(\pi\)RonCoff) [2, 3]. A typical IPCS consists of two RF ports in-line with the PCM (i.e., the RF path), separated by a small gap, and two terminals for thermal actuation using an embedded heater. The heater runs transversely to the direction of the RF path, under the PCM. The heater and the RF path are separated by a thin electrically isolating film (e.g., Si\(_3\)N\(_4\)). GeTe has been so far the material of choice for RF applications due to its low resistivity in the crystalline phase and relatively large resistivity contrast with the amorphous state, but recently an Sb\(_7\)Te\(_3\) IPCS was demonstrated with similar FOM and improved energy efficiency [3].

In this study, we report on the use of IPCS device structure as a platform for electro-thermal characterization of phase transition properties of PCM in nanoscale films at nanosecond temporal resolution. The isolation between the heater and the PCM layer electrically decouples the heating pulse and PCM probing. Thus, the phase transition, as well as temperature-dependent properties up to temperatures of \(~1100\) K, can be measured during heating pulse application with ns resolution. Furthermore, since the heater is buried underneath the PCM, our setup allows for 1) steady-state PCM temperature validation using scanning thermal microscopy (SThM) from the top surface, 2) separation between contribution of contact (interface) and bulk effects by varying overlap and underlap between the heater and the PCM contacts, and 3) test different materials of interest without significant change in the fabrication process. We use GeTe as a prototype material with known melting temperature, crystallization kinetics, and surface treatment for low ohmic contacts [4]. Measurements are carried out using RF probes for the heater and the PCM to reduce the overshoot and ringing of short-pulses and produce clean waveforms for nanosecond probing. The experimental results are compared to a detailed finite element electro-thermal model to extract key material properties. Overall, our platform can be used to uncover the intriguing kinetics of crystallization and amorphization in chalcogenides and other amorphous semiconductors.


6:00 AM S.EL09.04.04

Uncovering \(\beta\)-Relaxations in Amorphous Phase-Change Materials Shuai Wei\(^1\), Si-Xu Peng\(^2\), Yudong Cheng\(^1\), Julian
Relaxation processes are decisive for many relevant physical properties of amorphous materials. For amorphous phase-change materials (PCMs) employed in non-volatile memories, relaxation processes are, however, difficult to characterize due to the lack of bulk samples. Here, instead of bulk samples, we use powder mechanical spectroscopy for powder samples to detect the prominent excess wings – a characteristic feature of $\beta$-relaxations – in a series of amorphous PCMs at temperatures below the glass transition. By contrast, $\beta$-relaxations are vanishingly small in amorphous chalcogenides of similar composition, which lack the characteristic features of phase-change materials. This conclusion is corroborated upon crossing the border from PCMs to non-PCMs, where $\beta$-relaxations drop significantly. Such a distinction implies that amorphous PCMs belong to a special kind of covalent glasses whose locally fast atomic motions are preserved even below the glass transitions. These findings also suggest a correlation between $\beta$-relaxation and crystallization kinetics of PCMs, which may have technological implications for phase-change memory functionalities.

6:15 AM S.EL09.04.05
Impact of High Electric Field on Resistance Drift in Amorphous Ge$_2$Sb$_2$Te$_5$ Phase Change Memory Line Cells at Low Temperatures

ABM Hasan Talukder, Raihan Sayeed Khan, Helena Silva and Ali Gokirmak; University of Connecticut, United States

Phase change memory (PCM) technology utilizes the large resistivity contrast between the crystalline and amorphous phases of chalcogenide materials. However, the resistance of the amorphous phase deviates from its originally programmed value over time, which is commonly referred to as resistance drift. This resistance drift may lead to inaccurate read operations and thus poses a major challenge to the realization of multilevel cell (MLC) PCM.

We have performed electrical characterization of Ge$_2$Sb$_2$Te$_5$ (GST) line cells at low temperatures expecting to see very small or no drift since resistance drift has been understood to be caused by structural relaxation which is a thermally activated defect annihilation process [1]-[3]. However, we observed resistance drift at cryogenic temperatures with drift coefficients comparable to the room temperature value of $\sim$0.1 [4]. Furthermore, we observed a significant acceleration in resistance drift with high electric field stress in 80 K - 200 K temperature range. Resistance of the cells stabilizes after the electrical stress allowing stable field and temperature-dependent electrical characterization.

These results suggest that charge traps and charge injection to these traps play a significant role in the resistance drift of amorphous phase change materials.

Acknowledgments: This work is partially supported by NSF under award ECCS 1711626.

References:

6:30 AM S.EL09.04.06
Effect of Optical Illumination on Resistance Drift in Ge$_2$Sb$_2$Te$_5$ Line Cells

Raihan Sayeed Khan, Helena Silva and Ali Gokirmak; University of Connecticut, United States

The large resistivity contrast between the highly resistive amorphous phase and low resistive crystalline phase of phase change memory (PCM) provides opportunities for multi bit per cell memory and neuromorphic applications. However, the drift of resistance of amorphous phase limits the potential of PCM as multiple intermediate states can overlap over time. Although resistance drift is generally attributed to structural relaxation [1], we have observed significant resistance drift in Ge$_2$Sb$_2$Te$_5$ line cells at cryogenic temperatures and also being affected by optical illumination, indicating charge trapping [2]. A detailed understanding of the mechanisms behind resistance drift may allow for mitigating techniques. In this work, we
study the effect of optical illumination between 125 K and 300 K and also the effect of different optical illumination conditions on the drift coefficient.

References:

SESSION S.EL09.05: Phase-Change Materials
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL09

5:00 AM *S.EL09.05.01
Phase Change Memory from Fundamental Research to Industrial Development Zhitang Song; Chinese Academy of Sciences, China

Phase change random access memory (PCRAM) has been successfully applied in the computer storage architecture, as storage class memory, to bridge the performance gap between DRAM and Flash-based solid-state drive due to its good scalability, 3D-integration ability, fast operation speed and compatible with CMOS technology. A good understanding of phase change mechanism is of great help to design new phase change materials with fast operation speed, low power consumption and long-lifetime. In this presentation, we firstly review the development of PCRAM and different understandings on phase change mechanisms in recent years, and then propose a new view on the mechanism, which is based on the octahedral structure motifs and vacancies. Octahedral structure motifs are the based units during phase transition. Robust octahedra and plenty of vacancies in both amorphous and crystalline phase, respectively avoiding large atomic rearrangement and providing necessary space, are of crucial to achieve the nanosecond or even sub-nanosecond operation of PCRAM. Based on this mechanism, we introduce Sc-based robust octahedra in Sb$_2$Te$_3$ phase change materials, called Sc-Sb-Te, and achieve 700 ps operation speed. Recently, the concentration of dopants has also been optimized by correlative atom probe tomography and transmission electron microscopy investigations. Focusing on phase change materials and PCRAM for decades, we have successfully developed 128Mb embedded PCRAM chips, which can meet the requirements of most embedded systems.

5:15 AM *S.EL09.05.02
Amorphization and Cristallization of Ge Rich GeSbTe Thin Films for Embedded Memory Applications Stefania M. Privitera1, Corrado Bongiorno1, Veronica Sousa2, Gabriele Navarro2, Chiara Sabbione2, Marie Claire Cyrille2, Egidio Carria2 and Emanuele Rimini1; 1IMM-CNR, Italy; 2CEA-LETI, France; 3STMicroelectronics, Italy

GeSbTe alloys, widely employed for phase change non volatile memory, are usually not suitable in embedded and automotive applications, because of the low crystallization temperature. Doping, in particular with Ge, has been shown to be a viable way to extend the thermal stability of GeSbTe alloys [1,2]. However, once an optimised composition has been selected, during device operation, the material stoichiometry may change, due to the atomic migration induced by the high temperature and/or by the electric field [3]. These variations may lead to programming and retention performance degradation or even to device failure. It is therefore crucial to understand the extent of the atomic migration and its impact on the stoichiometry, as well as on the crystallization properties. In order to decouple the effect of the atomic diffusion at high temperature from that of the field induced electromigration, we have irradiated crystalline Ge rich GeSbTe thin films by laser. The films were prepared by sputter deposition in the amorphous phase, and then converted into the crystalline structure by annealing at 400°C. The irradiation has been performed by using a Yb-YAG laser (515 nm) with 600 ns pulse, operating at different energy densities. By changing the energy density, complete or partial melting and quenching, with amorphization of the film, can be achieved. In this way we are able to study the thermal diffusion processes decoupled from the field induced electromigration. After melting and quenching, the atomic elements distribution has been studied by Transmission Electron Microscopy (TEM) and Electron Energy Loss Spectroscopy (EELS). We find that, even without the electric field, the melting give rise to a prominent diffusion of Ge atoms. By employing finite elements computational analysis, a diffusion coefficient of Ge on the order of 5x10$^{-5}$ cm$^2$ s$^{-1}$ in the molten phase has been estimated.
After amorphization under different irradiation conditions, we have followed the crystallization upon thermal annealing by in-situ time resolved reflectivity measurement. Such a crystallization process, after the first melting and quenching, is expected to be different from the crystallization of the as deposited amorphous film, since the melting produces not only sub-critical crystalline nuclei, but also a modification of the stoichiometry. The study of the crystallization in such a “primed” material is very similar to the situation occurring in a real memory device after the first erasing step and therefore it is relevant for reliability evaluations.


5:30 AM S.EL.09.05.03

Thermal Properties of Carbon Nitride Toward Use as an Electrode in Phase Change Memory Devices Kiumars Aryana1, John Gaskins1, Joyeeta Nag2, John Read2, David Olson1, Michael Grobis2 and Patrick E. Hopkins1; 1University of Virginia, United States; 2Western Digital Corporation, United States

In phase change memory cells, the majority of heat is lost through the electrodes during the programming process that leads to significant drops in the performance of the memory device. In this investigation, we report on the thermal properties of thin film carbon nitride with modest electrical resistivity of 5-10 mW cm, low thermal conductivity of 1.47W/m/K, and low interfacial thermal conductance between carbon nitride and phase change material for length scales below 40 nm. The thermally insulating property of carbon nitride makes it a suitable thermal barrier, allowing for less heat loss during Joule heating within the memory unit. We compare carbon nitride thermal properties against commonly used electrodes and insulators such as tungsten and silicon nitride, respectively, to demonstrate the promise of carbon nitride as a potential material candidate for electrode applications in phase change memory devices.

5:45 AM S.EL.09.05.04

The Effect of Metal Reactivity on Critical Interfaces in GeTe-Based Devices Kayla A. Cooley and Suzanne E. Mohney; The Pennsylvania State University, United States

Phase change materials (PCMs) are well-known for their crystalline-to-amorphous transitions that are both quick and reversible, offering a large contrast in electrical and optical properties of the two phases. Responsible for enabling the development of rewritable CD and DVD technology, this class of materials has greatly contributed to the development of modern data storage, entertainment, and computing; and due to so many contributions, research continues to point to applications in which chalcogenide PCMs provide novel solid-state devices. One such PCM, germanium telluride (GeTe), has been the focus of numerous studies to develop next generation non-volatile memory cells, photonic devices, and radio frequency (RF) switches. The geometry of GeTe-based devices for radio frequency switches and non-volatile memory technologies often places GeTe thin films in contact with metal thin films. Despite the potential effect of metal/GeTe reactions on device performance, few studies have addressed the reactivity between elemental metals and GeTe or systematically approached the thermal stability of GeTe with metals. In response to this need, reactivity was determined by calculating ternary phase diagrams of metal-Ge-Te systems and performing transmission electron microscopy (TEM) both after metal deposition and after the samples were annealed for 12 h at 200 °C. GeTe is thermodynamically favored to react with many metals at room temperature. Nine of the 24 studied metals are not reactive with GeTe (Au, Ir, Mo, Os, Re, Ru, Ta, W, and Zn), while 15 metals have a thermodynamic driving force to react with GeTe at room temperature (Ag, Al, Cd, Co, Cu, Fe, Hf, Mn, Ni, Pd, Pt, Rh, Sc, Ti, and Y). Most of the unreactive metals, except Au and Zn, are not in thermodynamic equilibrium with GeTe at room temperature. These metals are refractory, and the lack of reactivity is ascribed to kinetic limitations. Solid-state reactions between contact metals and GeTe produce an unexpected trend between metal work function and metal/GeTe contact resistance ($R_c$), which is actually the opposite to what is projected by the well-known Schottky-Mott Law. For a $p$-type semiconductor like GeTe, high work function metals, like Ni and Pt, would be expected to provide the lowest $R_c$ values. However, comparing all contact metals (Au, Ni, Mo, Sn, Ti, Pt, and Cr), Mo-based contacts (with a work function of only 4.60 eV) offered the lowest contact resistance. From cross-sectional TEM analysis, only Au- and Mo-based contacts did not react with GeTe. Thus, the work function of the contact metal of the reactive contacts is no longer the deciding factor in setting $R_c$, and we explore explanations for this trend in our ongoing work.
Modeling Charge and Electro-Thermal Heat Transport in Phase Change Memory Cells

Md Tashfiq Bin Kashem, Jake Scoggin, Ali Gokirmak and Helena Silva; University of Connecticut, United States

In order to model phase change memory (PCM) cells, dynamic materials models have to be coupled with charge and heat transport models [1]-[7]. Since PCM cells experience high temperatures, very large thermal gradients (~ 50 K/nm) and high current densities during their normal reset and set operations, thermoelectric contributions are significant for both charge and heat transport in these cells. Furthermore, some of the assumptions made for large scale thermoelectric devices do not hold under these extreme conditions.

Charge transport in PCM cells can be modeled using a drift-diffusion approximation. However, electronic material properties such as carrier concentrations, mobilities and diffusivities are not well characterized for phase change materials. In this study, we construct (i) a drift-diffusion model using thermoelectric characteristics of the material, measured in a large temperature range, and (ii) an electrothermal heat transport model that does not assume mild temperature gradients only.

Our simulation results show that both Thomson heat (thermoelectric effects in the bulk materials) and Peltier heat (thermoelectric effects at the contact regions) play a significant role, and give rise to significantly asymmetric thermal profiles in symmetric PCM cells.

Acknowledgments: This work is partially supported by NSF under award DMR-1710468.

References:

Contact Resistance Measurements of GST 225 to TiN Bottom Electrode

Guy M. Cohen and Amlan Majumdar; IBM T.J. Watson Research Center, United States

The contact resistance between TiN and GST 225 was measured using the transfer length method (TLM) and the end resistance method for the crystalline and amorphous phases of GST 225. We found a 3000x increase in contact resistance when GST 225 over the TiN electrodes changed from crystalline to amorphous. When considering common phase change material (PCM) memory cell geometries, our measurements suggests that the contact resistance is a large component of the change in the resistance when the device is switched between the crystalline and the amorphous phases. In other words, the increase of the device resistance when the device is reset is substantially due to the increase in the contact resistance and not solely due the change in the bulk resistance of the PCM.

Combinatorial Exploration of Phase Change Memory Materials with Enhanced Properties

Heshan Yu1, Changming Wu2, Xiaohang Zhang1, Apurva Mehta3, Ritesh Agarwala4, Mo Li5, Gilad Kuson2 and Ichiro Takeuchi1; 1University of Maryland, United States; 2University of Washington, United States; 3Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, United States; 4University of Pennsylvania, United States; 5National Institute of Standards and Technology, United States

As one of the most promising candidates for developing new neuromorphic architectures for non-von Neumann computing and information storage, Ge2Sb2Te5(GST225) in photonic devices shows non-volatile, fast, and multi-step changes between
the amorphous state and the meta-stable states. In order to search for other composition ratios with desired properties, e.g. large figure of merit, lower switching energy, etc., we have systematically investigated a broad composition range of the Ge-Sb-Te (GST) system. The GST combinatorial spread was fabricated by co-sputtering Ge, Sb and Te targets and was confirmed by wavelength dispersive spectroscopy that the composition variation across the Si wafer covers most part of the GST phase diagram. X-ray diffraction measurements (synchrotron radiation), Raman spectroscopy and resistance mapping clearly show evolution of the structure and phase-change temperature in the GST system. Refractive index and extinction coefficient were calculated at each composition spot using a scanning ellipsometer: some composition ratios were found to have a small extinction coefficient in the amorphous state, a high phase-change temperature, and a large figure of merit. Then, the nano-size photonic devices fabricated by these ratios were measured and showed good reversibility (more than 40000 cycles) and multi-level symmetric switching (at least 15 levels), suggesting that such compositions can be promising for photonic devices for neuromorphic control. Further, we confirm that compositions with promising properties are near the boundary between the Sb-Te and the Ge-Sb-Te phases, indicating that co-existence of the phases at microstructural level may be playing a role in giving rise to their properties. This work is funded by an ONR MURI (Award No. N00014-17-1-2661).

6:45 AM S.EL09.05.09
Cw Laser Annealing Induces Stress Field During Phases Transition in Ge:Sb:Te$_5$ Layer Giuseppe D'Arrigo$^{1}$, Mario Scuderi$^{1}$, Antonio M. Mio$^{1}$, Gregory Favaro$^{2}$, Antonella Sciuto$^{1}$, Marzia Buscema$^{1}$, Alessandro Meli$^{1}$, Giovanni Li Destri$^{3}$, Egidio Carria$^{4}$, Domenico Mello$^{4}$, Michele Calabretta$^{4}$, Alessandro Sitta$^{4}$, Julian Pries$^{5}$, Matthias Wuttig$^{5}$ and Emanuele Rimini$^{1}$; $^{1}$CNR-IMM, Italy; $^{2}$Anton Paar USA Inc., Switzerland; $^{3}$Università di Catania, Italy; $^{4}$STMicroelectronics, Italy; $^{5}$RWTH Aachen University, Germany

The mechanical properties, Hardness and Young module, of crystalline micrometer stripes of Ge:Sb:Te$_5$ and of the surrounding 2.2 µm thick amorphous film have been measured simultaneously. Crystallization was performed by a Continuous Wave laser irradiation process in the range 1.25-3.2 mW. The density changes between the amorphous and the crystalline phase causes a relevant stress in the processed material. Usually the stress is measured by the wafer curvature. This methodology doesn’t allow a detailed investigation of the local mechanical modifications when the two phases amorphous and crystalline are contiguous, as in an optical or electrical storage device. The use of micrometer patterned structures and nano-indentation measurements allow us to determine the mechanical behavior of the two contiguous GST phases. The measured values of the mechanical property are more dispersed for the crystallized material than those for the contiguous amorphous phase. The Young module and the hardness are 51±8 GPa and 2880±450 MPa for the crystallized and 33±4 GPa and 1989±300 MPa for the amorphous phase respectively. Microcracks are also seen, together with fracture lines. The occurrence of delamination at laser power densities above 1.70 mW indicates that for these crystallized thicknesses the maximum tensile strength of the amorphous and crystalline phases was reached and exceeded. The phase transition has also been investigated by several analytical tools (TEM, SEM, Raman and XRD diffraction). A simulation code was adopted to compute the temperature-time-space profile as a function of the laser power. These results were used to compare the measured crystallized thickness to that calculated.

7:00 AM S.EL09.05.10
Metal Incorporation in Germanium Telluride—A First Principles Study with Experimental Observations Kayla A. Cooley$^{1}$, Nathan Kelibart$^{2}$, James G. Champlain$^{2}$, Laura B. Ruppalt$^{1}$, Ismaila Dabo$^{1}$ and Suzanne E. Mohney$^{1}$; $^{1}$The Pennsylvania State University, United States; $^{2}$US Naval Research Laboratory, United States

Intentionally introducing impurity atoms into a semiconductor has been a common method for modifying material properties that are critical to many electronic and optoelectronic devices. For GeTe, a phase change material (PCM), there has been interest in using metal incorporation for this approach to materials engineering. GeTe thin films doped and/or alloyed with metals have been reported to exhibit improved device performance, like improved crystallization speed, thermal stability, and power consumption. However, these films have often been fabricated using non-equilibrium methods with high metal concentrations (>10 at. %). Since switching between the low-resistance crystalline and high-resistance amorphous states requires a heating cycle, the stability of metal-incorporated GeTe (GeTe:metal) films is critical to practical implementation of these materials in electronic devices. Understanding the effect of metal-incorporation in GeTe films provides valuable insights for engineering future PCM devices, both in terms of doping and discovery of ternary PCMs.

In this work, we present first principles calculations concerning the stability of GeTe doped with select metals (Cu, Fe, Mn, Mo, and Ti), as well as the effect of increasing dopant atom concentration (2-6 at.%) on the crystal structure and electronic properties of GeTe. From density-functional theory calculations of the formation energy of the ternary solid (GeTe doped with 2-6 at. % of Cu$^{2+}$, Fe$^{2+}$, Mn$^{2+}$, Mo$^{2+}$, and Ti$^{2+}$), all metals favored substitution into the Ge site over the Te site. The formation energy of the GeTe:metal structure increases (or becomes less stable) with increasing metal incorporation for all
metals except Mn. Certain metals (Ti, Mo) clearly favor dopant atom clustering. In addition, different metal dopants have a varied distortion of the GeTe crystal structure and projected density of states. Computational results are compared to observed solubility trends in cross-sectional transmission electron microscopy (TEM) studies of metal/GeTe thin film systems (Cu, Mn, Mo, and Ti)\(^1\) and TEM, spectroscopic ellipsometry, and transport data from newly characterized co-sputtered GeTe:Fe films.


**7:15 AM S.EL09.05.11**

**Materials Gene Exploration and Modification for Phase-Change Memory Glass** Ming Xu and Xiangshui Miao; Huanzhong University of Science and Technology, China

Phase-change memory is the most promising candidate for the next generation memory technology. It utilizes the large property contrast between the amorphous and crystalline phases of phase change materials (PCMs), which switches to each other within nanoseconds. In the past decades, a lot of efforts have been devoted to explore how the structure defines the particular properties of PCMs, and it is discovered that the structure of the amorphous phase plays the key role in this case. For example, the fragility of the glass determines the crystallization speed (the programming speed in memory); the glass aging results in the resistance drift in the devices; the stability of the glass (data retention) is determined by the covalent bonds in this material. Since the amorphous phase is absent of long-range order and defects such as dislocation and grain boundary, the physical properties are usually determined by the short- and medium-range orders, and hence we call it the materials “gene” of glass.

We discovered in the our research that the local structure of PCMs could be described as “octahedral motifs”, which can be easily modified by adding different dopants. For example, the carbon, which forms tetrahedral clusters, can increases the stability of the glass to elongate the life of memory devices; the addition of Yi and Sc stabilizes the nuclei in the glass, remarkably accelerating the crystallization speed. The discovery of new PCMs enabled by the Materials Genome Engineering paves the way for the design of high-density phase change memory.

**7:30 AM S.EL09.05.12**

**Electron Beam Driven Phase Transitions in Phase-Change Materials and Phase Change Heterostructure** Jiangjing Wang\(^1\), Chun-Lin Jia\(^1,2\) and Wei Zhang\(^1\); \(^1\)Xi'an Jiaotong University, China; \(^2\)Forschungszentrum Jülich GmbH, Germany

Fast and reversible phase transitions in chalcogenide phase-change materials (PCMs), in particular, Ge-Sb-Te compounds, are not only of fundamental interests but also make PCMs based random access memory a leading candidate for nonvolatile memory, and even neuromorphic computing devices. For instance, a recently designed phase-change heterostructure (PCH), which consists of alternately stacked phase-change and confinement nanolayers to suppress the noise and drift, has attracted increasing attention. However, to RESET the memory cell, crystalline PCMs has to undergo phase transitions first to a liquid state and then to an amorphous state, corresponding to an abrupt change in electrical resistance. In this work, we demonstrate a progressive amorphization process in GeSb\(_2\)Te\(_4\) thin films under electron beam irradiation on a transmission electron microscope (TEM). Melting is shown to be completely absent by the in situ TEM experiments. The progressive amorphization process resembles closely the cumulative crystallization process that accompanies a continuous change in electrical resistance. The same nonthermal amorphization process was also verified in the phase-change nanolayers of PCH. The displacement forces induced by knock-on collision effect of E-beams drives this nonthermal amorphization process, thus our work suggests that if displacement forces can be implemented properly, it should be possible to emulate symmetric neuronal dynamics by using PCMs.

Key words: phase-change materials, phase change heterostructure, phase transition, electron beam irradiation, in situ TEM

**7:45 AM S.EL09.05.13**

**Electronic Properties of Phase Change Compounds in the Liquid State—Effective Charges for Electromigration and Semiconductor-Metal Transition from First Principles** Matteo Cobelli\(^1\), Mario Galante\(^2\), Daniele Dragoni\(^1\), Stefano Sanvito\(^2\) and Marco Bernasconi\(^1\); \(^1\)Università di Milano-Bicocca, Italy; \(^2\)Trinity College, Ireland

In the reset process of phase change memories, the active material is brought rapidly above the melting temperature by Joule heating. Atomic migration in the liquid state due to the high electric field can lead to alloy demixing and eventually to device failure. The electromigration force \(F\) responsible for ionic migration is proportional to the electric field via the effective charge \(Z^*\) \((F=Z^*E)\). Information on the effective charges is thus of great relevance for the electrothermal modeling of the device. However, experimental estimates of the effective charges in the liquid state suffer from large uncertainties. A possible
route to estimate $Z^*$ relies, in fact, on the modeling of the concentration profile of the different species in highly cycled memory cells which, however, depends on several mostly unknown parameters that have to be plug into phenomenological transport equations [1].

In this work, we show that a direct first principles calculation of the effective charges in metallic liquids is possible by computing the atomic forces in the presence of both an electric field and an electronic current within the Non-Equilibrium Green Function scheme implemented in the code Smeagol [2]. We will present results on the calculation of the effective charges, including the wind force, for the GeTe and Sb$_2$Te$_3$ phase change compounds in the liquid state.

Another feature of the liquid state that affects device operations is the opening of an electronic gap upon cooling from the melting point to the glass transition temperature during reset. The temperature at which the metallic liquid turns into a semiconductor is another important parameter for the electrothermal modeling of the device. By means of density functional molecular dynamics and the use of a hybrid exchange and correlation functional, we have estimated the temperature of gap opening in the supercooled liquid phase of GeTe and Ge$_2$Sb$_2$Te$_5$ compounds.


8:00 AM S.EL09.05.14

**In Situ Study of Vacancy Disordering in Crystalline Phase-Change Materials under Electron Beam Irradiation**

**Xudong Wang**, **Tingting Jiang**, **Jiangjing Wang** and **Wei Zhang**

1. Center for Advancing Materials Performance from the Nanoscale, State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, China; 2. Xi’an Jiaotong University Suzhou Institute, China

Fast and reversible phase transitions in chalcogenide phase-change materials (PCMs) play a key role in next-generation memory and computing chips. The Ge-Sb-Te compounds, such as Ge$_2$Sb$_2$Te$_5$ and GeSb$_2$Te$_4$, are under active investigations, not only because they serve as the key element in commercial products, but also because they provide a rich platform for fundamental research in materials science.

Disorder-driven metal insulator transition has been reported in crystalline Ge-Sb-Te phase-change materials (PCMs), where the high concentration and statistical distribution of atomic vacancies were identified as the key factor in shaping the localization properties of electrons and, thus, the electrical transport. Vacancy ordering has been consistently observed in crystalline Ge-Sb-Te thin films upon thermal annealing, triggering a structural transition from a cubic rocksalt structure to a layered hexagonal structure and an insulating to metallic transition.

In this work, we demonstrate an opposite vacancy disordering process upon extensive electron beam irradiation, which drives the reverse transition from the stable hexagonal phase to the metastable cubic phase. The combined in situ transmission electron microscopy experiments and density functional theory nudged elastic band calculations reveal three transition stages, including (I) the vacancy diffusion in the hexagonal phase, (II) the change in atomic stacking, and (III) the vanishing of vacancy-rich planes. The driving force of the vacancy disordering process is attributed to the kinetic knock-on collision effects of the high-energy focused electron beams, which prevail over the heating effects.

Our electron irradiation experiment not only provides an alternative approach to tune the vacancy distribution that is crucial for the disorder-driven metal-insulator transition of GST crystals, but also makes an instruction for the TEM measurement of structural details of a particular solid-state phase of PCMs that the three critical TEM parameters, namely, accelerating voltage, beam intensity and recording time, should be reduced as much as possible to avoid structural transitions during the measurement.


**Reconfigurable Infrared Flat Optics with Novel Phase Change Materials**

Christopher M. Roberts¹, Yifei Zhang², Mikhail Shalaginov², Paul Robinson¹, Paul Miller¹, Kevin Tibbetts¹, Sean Gorsky¹, Vladimir Liberman¹, Carlos A. Ríos Ocampo², Tian Gu², Myungkoo Kang³, Anupama Yadav⁴, Kathleen Richardson⁴, Juejun Hu² and Jeffrey Chou¹; ¹MIT Lincoln Laboratory, United States; ²Massachusetts Institute of Technology, United States; ³University of Central Florida, United States

Previously, we have reported on a novel class of chalcogenide phase change materials, based on Ge-Sb-Se-Te (GSST) alloys, with excellent infrared transparency from 1.5 to > 15 micron wavelengths. Increasing Se substitution leads to a progressive lowering of extinction coefficient. A material in this family with a particular useful stoichiometry, Ge₂Sb₂Se₄Te₁ (GSS₄T₁), possesses broadband transparency through the infrared range while maintaining a large index contrast between its amorphous and crystalline phases. Defining a figure of merit as \( \Delta n/k \) (where \( n,k \) are the real, imaginary parts of the refractive index), our materials shows >100x figure of merit (FOM) improvement over conventional GST throughout the infrared range.

In this talk, we describe novel applications enabled by reversible switching of low loss GSS₄T₁ material. In the first application, we exploit the exceptional FOM of the Se-doped PCM to realize a nonvolatile photonic switch with unprecedented high performance. Our device, based on a racetrack SiN resonator with a PCM gate, exhibits a large switching contrast ratio of 42 dB and a low insertion loss of < 0.5 dB, far outperforming previous nonvolatile switches as well as devices based on the classical GST-225 material with a similar configuration.

Additional novel applications are enabled by our development of wafer-scale pixelated electrical switchable PCM devices. The pixelated devices are fabricated in a CMOS-compatible clean room on 8 inch wafers utilizing a full Si-based fabrication tool set. Devices of various pixel sizes, from 1 to 30 micron have been fabricated. Additionally, fabrication of more complicated sub-pixel metasurfaces was demonstrated. Electrical switching measurement is obtained by applying electrical pulse trains through a programmable voltage generator into the gate of a high powered transistor. Microsecond switching of 30-micron and 1-micron pixels in a wafer-scale device has been demonstrated. Current devices have demonstrated over 1,000 switching cycles and further durability improvements are underway.

As an application of pixelated electrical device, we have demonstrated a concept of compact infrared reflection spectrometer with no moving parts. Here, we leverage the ability to obtain gradually changing reflection signature of the pixel with voltage between fully-converted crystalline and amorphous phases. This wavelength shift is essentially a nonlinear filter which can be used to reconstruct an input spectrum. Since the reflection response of the pixel states is pre-determined, a spectral response of the scene can be extracted once the pixel spectrum is fully characterized with a known calibrated spectral source. We have carried out such characterization utilizing a supercontinuum laser in the short-wave infrared part of the spectrum and the results of spectral signature extraction for three different incident spectral scenarios.

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**5:30 AM *S.EL09.06.02*

**Effects of Spatial Confinement on Phase-Change Materials**

Ann-Katrin U. Michel and David J. Norris; ETH Zürich, Switzerland

Phase-change materials (PCMs) allow for an ultrafast and reversible transition between their amorphous (a) and crystalline (c) state. This structural transition results in a pronounced change in their optical and electrical properties. The strong resistivity contrast of several orders of magnitude has been employed in electronic and neuromorphic memories, while the unity-scale refractive index change \( \Delta n = |n_c - n_a| \) has been applied in rewriteable optical-data-storage memories. Additionally, \( \Delta n \) is the subject of research in various photonic applications.¹ For tunable photonics, PCMs are very desirable, but expensive and laborious to produce. Thus, colloidal PCMs that can be easily synthesized could provide broader access to this material class and allow for deposition on a variety of substrates, including prepatterned holes and vertical interconnect accesses. However, due to the size reduction from GeTe thin films to small nanoparticles (NPs), new effects can arise. Examples are the occurrence of localized surface plasmon resonances in c-GeTe NPs,² and size dependence of the crystallization temperature \( T_c \).³ Thickness dependent temperature scaling was also reported for very thin sputtered PCM films, and related to their bonding characteristics.⁴ Recent results indicate that the
spatial confinement of PCMs into small NPs results in an increase of the optical band gap $E_g$, while maintaining the pronounced contrast between the band gaps for a- and c-PCMs $E_{ga}$ and $E_{gc}$ respectively.\cite{5}

Insights into small-size PCM NPs can promote the application of these materials in different fields, and add value to fundamental scientific questions, especially regarding the current debate on the unique chemical bonding in PCMs.\cite{6}

Despite the bottom-up synthesis of PCM NPs, structural confinement can be realized by sub-wavelength patterning. While laser pulses do not allow for switching on such small length scales, tip-induced crystallization can lead to features below 100 nm. The resulting so-called metasurfaces feature extremely strong field confinement and nearly $2\pi$ phase shift.\cite{7}


6:00 AM *S.EL09.06.03
Terahertz Spectroscopic Studies in Ge-Sb-Te Phase Change Materials Kotaro Makino; National Institute of Advanced Industrial Science and Technology, Japan

Phase change materials including Ge-Sb-Te (GST) alloys provide useful changes in the electronic and optical properties thanks to the reversible a structural phase transition between amorphous and crystalline phases. The phase change materials have been used for commercially-available optical and electrical memory technologies by exploiting the phase change property. In this context, GST is expected to be utilized also for terahertz (THz) wave engineering since the frequency of THz wave ranges between infrared light and radio wave. So far, we revealed that a THz pulse excitation is capable of structural control thorough unique nonlinear field-induced phenomena \cite{1,2}. In addition, we performed a THz emission spectroscopy as well as a THz time-domain spectroscopy and found that these spectroscopic measurements can be used for evaluation of the film quality and electronic characteristics of the GST. Based on the result of THz time-domain spectroscopy, we propose that the reversible and nonvolatile changes in the THz properties of GST are promising for a variety of applications e.g. THz photonics and THz amplitude modulator \cite{3}.


6:30 AM *S.EL09.06.04
Exploiting Phase Change Materials and Multi-Objective Optimization for Reconfigurable Multi-Functional Meta-Optics Sawyer D. Campbell, Yuhao Wu, Eric B. Whiting, Lei Kang, Pingjuan L. Werner and Douglas Werner; The Pennsylvania State University, United States

Phase change materials (PCMs) are an extremely attractive material platform for the realization of multi-functional and reconfigurable meta-optics. For example, PCMs can be exploited to synthesize metasurfaces and metamaterials to enable a variety of tunable devices such as beam-steerers, optical shutters, spectral filters, and adaptive focal length lenses \cite{1}–\cite{5}. However, the expanded degrees of design freedom that PCMs offer can make direct device design intractable for all but the most experienced engineers. This challenge is best overcome through the use of advanced inverse-design tools and state-of-the-art optimization algorithms. To this end, a number of successful meta-device inverse-design approaches have been demonstrated in the literature including those based on topology optimization, deep learning, and global optimization \cite{6}. While each method has its pros and cons, one method stands out as an ideal candidate for reconfigurable meta-optic design: multi-objective optimization. In contrast to ubiquitous single-objective optimization algorithms, which require users to combine multiple goals into a single cost function usually via a weighted sum, true multi-objective optimization (MOO) algorithms allow designers to minimize multiple competing objectives simultaneously without the need for \textit{a priori} information on how best to weight a single cost function \cite{7}, \cite{8}. Thus, MOO algorithms are perfectly suited for reconfigurable meta-optic design as each independent functionality can be assigned a unique cost function and optimized. Moreover, MOO algorithms provide the user with a collection of designs called the Pareto set that can be analyzed to determine the inherent tradeoffs between competing design objectives. In our presentation, we will introduce an efficient multi-objective optimization enabled design framework for the generation of multi-functional unit cells based on phase.
change materials. Additionally, several reconfigurable meta-optic design examples will be presented, and future research directions discussed.

References

7:00 AM S.E.L09.06.05
All-Dielectric Varifocal Metalens for Aberration-Free Imaging
Mikhail Shalaginov$^1$, Yifei Zhang$^1$, Sensong An$^2$, Myungkoo Kang$^1$, Kathleen Richardson$^1$, Hualiang Zhang$^2$, Tian Gu$^1$ and Juejun Hu$^1$;
$^1$Massachusetts Institute of Technology, United States; $^2$University of Central Florida, Orlando, United States

We present our results on design, fabrication and characterization of a tunable metalens based on optical phase change materials (O-PCMs). We first introduce a phase change meta-atom design concept enabling switching of metasurface devices between two arbitrary optical states. We then implement this principle to demonstrate a bifocal switchable metalens made of the low-loss non-volatile O-PCM Ge$_2$Sb$_2$Se$_4$Te$_1$ (GSST). The metalens can achieve large change in focal length, from 1.5 mm to 2 mm, which is caused by drastic change in meta-atoms refractive index. Additionally, the metalens exhibits focusing efficiencies above 20% in both amorphous and crystalline states. We further experimentally demonstrated aberration-free imaging using the lens and achieved diffraction-limited resolution in both states. This result represents the first experimental demonstration of a non-mechanical active metalens with diffraction-limited imaging capability.

7:15 AM S.E.L09.06.06
Electrically Tunable Dielectric Metasurfaces Enabled by Optical Phase Change Materials
Yifei Zhang$^1$, Junhao Liang$^1$, Mikhail Shalaginov$^1$, Bilal Azhar$^1$, Jeffrey Chou$^2$, Christopher M. Roberts$^2$, Skylar Deckoff-Jones$^2$, Clayton Fowler$^2$, Carlos A. Rios Ocampo$^1$, Sensong An$^2$, Claudia Gonçalves$^2$, Kathleen Richardson$^2$, Hualiang Zhang$^2$, Tian Gu$^1$ and Juejun Hu$^1$;
$^1$Massachusetts Institute of Technology, United States; $^2$Lincoln Laboratory, Massachusetts Institute of Technology, United States; $^3$The University of Massachusetts Lowell, United States; $^4$University of Central Florida, Orlando, United States

The nonvolatile reconfiguration capability of optical phase change materials (O-PCMs) makes them highly attractive for tunable dielectric metasurfaces. However, conventional switching methods based on either laser pulsing or electrical-current triggered transition require raster-scanned writing and dedicated off-chip switching instruments, therefore incompatible with large-scale integration. Here we report the design, fabrication and characterization of a scalable electrical switching platform for tunable dielectric metasurfaces based on O-PCMs.

We first introduce Ge$_2$Sb$_2$Se$_4$Te$_1$ (GSST), a novel O-PCMs we developed recently that is specifically targeted for high-performance photonic applications. We demonstrate that GSST exhibits low-loss at both phases over a broad wavelength range, while still possessing a huge optical contrast ($\Delta n = 1.7$). Its improved amorphous phase stability also gives rise to a larger critical thickness for complete switching. Comparing to a critical thickness of only 100 nm or less for traditional PCMs such as Ge$_2$Sb$_2$Te$_5$, GSST is a preferred material for providing desired phase coverage for metasurface applications. Geometrically optimized on-chip micro-heaters are implemented to achieve uniform temperature distribution within the metasurface region. This eliminates damage to the metasurface due to overheating. Devices of various heater dimensions, from 30 to 200 microns, have been fabricated. The fabricated devices are wire-bonded onto a custom printed circuit board.
carrier to enable in-situ device characterizations. We then implement the switching platform to demonstrate a tunable metasurface spectral filter. Multi-cycle bi-stable reversible switching is realized. Thanks to the huge optical contrast of GSST, the device provides a high reflectance modulation of 40%. In addition to bi-stable switching, broadband quasi-continuous resonance tuning over half an octave is also demonstrated. This is accomplished through controlling the fraction of crystallization of O-PCMs by varying pulse parameters. We further demonstrate a nonvolatile beam deflection control method with a tunable metasurface reflectarray. The fabricated device deflects incident laser beam from +1 to 0 diffraction order upon phase transition, and it exhibits significant switching contrast between its two phases. This result presents, to the best of our knowledge, the first experimental demonstration of a scalable switching platform for dielectric metasurfaces based on O-PCMs. We further demonstrate functional metasurface devices with bistable and quasi-continuous tuning capabilities. We believe that this platform will facilitate the development of numerous emerging applications capitalizing on its scalability and nonvolatile nature.

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SESSION S.EL09.07: Poster Session: Phase-Change Materials in Electronics and Photonics
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
5:00 AM - 8:00 AM
S-EL09

S.EL09.07.01
Comparison between Silicon and Silicon Nitride Platform for Nonvolatile Phase Change Photonic In-Memory Computing
Xuan Li\textsuperscript{1}, Nathan Youngblood\textsuperscript{2}, Zengguang Cheng\textsuperscript{1} and Harish Bhaskaran\textsuperscript{1}; \textsuperscript{1}University of Oxford, United Kingdom; \textsuperscript{2}University of Pittsburgh, United States

Demands for applying silicon photonics to high-performance computing systems have grown significantly in recent years due to the breakdown of Dennard scaling and information transfer bottlenecks in the conventional von Neumann architecture. Data processing on photonic platforms is a promising approach because of the potential advantages over electrical approaches where large bandwidth, high efficiency, ultrafast modulation speed, and low crosstalk are crucial. Critical photonic components, such as lasers, modulators, switches, filters, multiplexers, photodetectors, and memory cells, have been developed on different material platforms, such as silicon nitride (SiN), GeSi, III-V semiconductors, and others, with silicon on insulator (SOI) being the dominant platform. Owing to its compatibility with mature CMOS processes and integration with electrical devices, fabless and large scale silicon photonic integrated circuits (PICs) are available and thus offer a promising route to future commercialization.

Recently fully integrated photonic memory devices have been demonstrated on silicon nitride and silicon. This approach not only enables photonic data storage on-chip, but also shows multilevel storage, improved SNR, and reduced switching energy over available optical storage technology. Previous work on silicon nitride waveguides demonstrated both multilevel storage (> 32 levels) and computation in a fully optical framework. This was despite the fact that silicon nitride does not benefit from a high refractive index contrast (~2/1.5 in Si\textsubscript{3}N\textsubscript{4}/SiO\textsubscript{2} vs 3.5/1.5 in Si/SiO\textsubscript{2}) or the ability to integrate active photonics (such as modulators and photodetectors) directly in the waveguide. Silicon-On-Insulator (SOI), on the other hand, has both these advantages, leading to smaller footprint devices and easy integration with high-speed, CMOS-based electronics. In spite of rapid advances of demonstrations in this field on both silicon and silicon nitride platforms, a clear pathway towards choosing between the two has been lacking.

Here, we systematically evaluate and compare the computation performance of phase change photonics on a silicon platform and a silicon nitride platform. Our experimental results show that whilst Silicon platforms are superior to Silicon Nitride in terms of potential for integration, modulation speed, and device footprint, it requires trade-offs in terms of energy efficiency.
We then successfully demonstrate single-pulse modulation using phase-change optical memory (PCOM) on silicon photonic waveguides and demonstrate efficient programming, memory retention, and readout of > 4 bits of data per cell. This decreased the device footprint compared with silicon nitride photonics and reduced both the energy and time required for reaching arbitrary memory levels. We have characterized the reliability of this approach and outlined a comparison with other state-of-the-art programming methods. The use of silicon demonstrates a major step toward making phase-change photonic memory a viable and integrable technology. Our results have potential applications like deep learning based on vector-matrix multiplication and neuromorphic computing. Our approach paves the way for the in-memory computing on the silicon photonic platform.

S.EL09.07.03
TEM and EDX Analyses of Thermally Improved Phase-Change Memory by Optimized Encapsulation Layer Gauthier Lefèvre1, Anna-Lisa Serra2, Olga Cueto2, Niccolo Castellani2, Guillaume Bourgeois2, Nicolas Bernier2, Marie Claire Cyrille2, Mathieu Bernard2, Virginie Beugin2, Christophe Vallée1, Sylvain David1, Christelle Charpin2, Etienne Nowak2 and Gabriele Navarro2; 1 LTM-CNRS, France; 2 CEA-LETI, France

Phase-Change Memory (PCM) is a promising candidate for next generation of non-volatile memory [1]. PCM operations rely on the reversible phase transition between the amorphous and the crystalline phase, which occurs upon current-induced joule heating. Therefore, the reliability of the programming operation depends also on the thermal efficiency of the device [2]. Heat retention is thus essential in PCM and in complete contradiction with usual conception of electronic devices where thermal dissipation is a key point.

In this context, optimized thermal encapsulation in Ge-rich Ge-Sb-Te based PCM devices enables programming current reduction and improved data retention [3]. Indeed, an SiC encapsulation layer provides a more uniform heating of the active volume of the PCM cell, with respect to a standard SiN layer. Thanks to TEM and EDX analyses performed on state-of-the-art PCM heater-based devices, we demonstrate the higher uniformity of the heating process in the PCM cell during the programming operation achieved by optimized SiC encapsulation. Moreover, nano-diffraction patterns analysis highlights the crystalline morphology of the programmed active volume and of the surrounding material. Finally, we show the agreement between experimental data and TCAD simulations.


S.EL09.07.04
Structural Transitions and Switching Effect in Nanoscaled Ge2Sb2Te5 Films Modified by Bismuth Impurity Nurlan Almassov1, Andrei Sazonov2, Sanzhar Dyussembayev2, Oleg Prikhodko4, Nazim Guseinov4, Zhands Tolepov4 and Sergei Kozukhin2; 1 Nazarbayev University, Kazakhstan; 2 University of Waterloo, Canada; 3 Kazatomprom, Kazakhstan; 4 Al-Farabi Kazakh National University, Kazakhstan; 5 Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Russian Federation

The design of non-volatile memory cells based on phase change materials (PCM) is the subject of many studies. And one of the most promising materials are the films of Ge2Sb2Te5 chalcogenide glassy semiconductor (CGS). The operation of memory cell is based on a reversible glass-crystal phase transition, which occurs when a current pulse passes through the film's nano-volume. The embedding of metal impurity in the films can improve the property of memory cells. However, the features of phase transition in the metal-modified Ge2Sb2Te5 films are poorly understood. This work presents the results of the study of the structure observed in nanoscale films of Ge2Sb2Te5 modified by Bi (Ge2Sb2Te5-Bi). By the method of HR-TEM imaging it was found that the structure of Ge2Sb2Te5-Bi films presents the amorphous matrix with isolated crystalline nanoregions (nanoclusters) of metallic bismuth with average size ~ 8 nm. Local atomic structure of the films was studied by Raman spectroscopy. It was found that under the laser irradiation there is the structure transition of nanoscale Ge2Sb2Te5 films from amorphous into polycrystalline hexagonal stable state through metastable polycrystalline cubic phase. In contrast, in the Ge2Sb2Te5-Bi films the transition from amorphous to polycrystalline hexagonal stable state under the laser irradiation occurs without intermediate metastable cubic phase.

S.EL09.07.05
Analysis of the Limitation of the JMAK Equation for Crystallization of GST Based Phase Change Materials
An investigation into the relationship between crystal fraction and electrical conductivity for GST materials was performed. Transition from amorphous to conduction state for homogeneous nucleation of conductive crystallites in the resistive amorphous layer and limitation of the JMAK equation to modeling this transition is analyzed. In particular, the analysis relate to the validity of the model in terms of time-temperature description of crystallization and dependencies between minimum amount of crystal during nucleation and percolative threshold.

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M. Avrami, J. Phys. Chem. 8, 212
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Andrea Redaelli Editor, Phase Change Memory Device Physics, Reliability and Applications, Springer (2018)
Session Chair: Jiamian Hu
Sunday Afternoon, November 29, 2020
S.EL12

12:30 PM *S.EL12.01.01
Controlling Electronic Signals Based on Domain Walls in Improper Ferroelectrics
Dennis Meier; Norwegian University of Science and Technology, Norway

Oxide materials exhibit a broad range of tunable phenomena, including magnetism, multiferroicity, and superconductivity. Oxide interfaces are particularly intriguing. Their low local symmetry combined with the sensitivity to electrostatics and strain leads to unusual physical properties beyond the bulk properties. Recently, ferroelectric domain walls have attracted attention as a novel type of oxide interface; the walls are spatially mobile and allow controlling electronic signals at the atomic scale, holding great potential as multifunctional 2D systems for future nanoelectronics.

In my talk, I will present unique features that occur at improper ferroelectric domain walls in hexagonal manganites and discuss how these walls can be used to emulate the behavior of key electronic components. For our studies, we choose the p-type semiconductor ErMnO₃ as it naturally develops all fundamental types of ferroelectric domain wall at room temperature, namely neutral (side-by-side) as well as negatively (tail-to-tail) and positively charged (head-to-head) wall configurations. The walls are explicitly robust and, hence, represent an ideal template onto which the desired electronic behavior can be imposed. I will show how the electronic properties can be optimized and controlled, and discuss the possibility to use such walls for designing 2D digital switches and half-wave rectifiers, bringing us one step closer to domain-wall based devices and networks for next-generation nanotechnology.

12:45 PM *S.EL12.01.16
Ferroelectric and Magneto-Ionic Switching in Hafnia-Based Multiferroic Tunnel Junctions
Beatriz Noheda¹, Yingfen Wei¹, Sylvia Matzen², Cynthia Quinteros¹, Thomas Maroutian², Guillaume Agnus², Philippe Lecoeur², Pavan Nukala¹ and Mart Salverda¹; ¹University of Groningen, Netherlands; ² Universite Paris-Sud-Universite Paris-Saclay, France

Ferroelectric hafnia-based films show large electrical polarization at largely reduced dimensions. In addition they present low leakage as well as CMOS compatibility,[1] making them ideal candidates for memory and logic devices. Here we show that multiferroic tunnel junctions (MTJs) with ferroelectric Hf₀.₅Zr₀.₅O₂ barriers show both tunneling magnetoresistance effect (TMR) and tunneling electroresistance effect (TER), displaying four resistance states by magnetic and electric field switching.[2] Moreover, under electric field cycling of large enough magnitude, the TER can reach values as large as 10⁶%. Concomitant with this TER enhancement, the devices develop electrical control of spin polarization, with sign reversal of the TMR effect.[3] Currently, this intermediate state exists for a limited number of cycles and understanding the origin of these phenomena is key to improve its stability. Our study points to the magneto-ionic effect as the origin of the large TER and strong magneto-electric coupling, showing that ferroelectric polarization switching of the tunnel barrier is not the main contribution. The interplay between ferroelectric polarization and magneto-ionic coupling will be discussed.


1:00 PM *S.EL12.01.02
Automated Experiment in Piezoresponse Force Microscopy—From FerroBOT to Active Learning
Sergei V. Kalinin, Rama Vasudevan, Maxim Ziatdinov, Kyle P. Kelley, Liam Collins and Stephen Jesse; Oak Ridge National Laboratory, United States
Piezoresponse force microscopy (PFM) has become the standard tool for imaging and spectroscopy of ferroelectric and multiferroic materials, providing wealth of information on domain structures and switching behaviors. However, until now PFM, similar to other scanning probe microscopy techniques, was based on the classical rectangular scans and predefined voltage patterns. In this presentation, I introduce our recent work on combining PFM with automated experimentation, exploring image-based feedback, non-rectangular and adaptable scans, and autonomous experiments. As one such example, we demonstrate a fundamentally new approach for exploring polarization dynamics of specific domain elements and topological structures in ferroelectric materials manipulation based on in-situ image-based feedback in PFM. This approach was demonstrated for probing highly pinned domain wall dynamics in polydomain PZT, one of the traditionally most difficult objects for PFM studies. We demonstrate the creation of frustrated phases with significantly enhanced electromechanical response prior to the onset of the wall motion and discuss future strategies for fabrication of predefined topological defects and exploration of their dynamic properties. We further illustrate the incorporation of non-rectangular scans and discuss the strategies for automated experimentation in PFM based on the Gaussian Process modelling. Finally, we explore the opportunities for exploring the fundamental physics of ferroelectric materials enabled by the combination of the automated PFM experiment and combinatorial synthesis.

This research is supported by the by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division and the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, BES DOE.

1:15 PM *S.EL12.02.05
Emergent Phenomena at Oxide Interfaces with Strong Spin-Orbit Coupling Jobu Matsuno; Osaka University, Japan

We suggest that 5d electron systems are promising class of spintronic materials because of its strong spin-orbit coupling (SOC). A strong SOC inherent to 5d Ir oxides recently emerged as a new paradigm for oxide electronics. For example, we investigated novel phases of spin-orbital Mott insulators [1] and possible topological insulators [2] by tuning the electronic phases through superlattice technique. We also demonstrated a large spin Hall effect of IrO$_3$, one of the simplest 5d oxides, indicating that Ir oxides are promising class of spintronic materials [3]. In this talk, we focus on yet another topic on spintronics – magnetic skyrmion as a topological spin texture. We have studied transport properties of bilayers consisting of $m$ unit cells of ferromagnetic SrRuO$_3$ and 2 unit cells of SrIrO$_3$. We observed an anomaly in the Hall resistivity in addition to anomalous Hall effect (AHE); this is attributed to topological Hall effect (THE) [4]. The results suggest that magnetic skyrmions of 10–20 nm are generated by Dzyaloshinskii-Moriya interaction, which might be caused by both broken inversion symmetry at the interface and strong SOC of SrIrO$_3$. Even more surprising is that we can control both AHE and THE by electric field in the SrRuO$_3$-SrIrO$_3$ bilayers [5]. We observed the clear electric-field dependence only when SrIrO$_3$ is inserted between SrRuO$_3$ and a gate dielectric. The results established that strong SOC of nonmagnetic materials such as SrIrO$_3$ is essential in electrical tuning of these Hall effects. We are also searching for spin-current transport properties at the interfaces consisting of magnetic oxides and nonmagnetic Ir oxides. We will report on the latest results on them. Through these studies on oxide interfaces containing Ir oxides, we may have a chance to approach a triple point for topology, correlation, and spin-orbit coupling.

References:

1:30 PM *S.EL12.02.01
Dimensionality-Induced Change in Ferroelectric Topological Order in Oxide Superlattices Megan E. Holtz¹, Elliot S. Padgett¹, Rachel Steinhardt², Charles M. Brooks², D.G. Schlom², David A. Muller¹,³ and Julia Mundy¹; ¹Harvard University, United States; ²Cornell University, United States; ³Kavli Institute at Cornell for Nanoscale Science, United States

Topological defects can be formed at a phase transition where there is spontaneous symmetry breaking. These features play a central role in understanding phase transitions, ranging from superfluid $^4$He and high-temperature superconductors to cosmological systems. Certain hexagonal multiferroic materials also display topological defects including (charged) domain walls and ferroelectric vortices. In addition to serving as a model for their universality class, these sites can further host emergent phenomena including anomalous conduction and fractional electronic charges or quantized magnetic moments.
Here, we construct atomically-abrupt superlattices to study the ferroelectric order as a function of thickness. We observe controlled formation of charged ferroelectric domain walls. Electrostatic confinement of the walls and the associated vortices pushes the material from a $Z_6$ symmetry to a stripe phase with continuous $U(1)$ symmetry to a paraelectric phase with decreasing thickness. These materials also display unique topological features not observed in the bulk components. Together we demonstrate how dimensional confinement in artificial superlattices is a new probe for stabilizing new topologies in hexagonal ferroelectric systems.

1:45 PM DISCUSSION TIME

2:00 PM *S.EL12.01.06
Structural Peculiarities of Epitaxial PMN-PT Thin Films Matjaz Spreitzer, U. Gabor, J. Belhadi, I. Rafalovskyi, N. Daneu, Aleksander Matavz, V. Bobnar, Z. Samardzija and J. Hlinka; Jožef Stefan Institute, Slovenia

Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$ is a relaxor ferroelectric material that exhibits interesting dielectric and piezoelectric properties. Specifically, complex domain architectures are formed in compositions around the morphotropic phase boundary. The polar structure of thin films is additionally affected by the epitaxial strain. In order to understand the structure of these films, multi-scale analysis is needed, considering limitations of individual analytical technique. It will be presented how a combination of high-resolution X-ray diffraction, selected area electron diffraction, atomic-resolution scanning transmission electron microscopy, polarized Raman scattering and wavelength-dispersive X-ray spectroscopy can be used to elucidate the structure of this material. Furthermore, it will be shown how macroscopic piezoelectric and dielectric measurements in different configurations can aid in understanding the film structural characteristics. Growth-related aspects will also be discussed, with emphasis on the challenges and peculiarities occurring in the growth of films with volatile components. Routes for the preparation of single-phase films with near-nominal stoichiometry will be presented, along with the specific defects that appear with off-stoichiometry. The role of the substrate on the phase purity and film quality will also be discussed. It will be shown why in some cases a rough interface is preferred.

SESSION S.EL12.07: Live Keynote II: Nanomagnetism/Magnetoelectrics
Session Chairs: Massimo Ghidini and Jiamian Hu
Monday Afternoon, November 30, 2020
S.EL12

5:15 PM *S.EL12.04.02
Magnetoelectric Coupling by Piezoelectric Tensor Design Mark S. Rzchowski$^1$, J. Irwin$^1$, S. Lindemann$^1$, W. Maeng$^1$, J.J. Wang$^2$, V. Vaithyanathan$^3$, Jiamian Hu$^1$, Long-Qing Chen$^2$, D.G. Schlom$^3$ and Chang-Beom Eom$^1$; $^1$University of Wisconsin-Madison, United States; $^2$The Pennsylvania State University, United States; $^3$Cornell University, United States

Strain-coupled magnetoelectric (ME) phenomena in piezoelectric / ferromagnetic thin-film bilayers are a promising paradigm for sensors and information storage devices, where strain manipulates the magnetization of the ferromagnetic film. In-plane magnetization rotation with an electric field across the film thickness has been challenging due to the large reduction of in-plane piezoelectric strain by substrate clamping, and in two-terminal devices, the requirement of anisotropic in-plane strain. Here we show that these limitations can be overcome by designing the piezoelectric strain tensor using the boundary interaction between biased and unbiased piezoelectric. We fabricated 500 nm thick, (001) oriented [Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$]0.7-[PbTiO$_3$]0.3 (PMN-PT) unclamped piezoelectric membranes with ferromagnetic Ni overlayers. Guided by analytical and numerical continuum elastic calculations, we designed and fabricated two-terminal devices exhibiting electric field-driven magnetization rotation. We develop a method that can apply designed strain patterns to many other materials systems to control properties such as superconductivity, band topology, conductivity, and optical response. We also discuss how these effects depend on the crystallographic orientation.

5:30 PM *S.EL12.04.03
Control of Ferromagnetic Skyrmions Using Ferroelectric Polarization Tae Won Noh; Seoul National University, Korea (the Republic of)

Ferromagnetic skyrmion is a topologically protected whirling spin texture in nanoscale. Due to its small size, topologically-protected stability, and solitonic nature together, it holds great promise for future spintronics applications. To translate these
compelling features into practical spintronic devices, we should face a key challenge in achieving effective control of skyrmion properties, such as size, density, and thermodynamic stability. Recently, we reported the discovery of ferroelectrically tunable skyrmions in ultrathin BaTiO3/SrRuO3 bilayer heterostructures. The ferroelectric proximity effect occurring at the BaTiO3/SrRuO3 heterointerface can trigger a sizable Dzyaloshinskii-Moriya interaction. Thus the interaction between two ferroic materials can stabilize robust skyrmions with diameters of several tens of nanometers.[1] Moreover, by manipulating the ferroelectric polarization direction of the BaTiO3 layer, we could achieve local, switchable and nonvolatile control of both skyrmion density and thermodynamic stability. Such a ferroelectrically tunable skyrmion system can work as a new paradigm to simultaneously enhance the integratability and addressability of skyrmion-based functional devices.


5:45 PM *S.EL12.03.02
Challenges and Opportunities with X-Raying Novel Spin Textures Peter Fischer; Lawrence Berkeley National Lab, United States

Spin textures are the foundation of properties and behavior of magnetic materials and drive the functionality of magnetic devices. Topology and frustration that impact spin textures have recently attracted significant scientific interest and led to intense research e.g. in magnetic skyrmions (Sk) and artificial spin ice systems (ASI) addressing a broad spectrum of challenging scientific and technological questions, including stability, dynamics, nucleation, and transport. So far, SK and ASI have been treated foremost as two-dimensional spin textures, however, recent investigations have opened the door to a conceptually next leap, which are three-dimensional nanoscale size magnetic spin textures (3D-spin-textures) e.g., chiral bobbers, magnetic hopfions, and skyrmion tubes.

Advanced characterization tools that provide magnetic sensitivity to spin textures at high spatial resolution, ultimately at buried interfaces and in all three dimensions [1], and at high temporal resolution to capture the spin dynamics across scales, are therefore of large scientific interest.

Magnetic soft X-ray spectro-microscopies [2] provide unique characterization opportunities to study the statics and dynamics of spin textures in magnetic materials combining X-ray magnetic circular dichroism (X-MCD) as element specific, quantifiable magnetic contrast mechanism with spatial and temporal resolutions down to fundamental magnetic length, time, and energy scales.

Current developments of x-ray sources aim to increase dramatically the coherence of x-rays opening the path to new techniques, such as ptychography [3] or x-ray photo-correlation spectroscopy (XPCS) [4] that allow unprecedented studies of nanoscale heterogeneity, complexity, and fluctuations.

I will review recent achievements and future opportunities with magnetic x-ray spectro-microscopies. Examples will include static properties and dynamic behavior of various magnetic skyrmion [5,6] textures with potential application to novel magnetic logic and storage devices, as well as results from an XPCS study at LCLS with a novel 2-pulse scheme that allowed to discover an unexpected and drastic change of the correlation times in nanoscale spin fluctuations near phase boundaries, i.e., in the skyrmion phase, and near the boundary with the stripe phase of a multilayered Fe/Gd system [4].

Finally, I will present a study on ferromagnetic liquid droplets, which could establish a complete paradigm shift in magnetic materials, that combine characteristics of liquid, such as reconfigurability and short range spatial and temporal correlations with ferromagnetism, which so far has been confined to condensed matter [7].

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division Contract No. DE-AC02-05-CH1123 in the Non-Equilibrium Magnetic Materials Program (MSMAG).

References

6:00 PM *S.EL12.04.11
Observation, Manipulation and Understanding of Coupled Multiferroic Domains in Single-Phase Magnetoelectrics Tsuyoshi Kimura; The University of Tokyo, Japan

Symmetry breaking ascribed to the evolution of an order parameter is one of the most important concepts in ferroic materials
such as ferromagnets and ferroelectrics, and bears “domain” structures. The domain switching by an external field is the key principle to exploit them for practical applications. In multiferroics, materials possessing multiple ferroic order parameters, the respective order parameters form domains and multiple types of domain states coexist. It is well-accepted that couplings between the multiple order parameters and domain states are essential for macroscopic magnetoelectric phenomena in multiferroics. However, there are few reports that directly compare responses of coexisting domain states to external fields and macroscopic magnetoelectric properties. In this presentation, we show selective observations of multiple magnetic order parameters and domain structures in some single-phase magnetoelectrics. This work has been done in collaboration with H. Ueda, R. Misawa, T. Katsuyoshi, J. K. H. Fischer, K. Kimura, Y. Tanaka, Y. Wakabayashi, T. Honda, J. S. White, M. Kenzelmann, A. B. Harris, N. Leo, and M. Fiebig.

6:15 PM *S.EL12.04.07
Progress in Magnetoelectric Composites and Device Applications Shuxiang Dong, Zhaoqiang Chu, MohammadJavad PourhosseiniAsl and Zhonghui Yu; Peking University, China

Incorporating ferromagnetic, ferroelectric and ferroelastic orders inherently in a single-phase multiferroic material or manipulating one ferroic order with the others via interfacial coupling effects in multiferroic heterostructures has driven significant research activities aiming at the realization of their technological potential in the field of sensors, RF electronics, logic devices and memory etc. Magnetoelectric (ME) effect is essentially referred to as a change of electrical polarization (P) induced by external magnetic field (H) or a control of magnetization (M) via applied electric field (E). This report first introduces our recent progress in laminated ME composites consisting of a [011]-oriented Pb(Mg,Nb)O3-Pb(Ti,Zr)O3 (PMN-PZT) single-crystal fiber laminated with laser-treated amorphous FeBSi alloy (Metglas). High ME coupling coefficient around 10 kV/cm*Oe has been achieved. We will then review recent advances in multi-layered ME composites as well as their device applications including magnetic field/current sensors, dual-stimulus energy harvesters, ME memories, ME gyrators and tunable electronics. Some perspectives in terms of the future of magnetoelectric composites and devices will also be provided.

6:30 PM *S.EL12.03.03
Neuromorphic Computing with Spintronic Oscillators Alice Mizrahi1,2,3, Tifenn Hirtzlin1, Matthew Daniels2,3, Nicolas Locatelli1, Akio Fukushima4, Hit Kubota4, Shinsi Yuasa4, M D. Stiles3, Julie Grollier1 and Damien Auerlioz2; 1Université Paris-Saclay, France; 2University of Maryland, United States; 3National Institute of Standards and Technology, United States; 4National Institute of Advanced Industrial Science and Technology (AIST), Japan

Artificial neural networks are performing tasks, such as image recognition and natural language processing, that offer great promises for artificial intelligence. However, these algorithms run on traditional computers and consume orders of magnitude more energy more than the brain does at the same task. One promising path to reduce the energy consumption is to build dedicated hardware to perform artificial intelligence. Spintronic devices are particularly interesting because they allow for complex functionality with low energy consumption and small size.

I will discuss the role of magnetic tunnel junctions as building blocks for artificial neural networks in hardware. These bi-stable nanodevices which magnetic state can be both read and written electrically. Their high endurance, reliability and CMOS-compatibility have made them flagship devices for novel forms of computing. While their main use is as non-volatile memories (MRAM), they can also exhibit rich non-linear dynamics which emulate the basic functionalities of neurons.

In particular, I will focus on the superparamagnetic regime of magnetic tunnel junctions and stochastic oscillators capable of harnessing the energy of thermal noise. While stochasticity is traditionally unwanted for computing, I will show how it can be leveraged to reduce energy consumption. I will draw an analogy between stochastic magnetic tunnel junctions and stochastic spiking neurons, which emit randomly spaced voltage spikes. I will show how these devices can be assembled into an artificial neural network an perform computing. Such a system would be competitive with conventional electronics implementations, both in terms of area on chip and energy consumption.

These results open the path to low energy hardware implementation of neural networks, making it possible to perform cognitive tasks on chip.

6:45 PM *S.EL12.04.04
Enhanced Magnetostriiction in FeGa Epitaxial Thin Films John T. Heron1, Peter Meisenheimer1, Rachel Steinhart6, Shihao Zhuang1, Suk Hyun Sung1, Mark Nowakowski1, Steve Novakov1, Bhagwati Prasad4, Chris Zollner3, Zhe Wang2, Natalie Dawley2, Allen Hunter1, Sasikanth Maniratun3, Dmitri Nikonov4, Ian Young3, Long Qing Chen6, Jeffrey Bokor4,
Ramamoorthy Ramesh, Robert Hovden, Jiamian Hu, and D.G. Schlom; 1University of Michigan, United States; 2Cornell University, United States; 3University of Wisconsin–Madison, United States; 4University of California, Berkeley, United States; 5Intel Corporation, United States; 6The Pennsylvania State University, United States

Composite multiferroics, composed of a magnetostrictive ferromagnet and a piezoelectric ferroelectric, hold promise for magnetic field sensors and energy efficient beyond-CMOS logic by harnessing magnetoelectric transduction. Enhancing device performance requires highly magnetostrictive materials, however, relatively little attention has been given to engineering magnetostriction in thin films. One promising magnetostrictor system are the Fe1–xGax alloys yet in bulk, the magnetostriction coefficient of Fe1–xGax alloys versus gallium composition peaks near ~18% Ga due to a phase change from the disordered A2 phase to an ordered BCC phase (D03). Here we discuss a means to boost (by 200-300% relative to bulk) the magnetostriction of Fe1–xGax thin film alloys by extending the phase stability of the A2 phase to higher Ga compositions.

Transport-based magnetoelectric characterization of a Fe1–xGax-[Pb(Mg1/3Nb2/3)O3]0.7-[PbTiO3]0.3 (PMN-PT) composite multiferroic heterostructure shows are reversible 90 deg electrical switch of magnetic anisotropy and a room temperature converse magnetoelectric coefficient of 5.5×10⁻⁶ s m⁻¹.

7:00 PM *S.EL12.04.13
Active Control of Spin Waves in Multiferroic Heterostructures Sebastiaan van Dijken; Aalto University, Finland

Active manipulation of spin waves is essential for the development of magnon-based technologies. One route towards this goal exploits reprogrammable magnonic crystals. In such structures, a varying spatial modulation of magnetic properties using, for instance, electric currents [1] or optical pulses [2] controls the transmission of spin waves. Besides these dynamic approaches, field-induced toggling between ferromagnetic and antiferromagnetic states in magnetic stripe arrays has been shown to modify spin wave transport in a non-volatile way [3].

Multiferroic heterostructures comprising coupled ferromagnetic and ferroelectric layers offer an interesting alternative as programmable hybrids for magnonics. Attractive properties of multiferroic heterostructures include the imprinting of magnetic domain patterns, the creation of abrupt anisotropy boundaries, strong pinning of magnetic domain walls, and electric field control of magnetic anisotropy, magnetic switching, and magnetic domain wall motion [4-6].

Here, we demonstrate that multiferroic heterostructures provide a versatile platform for the emission of short-wavelength spin waves [7], the confinement of spin wave modes in structurally uniform films [8], and active manipulation of spin wave transmission [9]. The multiferroic heterostructures consist of a ferroelectric BaTiO3 substrate and a strain-coupled ferromagnetic film with a thickness of 20 – 50 nm. At room temperature, this material system comprises fully correlated stripe domains in the ferroelectric and ferromagnetic subsystems. Utilizing strong pinning of ferromagnetic domain walls onto ferroelectric boundaries, we demonstrate active manipulation of spin wave transmission from 0% to 100% by non-volatile reprogramming of the domain-wall spin structure in a magnetic field [9]. In addition to magnetic field control, we also present recent results on active manipulation of spin wave transmission using electric fields. This sought-after effect originates from local strain-induced changes of the magnetic anisotropy. We demonstrate that the transmission of spin waves can be fully turned on and off in certain frequency bands by the application of voltage pulses across the BaTiO3 substrate. The multiferroic heterostructures allow also for continuous tuning of the spin wave phase and amplitude, offering prospects for voltage-controlled magnonic logic.

5:00 AM *S.EL12.01.01
Controlling Electronic Signals Based on Domain Walls in Improper Ferroelectrics Dennis Meier; Norwegian University of Science and Technology, Norway

Oxide materials exhibit a broad range of tunable phenomena, including magnetism, multiferroicity, and superconductivity. Oxide interfaces are particularly intriguing. Their low local symmetry combined with the sensitivity to electrostatics and strain leads to unusual physical properties beyond the bulk properties. Recently, ferroelectric domain walls have attracted attention as a novel type of oxide interface; the walls are spatially mobile and allow controlling electronic signals at the atomic scale, holding great potential as multifunctional 2D systems for future nanoelectronics.

In my talk, I will present unique features that occur at improper ferroelectric domain walls in hexagonal manganites and discuss how these walls can be used to emulate the behavior of key electronic components. For our studies, we choose the p-type semiconductor ErMnO3 as it naturally develops all fundamental types of ferroelectric domain wall at room temperature, namely neutral (side-by-side) as well as negatively (tail-to-tail) and positively charged (head-to-head) wall configurations. The walls are explicitly robust and, hence, represent an ideal template onto which the desired electronic behavior can be imposed. I will show how the electronic properties can be optimized and controlled, and discuss the possibility to use such walls for designing 2D digital switches and half-wave rectifiers, bringing us one step closer to domain-wall based devices and networks for next-generation nanotechnology.

5:30 AM *S.EL12.01.02
Automated Experiment in Piezoresponse Force Microscopy—From FerroBOT to Active Learning Sergei V. Kalinin, Rama Vasudevan, Maxim Ziatdinov, Kyle P. Kelley, Liam Collins and Stephen Jesse; Oak Ridge National Laboratory, United States

Piezoresponse force microscopy (PFM) has become the standard tool for imaging and spectroscopy of ferroelectric and multiferroic materials, providing wealth of information on domain structures and switching behaviors. However, until now PFM, similar to other scanning probe microscopy techniques, was based on the classical rectangular scans and predefined voltage patterns. In this presentation, I introduce our recent work on combining PFM with automated experimentation, exploring image-based feedback, non-rectangular and adaptable scans, and autonomous experiments. As one such example, we demonstrate a fundamentally new approach for exploring polarization dynamics of specific domain elements and topological structures in ferroelectric materials manipulation based on in-situ image-based feedback in PFM. This approach was demonstrated for probing highly pinned domain wall dynamics in polydomain PZT, one of the traditionally most difficult objects for PFM studies. We demonstrate the creation of frustrated phases with significantly enhanced electromechanical response prior to the onset of the wall motion and discuss future strategies for fabrication of predefined topological defects and exploration of their dynamic properties. We further illustrate the incorporation of non-rectangular scans and discuss the strategies for automated experimentation in PFM based on the Gaussian Process modelling. Finally, we explore the opportunities for exploring the fundamental physics of ferroelectric materials enabled by the combination of the automated PFM experiment and combinatorial synthesis.

This research is supported by the by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division and the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, BES DOE.

6:00 AM S.EL12.01.03
Polar Metals Revisited Pankaj K. Sharma1,2; 1The University of New South Wales, Australia; 2ARC Centre of Excellence in Future Low-Energy Electronics Technologies, University of New South Wales, Australia

Ferroelectricity has often been associated with and observed in materials that are insulating or semiconducting rather than metallic because conduction electrons in metals screen out the static internal fields arising from a long-range dipolar order. In the 1960s, Anderson and Blount proposed materials with these seemingly incompatible characteristics, i.e., metals with a polar axis termed ferroelectric metals. Since then, ferroelectric metals were merely a theoretical construct until recent experimental observations suggesting otherwise. Despite the progress, electrically switchable intrinsic electric polarization, together with the direct observation of ferroelectric domains, has not yet been realized in a bulk crystalline metal, although incomplete screening by mobile conduction charges should, in principle, be possible.

Here, we provide evidence that native metallicity and ferroelectricity coexist in bulk crystalline van der Waals WTe2. We
show that, despite being a Weyl semimetal, WTe$_2$ has switchable spontaneous polarization and a natural ferroelectric domain structure at room temperature. This new class of materials has tantalizing potential for functional nanoelectronics applications.

6:15 AM S.EL12.01.04
Superior Polarization Retention through Engineered Domain Wall Pinning Dawei Zhang$^1$, Daniel Sando$^{1,1}$, Pankaj K. Sharma$^{1,1}$, Xuan Cheng$^2$, Fan Ji$^{1,1}$, Vivasha Govinden$^{1,1}$, Matthew Weyland$^{2,2}$, Valanoor Nagarajan$^{1,1}$ and Jan Seidel$^{1,1}$; $^1$UNSW, Australia; $^2$Monash University, Australia

In the quest towards commercialization of ferroelectric-based non-volatile nanoelectronic devices, the realization of robust polarization retention is of great significance. However, ferroelectric materials always suffer from polarization relaxation during the time, typically happening within from days to a few weeks, which leads to a final retention loss for the data storage. In this work, by exploiting the domain wall pinning through designer-defect engineering in epitaxial BiFeO$_3$ films, we have demonstrated an ultra-long polarization with virtually no degradation in switched nanoscale domains for periods longer than two years. This already represents a more than 4000 % improvement over the best values hitherto reported and is believed to have an ongoing retention. Transmission electron microscopy (TEM) with atomic resolution reveals that nanoscale defect pockets pervade the entire film thickness homogeneously. These defects act as highly efficient domain wall pinning centres, resulting in the superb retention. This is also corroborated by scanning probe microscopy-based dynamic switching measurements as the results show a remarkably increased activation field for domain wall movement, originating from the defect-engineered domain wall pinning. Our findings demonstrate that defects can be exploited in a positive manner to solve reliability issues in ferroelectric films used in functional devices.

6:30 AM *S.EL12.01.05
Cold Sintering of Novel Microwave Dielectric Ceramics Ian M. Reaney and Dawei Wang; Chinese Academy of Sciences, China

Cold sintering is a revolutionary new sintering process which densifies ceramics at < 200 °C using a combination of pressure and a transient aqueous phase. The most significant progress towards component/device fabrication has been in the area of MW technology and several new materials have recently emerged, including a range of temperature stable, low loss ceramics with permittivities from 8 to 40, as well as new magnetodielectrics. This contribution presents an overview of new developments in cold sintering for MW technology and suggests future directions that might result in ceramics directly deposited and integrated onto polymer circuit boards.

7:00 AM *S.EL12.01.06
Structural Peculiarities of Epitaxial PMN-PT Thin Films Matjaz Spreitzer, U. Gabor, J. Belhadi, I. Rafalovskyi, N. Daneu, Aleksander Matavz, V. Bobnar, Z. Samardzija and J. Hlinka; Jozef Stefan Institute, Slovenia

Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$ is a relaxor ferroelectric material that exhibits interesting dielectric and piezoelectric properties. Specifically, complex domain architectures are formed in compositions around the morphotropic phase boundary. The polar structure of thin films is additionally affected by the epitaxial strain. In order to understand the structure of these films, multiscale analysis is needed, considering limitations of individual analytical technique. It will be presented how a combination of high-resolution X-ray diffraction, selected area electron diffraction, atomic-resolution scanning transmission electron microscopy, polarized Raman scattering and wavelength-dispersive X-ray spectroscopy can be used to elucidate the structure of this material. Furthermore, it will be shown how macroscopic piezoelectric and dielectric measurements in different configurations can aid in understanding the film structural characteristics. Growth-related aspects will also be discussed, with emphasis on the challenges and peculiarities occurring in the growth of films with volatile components. Routes for the preparation of single-phase films with near-nominal stoichiometry will be presented, along with the specific defects that appear with off-stoichiometry. The role of the substrate on the phase purity and film quality will also be discussed. It will be shown why in some cases a rough interface is preferred.

7:30 AM S.EL12.01.09
Memory Window Improvement of HZO-Based FeFETs with HfO$_2$ Interlayers Zhouchangwan Yu, Fei Huang, Yoshio Nishi, Simon S. Wong and Paul McIntyre; Stanford University, United States

Since the discovery of ferroelectricity in HfO$_2$ thin films that either doped or alloyed with other metal oxide components, HfO$_2$ based ferroelectric field-effect transistors (FeFETs) have gained increasing interest as a candidate emerging memory due to their ability to scale to very small device dimensions, and their CMOS compatibility. For a FeFET with metal-
ferroelectric-insulator-semiconductor (MFIS) gate stack, the insulator layer interposed between the ferroelectric and the semiconductor channel plays an important role to achieve a wide memory window (MW) and good endurance and retention. In this work, we experimentally demonstrate FeFETs with very large MW of 3.3 V by utilization of HfO$_2$ interlayers both on top of and under the ferroelectric Hf$_{0.5}$Zr$_{0.5}$O$_2$ (HZO) layer.

Based on the studies of metal-ferroelectric-metal (MFM) capacitors and MFIS gate stacks with ferroelectric HZO of 10 nm, the thicknesses of top and bottom HfO$_2$ interlayers are optimized to be 2 nm and 1 nm, respectively, in order to achieve maximum MW and minimum polarization “wake-up” effect. The MFIS without HfO$_2$ interlayers shows MW of 2.0 V, while the MFIS with HfO$_2$ interlayers shows MW greater than 3.0 V. The thickness of bottom HfO$_2$ layer of 2 nm is required to improve the MW, and the possible effect is that it forms a thin continuous film that facilitate the later ALD growth of HZO, which may benefit the orthorhombic phase formation.

It has been reported that FeFETs with 20 nm thick HfO$_2$ layer have a MW of 2.9 V, switched by +5 V and -5 V pulses on the gate.[i] By utilizing HfO$_2$ interlayers, our FeFETs has only 13 nm of HZO of HfO$_2$ layers in total, and exhibit a wider MW of 3.3 V, switched by +4 V and -4 V. In addition, our FeFET devices display good retention at 85°C and maintain a MW of 1.8 V extrapolated for 10 years. As for write disturb, the devices can withstand disturbs in a V$_{dd}/2$ scheme up to the tested 10$^6$ cycles without degradation of I$_{on}/I_{off}$ ratio.


7:45 AM S.EL12.01.13

Strain-Induced Ferroelectricity in Freestanding SrTiO$_3$ Membranes Ruijuan Xu$^1$, Jiawei Huang$^2$, Edward Barnard$^3$, Seung Sae Hong$^1$, Ed Wong$^3$, Varun Harbola$^1$, Prastuti Singh$^1$, Bai Yang Wang$^1$, Shi Liu$^2$ and Harold Y. Hwang$^1$; $^1$Stanford University, United States; $^2$Westlake University, China; $^3$Lawrence Berkeley National Laboratory, United States

SrTiO$_3$ is known to exhibit quantum paraelectricity in which quantum fluctuations suppress ferroelectric ordering at low temperature$^1$. Despite the intrinsic paraelectric nature of SrTiO$_3$, it is possible to stabilize ferroelectricity via a variety of means such as substrate-induced strain tuning$^2$, cation substitution$^3$, $^{18}$O isotope substitution$^4$, and defect engineering$^5$, etc. In particular, the epitaxial strain applied via lattice mismatch in thin film heterostructures can significantly enhance the ferroelectric transition temperature $T_c$ and even stabilize ferroelectricity at room temperature. However, since a given substrate provides a fixed and discrete lattice parameter that lacks mechanical flexibility, this approach is limited in the ability to dynamically control the strain state in a widely accessible range. In order to tune strain in a dynamic and continuous fashion, here we utilize freestanding SrTiO$_3$ crystalline membranes to extend the lattice control of ferroelectric ordering in such materials$^6$. By dissolving a water-soluble epitaxial buffer layer, we can release SrTiO$_3$ films from substrates, and transfer the resulting freestanding membranes onto flexible polymer substrates that can be stretched to induce various strain states. Using optical second harmonic generation microscopy, we probe the ferroelectric phase transition as a function of strain wherein we observe $T_c$ is significantly enhanced by strain. Upon applying 1.5% uniaxial strain, we observe robust room-temperature ferroelectricity with the notable feature of 180° ferroelectric domains using piezoresponse force microscopy. First-principle calculations and molecular dynamics simulations further reveal the structural nature at each given strain state and the order-disorder character of the phase transition in strained SrTiO$_3$ membranes. Overall, our work provides new insights regarding strain induced phenomena in oxide membranes and also demonstrates a new approach to dynamically control ferroelectric ordering in SrTiO$_3$.

References
Modeling Morphotropic Phase Boundary in Lead Zirconate Titanate as a Frustrated State

Ying Shi Teh and Kaushik Bhattacharya; California Institute of Technology, United States

The microstructure of lead zirconate titanate (PZT) at its morphotropic phase boundary (MPB) has attracted much interest due to its exceptional dielectric and ferroelectric properties. One long-held hypothesis is that a monoclinic phase exists at the narrow composition regime near the MPB of PZT to bridge the transition between rhombohedral and tetragonal phases. However, till today, there remains no agreement regarding the specific monoclinic structure. Motivated by the disordering in the chemical composition of a solid solution, we propose an extension of the random field Ising model with dipolar state that includes long-range dipole-dipole interactions to study MPB in PZT. A Monte Carlo approach is then adopted to obtain low-energy configurations of the model. The method is formulated to suit the GPU architecture, hence allowing to solve large-scale cases that better capture composition disordering and domain pattern. Our model predicts a sharp transition from rhombohedral phase to tetragonal phase as the composition of lead titanate in PZT is increased. At the MPB, it shows a frustrated state mixed with domains of both rhombohedral and tetragonal phases. The average domain size undergoes a sudden dip while the domain walls no longer follow the low-order crystallographic directions at this region. These findings are consistent with experimental observations. Overall, this model presents a picture of the competition between composition disordering and long-range interactions, and clarifies the structural inhomogeneity at the MPB.

Ferroelectric and Magneto-Ionic Switching in Hafnia-Based Multiferroic Tunnel Junctions

Beatriz Noheda1,1, Yingfen Wei1, Sylvia Matzen2, Cynthia Quinteros1, Thomas Maroutian2, Guillaume Agnus2, Philippe Lecoeur2, Pavan Nukala1 and Mart Salverda1; 1University of Groningen, Netherlands; 2- Universite Paris-Sud-Universite Paris-Saclay, France

Ferroelectric hafnia-based films show large electrical polarization at largely reduced dimensions. In addition, they present low leakage as well as CMOS compatibility, making them ideal candidates for memory and logic devices. Here, we show that multiferroic tunnel junctions (MTJs) with ferroelectric Hf0.5Zr0.5O2 barriers show both tunneling magnetoresistance effect (TMR) and tunneling electroresistance effect (TER), displaying four resistance states by magnetic and electric field switching.[2] Moreover, under electric field cycling of large enough magnitude, the TER can reach values as large as 10%. Concomitant with this TER enhancement, the devices develop electrical control of spin polarization, with sign reversal of the TMR effect.[3] Currently, this intermediate state exists for a limited number of cycles and understanding the origin of these phenomena is key to improve its stability. Our study points to the magneto-ionic effect as the origin of the large TMR and strong magneto-electric coupling, showing that ferroelectric polarization switching of the tunnel barrier is not the main contribution. The interplay between ferroelectric polarization and magneto-ionic coupling will be discussed.


Control of Transport Properties of Hybrid Molybdenum Disulfide (MoS2)—Ferroelectric Devices via Domain Engineering

Alexey Lipatov1, Tao Li2, Nataliia Vorobeva1, Alexander Sinitskii1 and Alexei Gruverman1; 1University of Nebraska–Lincoln, United States; 2Xi'an Jiaotong University, China

We introduce a concept of programmable ferroelectric devices comprised of two-dimensional (2D) and ferroelectric (FE) materials. It enables precise modulation of the in-plane conductivity of a 2D channel material through nanoeengineering of FE domains with out-of-plane polarization. The functionality of these new devices has been demonstrated using field-effect transistors (FETs) fabricated with monolayer molybdenum disulfide (MoS2) channels on the Pb(Zr,Ti)O3 substrates. Using piezosresponse force microscopy, we show that local switching of FE polarization by a conductive probe can be used to tune the conductivity of the MoS2 channel. Specifically, patterning of the nanoscale domains with downward polarization creates
conductive paths in a resistive MoS$_2$ channel so that the conductivity of an FET is determined by the number and length of the paths connecting source and drain electrodes. In addition to the device programmability, we demonstrate the device ON/OFF cyclic endurance by successive writing and erasing of conductive paths in a MoS$_2$ channel. These findings may inspire the development of advanced energy-efficient programmable synaptic devices based on combination of 2D and FE materials.

9:00 AM S.EL12.01.18
Nanoscale Structural Ripples and Flexoelectric Effects in Free-Standing Single-Crystal Complex Oxide Ferroelectric Materials Saidur R. Bakaul$^1$, Jaegyu Kim$^2$, Seungbum Hong$^2$, Mathew Cherukara$^1$, Tao Zhou$^1$, Liliana Stan$^1$, Claudio Serrao$^3$, Sayeef Salahuddin$^1$, Amanda Petford-Long$^1$, Dillon D. Fong$^1$ and Martin V. Holt$^1$; $^1$Argonne National Laboratory, United States; $^2$Korea Advanced Institute of Science and Technology, Korea (the Republic of); $^3$University of California, Berkeley, United States

Recent studies have reported that freestanding epitaxial complex oxide thin films [1, 2] exhibit physical properties significantly different from original, as-grown films. For instance, the collapse of crystalline order has been reported in ultrathin, freestanding SrTiO$_3$ layers, induced by the electron-volt-level energy of bond breaking that is released from the interfacial layer during the transfer process. How such an energy landscape and bond rearrangement in one layer would necessarily affect other layers of a single crystal complex oxide thin film, i.e., in a three-dimensional object, is poorly understood. Unlike 2D materials such as graphene, complex oxides have strong interlayer bonds, which allows for long-range, three-dimensional mechanical energy propagation. The interfacial bond energy in typical complex oxide heterostructures is quite high and therefore, atomistic changes at the interface will alter the properties of all the layers, resulting in a very different mechanical and electrostatic energy landscape in the entirety of the material.

In this work, [3] we present the effect of interfacial bond-breaking on the structural and ferroelectric (FE) properties of epitaxially-grown PbZr$_{0.2}$Ti$_{0.8}$O$_3$ (PZT) thin films at mesoscopic length scale. PZT film grown on La$_{0.7}$Sr$_{0.3}$MO$_3$ (LSMO) buffered STO substrate is released by breaking the bond at the LSMO-PZT interface using a layer transfer technique. Utilizing the synchrotron X-ray nanoprobe technique we reveal that the bond-breaking results in nanoscale structural ripples in atomic planes of the FE material. The ripples are formed due to the lack of mechanical boundaries in all three dimensions. We estimate that such ripples can create a strong local strain gradient and flexoelectric field that is comparable to the coercive field of the FE film. In-situ piezo force microscopy and electronic transport measurements show that the flexoelectric effect generated from such ripples in atomic planes strongly blocks the FE domain wall motion and reduces the velocity by several orders magnitude. We will present and discuss the effect of these ripples on the energy landscape that controls domain wall motion and polarization reversal behavior.

Reference:

SESSION S.EL12.02: Functional Oxides
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL12

5:00 AM *S.EL12.02.01
Dimensionality-Induced Change in Ferroelectric Topological Order in Oxide Superlattices Megan E. Holtz$^1$, Elliot S. Padgett$^1$, Rachel Steinhardt$^2$, Charles M. Brooks$^2$, D.G. Schlom$^2$, David A. Muller$^{1,3}$ and Julia Mundy$^1$; $^1$Harvard University, United States; $^2$Cornell University, United States; $^3$Kavli Institute at Cornell for Nanoscale Science, United States

Topological defects can be formed at a phase transition where there is spontaneous symmetry breaking. These features play a central role in understanding phase transitions, ranging from superfluid $^4$He and high-temperature superconductors to cosmological systems. Certain hexagonal multiferroic materials also display topological defects including (charged) domain walls and ferroelectric vortices. In addition to serving as a model for their universality class, these sites can further host emergent phenomena including anomalous conduction and fractional electronic charges or quantized magnetic moments.
Here, we construct atomically-abrupt superlattices to study the ferroelectric order as a function of thickness. We observe controlled formation of charged ferroelectric domain walls. Electrostatic confinement of the walls and the associated vortices pushes the material from a $Z_6$ symmetry to a stripe phase with continuous $U(1)$ symmetry to a paraelectric phase with decreasing thickness. These materials also display unique topological features not observed in the bulk components. Together we demonstrate how dimensional confinement in artificial superlattices is a new probe for stabilizing new topologies in hexagonal ferroelectric systems.

5:30 AM S.EL12.02.03
DFT Models of Negative Capacitance in Hafnium/Zirconium Oxide Polymorphs Kisung Chae1,2, Kyeongjae Cho2 and Andrew C. Kummel1; 1University of California, San Diego, United States; 2The University of Texas at Dallas, United States

Ferroelectric (FE) hafnium/zirconium oxide (HZO) thin films have shown many advantages in next-generation device applications such as negative capacitance gate oxides and FE random access memory (FERAM) or multi-state memory. In addition, spontaneous formation of atomically sharp phase and domain boundaries is prevalently observed in the HZO thin films due to structural similarity of the various polymorphs based on fluorite parent structure. Here, density functional theory (DFT) is employed to show that the FE o-phase could be stabilized by significant in-plane tension formed during the thermal annealing process, in which the as-deposited amorphous phase is crystallized into the more dense crystalline phases. The in-plane tension being the stabilization mechanism is in agreement with experiments but in contrast to some of the previous calculations which argued that in-plane compression is responsible for the stabilization of the o-phase. Furthermore, DFT is employed to model stacks of FE and paraelectric (PE) phases to provide an atomic model of negative capacitance. It is shown that the unfavorable interaction of the PE phase with the field from vertically polarized FE phase induce polarization rotation, phase change and domain wall formation consistent with negative capacitance. Furthermore, the rotation of polarization initiates at the PE/FE interface and propagates into the FE layer, while mixed FE phases with the vertical/rotated polarizations show shallow energy minima, and are further stabilized by applying an external electric field. Validation of negative capacitance in atomic models will further enable atomic models of stacks with high k value and their switching behavior in response of external electric fields, mechanical strain, and defects.

This work was supported by DARPA SRC JUMP ASCENT theme 1 task 59.

5:45 AM *S.EL12.02.04
Reconfiguring Functional Oxides in Atomically Controlled Thin Films Gertjan Koster; University of Twente, Netherlands

Consumer electronics and electronics is driven by low cost, reliable performance and low energy consumption. To truly enable innovations, new solutions have to be found in new materials. Oxides show multiple functional properties and therefor offer multiple solutions in one material. Moreover, the reconfiguring functionality of materials by using epitaxy or self-assembly etc. (e.g., non-magnetic to ferromagnetic, dielectric to piezoelectric properties or insulating to metallic) has been demonstrated. The success of reconfiguring many of these oxides critically depends on the atomically controlled thin film deposition techniques such as pulsed laser deposition but till now typically laboratory scale single crystalline wafers have been used. Important progress has been made in terms of plasma scanning techniques on large wafers and compatibility with technical materials (Si). However, fundamental knowledge of a scanning plasma and the composition of the thin films, which is essential in obtaining reliable reconfigured functional properties, is lacking.

In this presentation I will discuss examples of manipulation of magnetic properties in thin films and the possibility of reconfigurable functionality, also on technical wafers such as Si. We showed how to manipulate magnetic and electronic anisotropic properties in manganite heterostructures by engineering the oxygen network on the unit-cell level. In addition, the critical temperature of the metal-to-insulator transition as well as the magnetic transition temperature in RENiO$_3$ can be tuned anisotropic properties in manganite heterostructures by engineering the oxygen network on the unit-cell level. In addition, the reconfigurable functionality, also on technical wafers such as Si. We showed how to manipulate magnetic and electronic

6:15 AM *S.EL12.02.05
Emergent Phenomena at Oxide Interfaces with Strong Spin-Orbit Coupling Jobu Matsuno; Osaka University, Japan

We suggest that 5$d$ electron systems are promising class of spintronic materials because of its strong spin-orbit coupling (SOC). A strong SOC inherent to 5$d$ Ir oxides recently emerged as a new paradigm for oxide electronics. For example, we investigated novel physics of spin-orbital Mott insulators [1] and possible topological insulators [2] by tuning the electronic phases through superlattice technique. We also demonstrated a large spin Hall effect of IrO$_2$, one of the simplest 5$d$ oxides, indicating that Ir oxides are promising class of spintronic materials [3]. In this talk, we focus on yet another topic on spintronics – magnetic skyrmion as a topological spin texture. We have studied
transport properties of bilayers consisting of $m$ unit cells of ferromagnetic SrRuO$_3$ and 2 unit cells of SrIrO$_3$. We observed an anomaly in the Hall resistivity in addition to anomalous Hall effect (AHE); this is attributed to topological Hall effect (THE) [4]. The results suggest that magnetic skyrmions of 10–20 nm are generated by Dzyaloshinskii-Moriya interaction, which might be caused by both broken inversion symmetry at the interface and strong SOC of SrIrO$_3$. Even more surprising is that we can control both AHE and THE by electric field in the SrRuO$_3$-SrIrO$_3$ bilayers [5]. We observed the clear electric-field dependence only when SrIrO$_3$ is inserted between SrRuO$_3$ and a gate dielectric. The results established that strong SOC of nonmagnetic materials such as SrIrO$_3$ is essential in electrical tuning of these Hall effects.

We are also searching for spin-current transport properties at the interfaces consisting of magnetic oxides and nonmagnetic Ir oxides. We will report on the latest results on them. Through these studies on oxide interfaces containing Ir oxides, we may have a chance to approach a triple point for topology, correlation, and spin-orbit coupling.

References:

5:00 AM *S.EL12.03.02

Challenges and Opportunities with X-Raying Novel Spin Textures Peter Fischer; Lawrence Berkeley National Lab, United States

Spin textures are the foundation of properties and behavior of magnetic materials and drive the functionality of magnetic devices. Topology and frustration that impact spin textures have recently attracted significant scientific interest and led to intense research e.g. in magnetic skyrmions (Sk) and artificial spin ice systems (ASI) addressing a broad spectrum of challenging scientific and technological questions, including stability, dynamics, nucleation, and transport. So far, Sk and ASI have been treated foremost as two-dimensional spin textures, however, recent investigations have opened the door to a conceptually next leap, which are three-dimensional nanoscale size magnetic spin textures (3D-spin-textures) e.g., chiral bobbers, magnetic hopfions, and skyrmion tubes.

Advanced characterization tools that provide magnetic sensitivity to spin textures at high spatial resolution, ultimately at buried interfaces and in all three dimensions [1], and at high temporal resolution to capture the spin dynamics across scales, are therefore of large scientific interest. Magnetic soft X-ray spectro-microscopies [2] provide unique characterization opportunities to study the statics and dynamics of spin textures in magnetic materials combining X-ray magnetic circular dichroism (X-MCD) as element specific, quantifiable magnetic contrast mechanism with spatial and temporal resolutions down to fundamental magnetic length, time, and energy scales.

Current developments of x-ray sources aim to increase dramatically the coherence of x-rays opening the path to new techniques, such as ptychography [3] or x-ray photo-correlation spectroscopy (XPCS) [4] that allow unprecedented studies of nanoscale heterogeneity, complexity, and fluctuations.

I will review recent achievements and future opportunities with magnetic x-ray spectro-microscopies. Examples will include static properties and dynamic behavior of various magnetic skyrmion [5,6] textures with potential application to novel magnetic logic and storage devices, as well as results from an XPCS study at LCLS with a novel 2-pulse scheme that allowed to discover an unexpected and drastic change of the correlation times in nanoscale spin fluctuations near phase boundaries, i.e., in the skyrmion phase, and near the boundary with the stripe phase of a multilayered Fe/Gd system [4].

Finally, I will present a study on ferromagnetic liquid droplets, which could establish a complete paradigm shift in magnetic materials, that combine characteristics of liquid, such as reconfigurability and short range spatial and temporal correlations with ferromagnetism, which so far has been confined to condensed matter [7].

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division Contract No. DE-AC02-05-CH1123 in the Non-Equilibrium Magnetic Materials Program
5:30 AM *S.EL12.03.03
Neuromorphic Computing with Spintronic Oscillators Alice Mizrahi1,2,3, Tifenn Hirtzlin1, Matthew Daniels2,3, Nicolas Locatelli1, Akio Fukushima4, Hit Kubota4, Shinshi Yuasa4, M D. Stiles5, Julie Grollier1 and Damien Auerlloz1; 1Université Paris-Saclay, France; 2University of Maryland, United States; 3National Institute of Standards and Technology, United States; 4National Institute of Advanced Industrial Science and Technology (AIST), Japan

Artificial neural networks are performing tasks, such as image recognition and natural language processing, that offer great promises for artificial intelligence. However, these algorithms run on traditional computers and consume orders of magnitude more energy more than the brain does at the same task. One promising path to reduce the energy consumption is to build dedicated hardware to perform artificial intelligence. Spintronics devices are particularly interesting because they allow for complex functionality with low energy consumption and small size.

In particular, I will focus on the superparamagnetic regime of magnetic tunnel junctions. Here, they behave as stochastic oscillators capable of harnessing the energy of thermal noise. While stochasticity is traditionally unwanted for computing, I will show how it can be leveraged to reduce energy consumption. I will draw an analogy between stochastic magnetic tunnel junctions and stochastic spiking neurons, which emit randomly spaced voltage spikes. I will show how these devices can be assembled into an artificial neural network an perform computing. Such a system would be competitive with conventional electronics implementations, both in terms of area on chip and energy consumption.

These results open the path to low energy hardware implementation of neural networks, making it possible to perform cognitive tasks on chip.

6:00 AM S.EL12.03.05
Field-Free Spin-Orbit Torque Perpendicular Magnetization Reversal Enabled by Interfacial Dzyaloshinskii-Moriya Interaction Minyi Dai and Jiamian Hu; University of Wisconsin-Madison, United States

Perpendicular magnetization reversal through spin orbit torque (SOT) is of great recent interest due to its potential application in spin-orbit torque magnetoresistive random access memory (SOT-MRAM). Typically, a simultaneous application of in-plane bias magnetic field is required to break in-plane symmetry, which would cause crosstalk between neighboring memory units and thus impede the development of high-density SOT-MRAM. Here, we propose a new approach to realize field-free SOT-mediated perpendicular magnetization reversal using micromagnetic simulations implemented in both our in-house package and MuMax3. Using realistic materials parameters from documented experimental measurements, our simulations suggest that such reversal can occur in a MgO/CoFeB/Pt multilayer stack when the disk size of CoFeB, the strength of Dyzaloshinskii-Moriya interaction at the CoFeB/Pt interface, and the magnitude of the driving in-plane current are all controlled within intermediate range. The kinetic mechanism of such new approach is presented and also understood by analogy to classical nucleation and growth theory.

6:15 AM S.EL12.03.07
Fabrication and Characterization of Layer-by-Layer Assembly of Spin Crossover Thin Films Kayleigh A. McElveen1, Guanhua Hao1, Prescott Evans1, Peter Dowben1, Andrew Yost2,1 and Rebecca Lai1; 1University of Nebraska-Lincoln, United States; 2Oklahoma State University, United States
Iron (II) complexes have a ligand field energy and exchange-interaction energy that are within a few eV; therefore, the spin crossover (SCO) from low spin (LS) to high spin (HS) can be controlled using an external stimuli—temperature, pressure, light, etc. Similar to other bistable materials, iron (II) SCO complexes could find applications in technologies such as quantum logic operators and memory storage devices. However, most research on SCO complexes is performed on powder samples, which are incompatible with the industry’s needs for thin films with thickness control. In this study, we aim at developing a layer-by-layer assembly method to fabricate iron (II) SCO thin films. This thin film fabrication method has several advantages, including the precise control of film thickness by simply adjusting the number of layers. Prior to thin film fabrication, \([\text{Fe(pyrazine)}\{\text{M(CN)}_4\}]\) (\(M = \text{Pt or Pd}\)) bulk powders were synthesized so that their SCO properties could be used as a reference for their thin film counterparts. The SCO behavior of the Pt and Pd powders was confirmed with a vibrating sample magnetometer (VSM), and both powders displayed abrupt, room temperature hysteresis with widths of 45 K centered around 300 K. The abrupt spin transition is indicative of strong cooperativity between the metal centers. Rietveld analysis of x-ray diffraction (XRD) data further confirmed that the Pt and Pd powders were crystalline, showing nearly identical diffraction patterns in space group P4/m. Next, we employed the layer-by-layer solution deposition method to fabricate \([\text{Fe(pyrazine)}\{\text{M(CN)}_4\}]\) (\(M = \text{Pt or Pd}\)) thin films on gold substrates. The resultant Pt and Pd thin films were analyzed using x-ray absorption spectroscopy (XAS) to demonstrate the differences in spin state ratios during heating and cooling cycles. A 25-layer Pd thin film was determined to have a thickness of 0.760 ± 0.04 μm using a scanning electron microscope (SEM). The SCO behavior of the Pd thin film was analyzed using a superconducting quantum interference device (SQUID), and the results suggest the presence of an incomplete spin transition with some evidence of hysteresis. Based on the results from comparing the SCO behavior of thin films with varying number of layers (i.e., film thickness), the SCO behavior appears to improve with film thickness. This alludes to the fact that by increasing the number of layers to beyond 25, this method can potentially be used to fabricate thin films with optimal SCO behavior. When compared to the bulk powder results, the hysteresis loop of the thin film was not abrupt and the spin transition was incomplete, but the general shape was similar and both loops were centered around room temperature. Although further optimization is required to improve the quality of the films, our initial results have demonstrated the use of this simple solution-phase deposition method in the fabrication of SCO thin films.

SESSION S.EL12.04: Multiferroic and Magnetoelectric Materials

5:00 AM *S.EL12.04.02
Magnetoelectric Coupling by Piezoelectric Tensor Design Mark S. Rzchowski¹, J. Irwin¹, S. Lindemann¹, W. Maeng¹, J.J. Wang², V. Vaithyanathan¹, Jianhui Hu¹, Long-Qing Chen², D.G. Schlom³ and Chang-Beom Eom¹; ¹University of Wisconsin-Madison, United States; ²The Pennsylvania State University, United States; ³Cornell University, United States

Strain-coupled magnetoelectric (ME) phenomena in piezoelectric / ferromagnetic thin-film bilayers are a promising paradigm for sensors and information storage devices, where strain manipulates the magnetization of the ferromagnetic film. In-plane magnetization rotation with an electric field across the film thickness has been challenging due to the large reduction of in-plane piezoelectric strain by substrate clamping, and in two-terminal devices, the requirement of anisotropic in-plane strain. Here we show that these limitations can be overcome by designing the piezoelectric strain tensor using the boundary interaction between biased and unbiased piezoelectric. We fabricated 500 nm thick, (001) oriented \([\text{Pb(Mg1/3Nb2/3)}_3\text{O}_3][\text{PbTiO}_3]_0.7\) unclamped piezoelectric membranes with ferromagnetic Ni overlayers. Guided by analytical and numerical continuum elastic calculations, we designed and fabricated two-terminal devices exhibiting electric field-driven magnetization rotation. We develop a method that can apply designed strain patterns to many other materials systems to control properties such as superconductivity, band topology, conductivity, and optical response. We also discuss how these effects depend on the crystallographic orientation.

5:30 AM *S.EL12.04.03
Control of Ferromagnetic Skyrmions Using Ferroelectric Polarization Tae Won Noh; Seoul National University, Korea (the Republic of)

Ferromagnetic skyrmion is a topologically protected whirling spin texture in nanoscale. Due to its small size, topologically-
protected stability, and solitonic nature together, it holds great promise for future spintronics applications. To translate these compelling features into practical spintronic devices, we should face a key challenge in achieving effective control of skyrmion properties, such as size, density, and thermodynamic stability. Recently, we reported the discovery of ferroelectrically tunable skyrmions in ultrathin BaTiO3/SrRuO3 bilayer heterostructures. The ferroelectric proximity effect occurring at the BaTiO3/SrRuO3 heterointerface can trigger a sizable Dzyaloshinskii-Moriya interaction. Thus the interaction between two ferroic materials can stabilize robust skyrmions with diameters of several tens of nanometers.[1] Moreover, by manipulating the ferroelectric polarization direction of the BaTiO3 layer, we could achieve local, switchable and nonvolatile control of both skyrmion density and thermodynamic stability. Such a ferroelectrically tunable skyrmion system can work as a new paradigm to simultaneously enhance the integratability and addressability of skyrmion-based functional devices.


6:00 AM *S.EL12.04.04
Enhanced Magnetostriction in FeGa Epitaxial Thin Films John T. Heron1, Peter Meisenheimer1, Rachel Steinhardti, Shihao Zhuang2, Suk Hyun Sung3, Mark Nowakowski2, Steve Novakov1, Bhagwati Prasad4, Chris Zollner2, Zhe Wang2, Natalie Dawley2, Allen Hunter1, Sasikanth Manipatruni3, Dmitri Nikonov5, Ian Young3, Long Qing Chen6, Jeffrey Bokor4, Ramamooorthy Ramesh4, Robert Hovden1, Jiamian Hu3 and D.G. Schlom2; 1University of Michigan, United States; 2Cornell University, United States; 3University of Wisconsin–Madison, United States; 4University of California, Berkeley, United States; 5Intel Corporation, United States; 6The Pennsylvania State University, United States

Composite multiferroics, composed of a magnetostrictive ferromagnet and a piezoelectric ferroelectric, hold promise for magnetic field sensors and energy efficient beyond-CMOS logic by harnessing magnetoelectric transduction. Enhancing device performance requires highly magnetostrictive materials, however, relatively little attention has been given to engineering magnetostriction in thin films. One promising magnetostrictor system are the Fe_{1-x}Ga_x alloys yet in bulk, the magnetostriction coefficient of Fe_{1-x}Ga_x alloys versus gallium composition peaks near ~18% Ga due to a phase change from the disordered A2 phase to an ordered BCC phase (D0_2). Here we discuss a means to boost (by 200-300% relative to bulk) the magnetostriction of Fe_{1-x}Ga_x thin film alloys by extending the phase stability of the A2 phase to higher Ga compositions. Transport-based magnetoelectric characterization of a Fe_{1-x}Ga_x - [Pb(Mg_{0.13}Nb_{0.23})O_3]_{0.7}-[PbTiO_3]_{0.3} (PMN-PT) composite multiferroic heterostructure shows are reversible 90 deg electrical switch of magnetic anisotropy and a room temperature converse magnetoelectric coefficient of $5.5 \times 10^{-6}$ s m$^{-1}$.

6:30 AM *S.EL12.04.06
Deterministic and Robust Magnetic Rotation with an Electric Field in a Concave Triangular Nanomagnet Ren-Ci Peng1, Long-Qing Chen1, Ziyao Zhou1 and Ming Liu1; 1Xi’an Jiaotong University, China; 2The Pennsylvania State University, United States

Deterministic magnetic switching driven by electric fields rather than power-dissipating currents on the nanoscale is fundamentally challenging yet promising for applications to energy-efficient and high-density spintronic devices. Here, we demonstrate an electric-field-controlled deterministic, robust and reversible 120° rotation of ‘Y’-like magnetic state in a patterned nanoscale multiferroic heterostructure consisting of a concave triangular nanomagnet on the Pb(Mg{0.13}Nb_{0.23})O_3-PbTiO_3 film. The nanomagnet is juxtaposed with an overlying antiferromagnetic layer to acquire an exchange bias from their interface. Using phase-field simulations, we find that the rotation of ‘Y’-like magnetic state is controlled by a synergistic effect of strain-mediated electric-field-induced uniaxial magnetoelastic anisotropy, magnetic in-plane shape anisotropy of the concave-triangle-shaped nanomagnet, and an interfacial exchange-bias field. It is also shown that deterministic magnetic state switching can be accomplished by a pulsed strain, the duration of which can span from a few seconds or longer down to a few nanoseconds, providing great design flexibility. We also discussed the dynamics of electric-field-driven switching of ‘Y’-like magnetic state as well as the influence of lateral size, thickness and shape variation (i.e. concave radius) of the nanomagnet on the critical strain for the switching. These results offer a new and technologically viable route to designing nanomagnet-based nonvolatile spin memories with high density and low power.

6:45 AM *S.EL12.04.07
Progress in Magnetoelectric Composites and Device Applications Shuxiang Dong, Zhaoqiang Chu, Mohammad Javad Pourhosseini Asl and Zhonghui Yu; Peking University, China

Incorporating magnetomagnetic, ferroelectric and ferroelastic orders inherently in a single-phase multiferroic material or manipulating one ferroic order with the others via interfacial coupling effects in multiferroic heterostructures has driven significant research activities aiming at the realization of their technological potential in the field of sensors, RF electronics,
induced by external magnetic field (H) or a control of magnetization (M) via applied electric field (E). This report first introduces our recent progress in laminated ME composites consisting of a [011]-oriented Pb(Mg,Nb)O3-Pb(Ti,Zr)O3 (PMN-PZT) single-crystal fiber laminated with laser-treated amorphous FeBSi alloy (Metglas). High ME coupling coefficient around 10 kV/cm*Oe has been achieved. We will then review recent advances in multi-layered ME composites as well as their device applications including magnetic field/current sensors, dual-stimulus energy harvesters, ME memories, ME gyrators and tunable electronics. Some perspectives in terms of the future of magnetoelectric composites and devices will also be provided.

7:15 AM S.EL12.04.09
Synthesis of Multiferroic Nanoparticles and Their 3D Printed Silicon Elastomer Polymer Composites Felicia Horne1, Soodabeh Azadehranjbar2, Zahra Ahmadi2, Archit Dhingra2, Peter Dowben2, Jeffrey Shield2, Naga S. Korivi1 and Vijaya K. Rangari1; 1Tuskegee University, United States; 2University of Nebraska, United States

There is great interest in composites of polymers and multiferroic nanoparticles for advanced electronic applications. There has been very little work done in the rapid prototyping of such composites. We report the fabrication of composites of silicone elastomer, and barium titanate/iron oxide nanoparticles. Multiferroic nanoparticles of Barium titanate/iron oxide were synthesized using sonochemical reaction of iron acetate, urea, barium titanate nanoparticles in a solvent. This results in iron oxide nanoparticles formed on and near the barium titanate nanoparticles. A subsequent sintering process improves the crystalline nature of the iron oxide. The barium titanate/iron oxide nanoparticles are combined with a moldable silicone elastomer (Dowsil MS-4007) at 5% weight ratio and loaded onto an extrusion head of a commercial 3D printer. Printing on a base maintained at 100°C results in the formation of solid nanocomposite layers. Observations will be presented from characterization of these layers by electrical and magnetic studies, microscopy, mechanical and thermal studies.

7:25 AM *S.EL12.04.11
Observation, Manipulation and Understanding of Coupled Multiferroic Domains in Single-Phase Magnetoelectrics Tsuyoshi Kimura; The University of Tokyo, Japan

Symmetry breaking ascribed to the evolution of an order parameter is one of the most important concepts in ferroic materials such as ferromagnets and ferroelectrics, and bears “domain” structures. The domain switching by an external field is the key principle to exploit them for practical applications. In multiferroics, materials possessing multiple ferroic order parameters, the respective order parameters form domains and multiple types of domain states coexist. It is well-accepted that couplings between the multiple order parameters and domain states are essential for macroscopic magnetoelectric phenomena in multiferroics. However, there are few reports that directly compare responses of coexisting domain states to external fields and macroscopic magnetoelectric properties. In this presentation, we show selective observations of multiple magnetic order parameters and domain structures in some single-phase magnetoelectrics. This work has been done in collaboration with H. Ueda, R. Misawa, T. Katsuyoshi, J. K. H. Fischer, K. Kimura, Y. Tanaka, Y. Wakabayashi, T. Honda, J. S. White, M. Kenzelmann, A. B. Harris, N. Leo, and M. Fiebig.

7:55 AM S.EL12.04.12
Electrical and Magnetic Properties of Thin Single Crystal Cr₂O₃ Films Nguyen M. Vu1, Xiangpeng Luo1, Steve Novakov1, Wencan Jin2, Johanna Nordlander3, Peter Meisenheimer1, Morgan Trassin3, Liuyan Zhao1 and John T. Heron1; 1University of Michigan, United States; 2Auburn University, United States; 3ETH Zürich, Switzerland

Magnetoelectric materials have been of great interest due to their potential for low-power spintronic devices via the electric field switching of magnetization. Antiferromagnet Cr₂O₃ is one of a very few room temperature magnetoelectrics and possesses unique properties such as uncompensated surface spins and perpendicular magnetic anisotropy. [1] Since the first demonstration of the electric field control of exchange bias in bulk single crystal Cr₂O₃ heterostructures [2], intense effort has focused the demonstration of magnetoelectric switching using Cr₂O₃ thin films at room temperature. [3,4] The existence of twin domains in thin films grown on metallic electrodes, however, leads to high leakage current and dielectric breakdown fields that can only be circumvented by growing rather thick films (250-500 nm). [4,5] By using an isostructural epitaxial oxide electrode, V₂O₅, recent studies have shown the reduction and even possible elimination of twin domains in Cr₂O₃ films. [3] Dielectric and magnetoelectric switching studies of 200 nm thick films show bulk like performance, however, for next generation logic and memory the films must be scaled down. [6]

Here we present an investigation of the electrical endurance and magnetic properties of very thin (30-60 nm) single crystal Cr₂O₃ films grown by pulsed laser deposition onto V₂O₅ buffered (0001) oriented Al₂O₃ substrates. Our results show that 60 nm single crystal thin film has bulk-like resistivity (10^{12} cm) and significantly improved breakdown voltage (150-300)
MV/m). Using magnetometry, we investigate exchange bias of thin film Cr2O3/ferromagnet heterostructure. The blocking temperature is found to be at 285 K which is higher compared to twinned films with similar or greater thickness in literature. Further, Second Harmonic Generation confirms bulk magnetoelectric order of our single crystal thin film at room temperature. These results indicate the importance of crystallinity to realize bulk like properties in very thin films at room temperature.


Active Control of Spin Waves in Multiferroic Heterostructures Sebastiaan van Dijken; Aalto University, Finland

Active manipulation of spin waves is essential for the development of magnon-based technologies. One route towards this goal exploits reprogrammable magnonic crystals. In such structures, a varying spatial modulation of magnetic properties using, for instance, electric currents [1] or optical pulses [2] controls the transmission of spin waves. Besides these dynamic approaches, field-induced toggling between ferromagnetic and antiferromagnetic states in magnetic stripe arrays has been shown to modify spin wave transport in a non-volatile way [3].

Multiferroic heterostructures comprising coupled ferromagnetic and ferroelectric layers offer an interesting alternative as programmable hybrids for magnonics. Attractive properties of multiferroic heterostructures include the imprinting of magnetic domain patterns, the creation of abrupt anisotropy boundaries, strong pinning of magnetic domain walls, and electric field control of magnetic anisotropy, magnetic switching, and magnetic domain wall motion [4-6].

Here, we demonstrate that multiferroic heterostructures provide a versatile platform for the emission of short-wavelength spin waves [7], the confinement of spin wave modes in structurally uniform films [8], and active manipulation of spin wave transmission [9]. The multiferroic heterostructures consist of a ferroelectric BaTiO3 substrate and a strain-coupled ferromagnetic film with a thickness of 20 – 50 nm. At room temperature, this material system comprises fully correlated stripe domains in the ferroelectric and ferromagnetic subsystems. Utilizing strong pinning of ferromagnetic domain walls onto ferroelectric boundaries, we demonstrate active manipulation of spin wave transmission from 0% to 100% by non-volatile reprogramming of the domain-wall spin structure in a magnetic field [9]. In addition to magnetic field control, we also present recent results on active manipulation of spin wave transmission using electric fields. This sought-after effect originates from local strain-induced changes of the magnetic anisotropy. We demonstrate that the transmission of spin waves can be fully turned on and off in certain frequency bands by the application of voltage pulses across the BaTiO3 substrate. The multiferroic heterostructures allow also for continuous tuning of the spin wave phase and amplitude, offering prospects for voltage-controlled magnonic logic.

**S.EL12.05.01**

**Multi-level Tactile Ferroelectric Field Effect Transistor Sensing Memory**  
Kyuho Lee and Cheolmin Park; Yonsei University, Korea (the Republic of)

A tactile memory, which can sense and memorize the external stimuli, has been reported up to date with great potential in emerging wearable electronics. To realize bi-functional systems for sensing and memorizing, two device platforms integrated with tactile sensor and memory have drawbacks from physically bulky systems as well as increase of circuit resistance from wire connection, giving rise to low sensing sensitivity. In particular, a binary memory with bi-level state of ON/OFF has limitation in storing multi-level sensing information that requires multiple memory array. A multi-level memory-based single device platform without the integration is, therefore, on demand.

Herein, we demonstrate a non-volatile multi-level tactile memory based on a single ferroelectric-gate field-effect transistor (Fe-FET) allowing for intelligent electronic skins (e-skins), which can sense, memorize, and then retrieve the tactile information. Pressure-sensitive top-gate shape formation can precisely sense and memorize the external pressure stimuli by making an underlying ferroelectric film polarized according to the size of the contact area between top-gate and ferroelectric film, giving rise to variation of gate voltage supply. Our tactile 1-transistor memory exhibits high sensitivity of >90 kPa⁻¹ at low pressure stimuli of <1.5 kPa, and shows good reliability in multiple programming and erasing up to 50 cycles and long-term stability even with bending radius of 6 mm. Tactile memory arrays showing precise spatial positioning of external stimuli with non-volatile multi-level sensing, memorizing, and then retrieving after one week have broad applications suitable for wearable human-interactive electronics.

**S.EL12.05.05**

**Effect of Sintering Temperature/Particle Size on Structural, Magnetic and Transport Properties of Polycrystalline Nd₀.₅Ca₀.₅MnO₃ Manganites**  
Dharmendra Raghav¹, Harikrishna Singh² and Ghanshyam D. Varma¹; ¹Indian Institute of Technology Roorkee, India; ²C.S.I.R. N.P.L., India

Nanosized materials, such as nanoparticles, nanowires, nanotubes, and nanocomposites are currently the focus of intense investigations due both to the physics they involve and to their potential for revolutionary technological applications. The applications are expected to be in a wide variety of diverse areas, such as logic circuits, magneto-electronic devices, magnetic data storage, medicine, and biotechnology. The phenomena and properties behind these applications are unique to nanodimensions, such as quantum confinement effects and enhanced surface to volume ratio. So, we have investigated the effect of particle size/sintering temperature on structural, magnetic and transport properties in Nd₀.₅Ca₀.₅MnO₃ system. Different size materials have been synthesized using Sol-gel method and sintered at 900 , 1100 and 1300 degree Centigrade to get the samples of different particle sizes. Phase pureness of the samples has been confirmed by Rietveld refinement of the powder X-Ray diffraction (XRD) data, which authenticates orthorhombic structure with Pnma space group. All three lattice constants (a, b and c), bond lengths and bond angles decrease with increasing particle size. The magnetization measurements (H@500 Oe) as a function of temperature exhibit paramagnetic (PM) to ferromagnetic (FM) transition and also brings out that (i) the divergence between the zero field cooled (ZFC) and field cooled cooling (FCC) magnetization decreases with increasing particle size, (ii) all samples show charge ordering at 250 K, (iii) the sharp drop of ZFC magnetization for all samples. At low temperatures a glassy behaviour is visible at higher particle size. The isothermal magnetization loops confirm the increase in the FM component at higher particle size at low temperature (20 K). The temperature dependent resistivity of all samples have been measured without magnetic field and resistivity measurements show no insulator to metal transition at lower sintering temperature but at higher sintering temperature the metal to insulator transition has been found. The data of resistivity have been fitted by using variable range hopping model (VRH). Characteristic temperature (Tᵥ), localization length (1/α) and average hopping distance (R) have been calculated by using this model. X-ray photoemission spectra of Mn2p and Mn2s core-level confirm dual valence state of Mn (Mn³⁺ and Mn⁴⁺), which is responsible for the magnetic behaviour of NCMO system. The correlation between the transport and observed magnetic properties of sintered NCMO samples will be described and discussed in paper.

**S.EL12.05.14**

**Domain Size Effects on Piezoelectricity in Lead-Free Ferroelectric Single Crystals**  
Bo Wang¹, J.J. Wang¹, Fei Li²,¹ and Long-Qing Chen¹; ¹Pennsylvania State University, University Park, United States; ²Xi’an Jiaotong University, China

Domain size is known to play a critical role in electromechanical properties of domain-engineered ferroelectric single
For lead-based relaxor-PbTiO$_3$ crystals, nanosized polar regions are believed to be the origin of giant piezoelectricity. For lead-free systems such as [111]-poled tetragonal ferroelectric BaTiO$_3$ crystals, enhanced piezoelectricity has been reported by reducing the domain size from hundreds to several microns. These examples lead to a long-standing belief that the smaller the domain size, the higher the piezoelectricity. Our recent study reveals an alternative route to improve piezoelectricity by increasing the size of domains through AC poling in relaxor-PbTiO$_3$. In this poster, we will discuss the general domain size effect on piezoelectricity in prototypical non-lead perovskites in tetragonal, orthorhombic, and rhombohedral ferroelectric phases, such as BaTiO$_3$, K$_{0.5}$Na$_{0.5}$NbO$_3$, and BiFeO$_3$, by examining the effective piezoelectric coefficients of engineered domain structures using a combination of thermodynamic analysis and phase-field simulations. We find that the domain size effect on piezoelectricity depends on the symmetry of the ferroelectric phase. The size effect becomes significant when the domain is reduced to a critical size (~ sub-100 nm) which depends on the proximity to a ferroelectric-ferroelectric phase transition and on the width of domain walls. Moreover, the domain size effect has a strong anisotropy, giving rise to opposite trends for different piezoelectric tensor components as well as varying along different probing directions. By separating the contributions from domains and domain walls, we reveal that the size effect is majorly originated from the modification of thermodynamic states of domains due to the presence of domain walls. We also reveal that the domain size effect on piezoelectricity can be understood as a competition between the domain size effects on the dielectric permittivity and on the polarization rotation. The former is related to the flattening of free energy landscapes, while the latter is due to the built-in fields between domain walls. Besides, we predict a convenient way of controlling the domain size by poling via an alternating electric field. This work offers a thermodynamic-based understanding of the domain size effect and brings new insights into the fundamental knowledge of the processing-microstructure-property relationship in piezoelectric single crystals.

**SYMPOSIUM S.EL13**

Processing, Microstructure and Multifunctioning of Organic Semiconductors  
November 21 - November 30, 2020

**Symposium Organizers**  
Hanying Li, Zhejiang University  
Jianguo Mei, Purdue University  
Joon Hak Oh, Seoul National University  
Erin Ratcliff, University of Arizona

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**SESSION S.EL13.08: Live Keynote: Processing, Microstructure and Multifunctioning of Organic Semiconductors**  
Session Chairs: Jianguo Mei and Erin Ratcliff  
Saturday Morning, November 28, 2020  
S.EL13

**10:15 AM *S.EL13.03.04**  
**Bio-Inspired Organic Artificial Nerves for Peripheral Nerve Emulation** Tae-Woo Lee$^1$, Zhenan Bao$^2$, Yeongjun Lee$^1$, Jin Young Oh$^2$, Yeongin Kim$^2$, Alex Chortos$^2$, Wentao Xu$^1$ and Dae-Gyo Seo$^1$; $^1$Seoul National University, Korea (the Republic of); $^2$Stanford University, United States

Biological nerves have evolved toward functionalities to efficiently process complex information in real-time. Unlike biological nerve system, von Neumann based computing system performs in centralized and sequential form which has
difficulty in event driven and parallel operation. In this regard, there has been many efforts to adopt the superior characteristic of biological nervous system and the concept of neuromorphic electronics have emerged. As the synaptic behavior can be implemented through single artificial synaptic device, it can emulate the functions of biological sensory and motor neurons when combined with sensors and actuators. Making the artificial nervous system desirable for soft robotics and neuroprosthetics have been widely investigated.

Here, artificial nervous systems were developed by using organic electronics to emulating peripheral nervous system. Pressure sensors (artificial mechanoreceptors), organic ring oscillators (artificial nerve fibers), and synaptic transistors were integrated to emulate the biological sensory nerve system. By forming hybrid reflex arc which connects artificial sensory nerve and biological motor nerves the applicability for neural prostheses was verified and the biological motor nerves were actuated depending on external pressure information. In addition, by integrating a stretchable artificial synapse, and a polymer actuator (an artificial muscle), stretchable artificial sensorimotor nervous system was developed. The optogenetics was emulated by contracting the artificial muscle with light stimulation. In parallel, the system distinguished the alphabet Morse code which showed the potential as an optical wireless communication method for human-machine interface.

Furthermore, by integrating a triboelectric sensor for an artificial auditory system, artificial auditory system was emulated. We modulated morphology of organic semiconductors of the artificial synapses to implement the specific recover time of biological synapse facilitation. Our organic artificial nerve systems suggest promising strategy for bioinspired electronics, soft robotics, and neuroprosthetics.

10:30 AM *S.EL13.01.09
The Mixed Conductivity in Highly-Ordered Polypyrrole Hybrid Materials Myung-Han Yoon, Ji Hwan Kim, Zubair Ahmad and Jaesuk Lee; Gwangju Institute of Science and Technology, Korea (the Republic of)

In this research, we report the effect of crystallinity on the mixed conductivity of highly-ordered polypyrrole film. Polypyrrol-4,4'-biphenylidisulfonic acid (poly(Py:BPDSA:Py)) hybrid was synthesized by oxidative polymerization after connecting two pyrrole monomers with various stoichiometric ratios of BPDSA in the aqueous solution. The structural and electrical/ electrochemical analysis revealed that the increase in BPDSA content enlarges the crystallite size from 18.9 to 52.1 nm, the ratio of crystalline to amorphous domains by 6 times, the electrical conductivity from 174 to 406 S/cm, and the volumetric capacitance from 85 to 672 C/cm³, while the doping concentration extracted from Hall measurement and electrochemical analysis remains unchanged. On the other hand, the resultant poly(Py:BPDSA:Py)-based organic electrochemical transistors (OECTs) showed the maximum value of transconductance (0.5 mS) at the intermediate composition of BPDSA, which can be attributed to the retardation of ion movement in highly crystalline polymeric film. The repeated OECT operation revealed the stable current on-off ratio over 2 x10⁵ without the significant loss in transconductance. All these results suggest that the mixed conductivity of poly(Py:BPDSA:Py) can be strategically modulated by engineering the crystallite size.

10:45 AM *S.EL13.05.04
Nanocrystalline Organic Semiconductor Photocatalysts—A Dominance of Oxygen Reduction Reactions Eric D. Glowacki¹,²; ¹Linkoping University, Sweden; ²Warsaw University of Technology, Poland

Semiconductor-based catalysts can convert solar energy into chemical fuels such as hydrogen, hydrogen peroxide, or hydrocarbons produced via carbon dioxide reduction. Long overlooked due to stability concerns, some organic semiconductors have recently emerged as promising electrocatalysts and photocatalysts for operation in aqueous environments. Our attention has focused on nanocrystalline pigment-type organic semiconductors, which stand out due to stability and performance. Generally, we have found a high selectivity of organic semiconductors for oxygen reduction reactions, by both one-electron and two-electron pathways. The products of these reactions are superoxide or hydrogen peroxide. We find this occurs on numerous organic semiconductors and conducting polymers in a pH range from 1 to 12. The large pH stability window is remarkable when compared with inorganic counterparts. We have found that while photogenerated electrons reduce oxygen, the fate of the holes represents a complex picture. When the nanocrystalline semiconductor is used as a photocathode and efficient p-type transport is available, photogenerated holes can easily be extracted to an external circuit. If this is not possible or inefficient, the hole will either oxidize electron-donors in solution or precipitate autoxidation reactions of the semiconductor itself. The factors affecting this photocorrosion effect will be discussed, as well as principles leading to stabilization of the semiconductor catalyst. The possibilities of solar energy conversion into the high-energy molecule H₂O₂ enabling carbon-neutral energy storage in liquid form, in contrast to gaseous H₂, will be covered. Organic semiconductors have potential to become a powerful class of intrinsic catalysts, tunable by molecular design.

11:00 AM *S.EL13.04.04
Patterning Organic and Hybrid Semiconductor Microstructures for Electronics and Optoelectronics Aram Amassian; North Carolina State University, United States

The transport properties and device performance of organic semiconductors is determined by the microstructure and morphology of polycrystalline thin films, including grain size, domain orientation and grain boundaries. For device applications, such as field-effect transistors, controlling the domain orientation and grain boundaries is particularly important as this mediates charge transport in the channel of the device. More generally, the opportunity to fabricate single crystal domains to match the device architecture would be a very promising pathway to unlock the intrinsic properties of organic and hybrid semiconductors. This presentation will discuss recent efforts to reduce and even eliminate grain boundaries in solution-processed organic and hybrid semiconductor films, with such applications as high performance field-effect transistors, photodetectors and light emitting devices envisioned. Approaches based on patterning the microstructure of thin films post-deposition or in situ will be discussed, as well as additive manufacturing-based coating and printing methods of delivering materials with single crystal-like properties at designated locations.

11:15 AM *S.EL13.01.11
Gating Semiconducting Polymers with Ionic Conductors Michael L. Chabinyc; University of California, Santa Barbara, United States

Electrical doping of semiconducting polymers requires introduction of counter ions to maintain electroneutrality. These counter ions can modify electronic charge transport by changing the microstructure of the semiconductor and by electrostatic interactions between the charge carriers and their counter ion. We will discuss our recent work using single ion conducting polymers, known as polymeric ionic liquids, as the dielectric in transistors with semiconducting polymers. Polymeric ionic liquids (PILs) have tethered ionic functional groups on their backbone with an untethered counter ion leading to single ion conductivity. By appropriate molecular design of the PIL, the operation of polymer transistors can be switched from an electrical double layer mechanism to electrochemical doping of the bulk. The behavior of transistors with PIL gates reveals the differences in the electrical conductivity at the surface and bulk of semiconducting polymers at high charge carrier concentrations. The role of the infiltration of ions on the electronic density of states of semiconducting polymers can also be determined by measurements of the thermopower of electrochemical transistors. Our results show that electrochemical doping leads to a broadening of the DOS and helps to rationalize recent models for charge transport in semiconducting polymers at high carrier densities.

11:30 AM *S.EL13.03.05
Charge Transport and Thermoelectric Properties of High Mobility Conjugated Polymers Henning Sirringhaus; Cambridge University, United Kingdom

Over recent years several new classes of conjugated polymers have shown promise as materials for polymer field-effect transistors with high field-effect mobilities. Many of the recently discovered high mobility polymers, in particular donor-acceptor copolymers, owe their excellent charge transport properties to a low degree of energetic disorder associated with a well-defined backbone conformation with small variations in torsion angles. In this presentation we will present our current understanding of the transport physics of these materials and focus in particular on the relationship between molecular structure, thin film processing and charge transport and thermoelectric properties of these materials. We will discuss new approaches for the doping of these polymers and for understanding their thermoelectric physics.
polymer precursors for electro-patterning nano-resolution patterns using conducting or current-sending AFM. The method involves the rational approach of preparing organic pi-conjugated polymers capable of crosslinking and also electrochemical activity. The interest is on light-emitting diode (LED) devices and photovoltaic (PV) devices. Application of a bias-voltage from an AFM tip is used for electron nanopatterning but also junction-tunneling allows for signal voltage-current measurement – making them useful for memory devices or sensing. We will also describe the use of colloidal nanosphere lithography in producing arrays of conducting polymers with I-V behavior as probed by conducting SPM methods. These techniques demonstrate the ability to bring materials properties from bulk behavior up to the nanoscale.

5:15 AM *S.EL13.01.04

**Graphene-Templated Growth of Organic Semiconductors for Organic Electronics** Kilwon Cho, Nguyen Ngan Nguyen and Hyo Chan Lee; Pohang University of Science and Technology, Korea (the Republic of)

High-performance organic electronic devices require organic semiconductor (OSC) thin films to possess desired microstructures. An effective approach is the use of graphene as a template for controlling growth behavior of OSC crystals. Unlike on ordinary substrates, the growth modes of OSCs on graphene are not only determined by the graphitic surface structure but also electronic characteristics of graphene. In this talk, I will discuss how OSC molecules assemble on graphene surface under the influence of graphene’s doping effect. Also, I will discuss a result that the OSC films grown on a graphene template under an optimized condition provide favorable vertical and lateral transport pathways for charge carriers and excitons in organic transistor and photovoltaic devices.

5:45 AM S.EL13.01.05

**High Efficiency Actuators from Cellulose Acetate-Polyaniline Based Bilayer** Najathulla Bhagavathi Chalil, Mudrika Khandelwal and Atul Deshpande; Indian Institute of Technology Hyderabad, India

Polyaniline is a well known conducting polymer preferred owing to facile synthesis and various oxidation states. Polyaniline, on application of a potential bias attracts oppositely charged ions causing volume expansion. This reversible expansion is exploited to prepare bilayer actuator with cellulose acetate electrospun mat as the substrate. A stable deflection of over 1 mm was observed at 1 V. Effect of amount and properties of polyaniline on deflection is studied along with energy conversion efficiency. This electro-chemical actuator can have potential applications in biomimetic soft robotics.

6:00 AM *S.EL13.01.06

**Engineering Uniform Nanorod Arrays Optimized for Light Energy Harvesting** Stephanie Lee; Stevens Institute of Technology, United States

Organic photovoltaics typically comprise two components in the photoactive layer – an electron donor and an electron acceptor – to overcome large excitonic binding energies in these Van der Waals systems. With typical exciton diffusion lengths in organic semiconductors on the order of 10 – 100 nm, the ideal structure of OPV photoactive layers comprises interdigitated crystalline domains of the electron donor and acceptor on the hundreds of nanometers lengths scale. Here, we present a novel strategy to form single-crystalline organic semiconductor nanoparticle arrays in situ during solution-phase deposition, with the size, orientation and spacing determined by nanostructured scaffolds at the substrate interface. Specifically, nanoporous scaffolds are introduced to the surface of device platforms that confine organic semiconductor nucleation at the air-solution-surface interface during a continuous dip coating process. These nuclei preferentially orient with their fast growth direction aligned parallel to the long axis of the pores. Subsequent crystallization proceeds beyond the scaffold to form uniform arrays of high-density, vertical nanorods with large exposed surface area. X-ray diffraction analysis has revealed that the vertical nanorods are oriented with the π-stack direction perpendicular to the substrate surface, the optimal orientation for light absorption and charge transport in organic solar cells and other devices with a sandwich electrode configuration. The height, diameter, and spacing of these nanorods are further tunable by varying the scaffold geometry and deposition conditions. Critically, this generalizable method to form uniform nanoparticle arrays is compatible with continuous processing methods that will enable the large-scale manufacturing of such materials.

Microscopic Gate-Modulation Imaging for Visualizing Undefined Operating States in Organic Single-Crystal Transistors Satoshi Matsuoka¹, Tomoki Kimura¹, Jun'ya Tsutsumi² and Tatsuo Hasegawa¹; ¹The University of Tokyo, Japan; ²National Institute of Advanced Science and Technology, Japan

A high-resolution microscopic gate-modulation imaging (μ-GMI) technique is recently developed to visualize spatial distribution of accumulated charges in operating organic field-effect transistors (OFETs) [1-4]. This technique utilizes high dynamic-range CMOS area-image sensor, which allows us to detect very slight change (up to 0.01%) of local optical absorption intensity in the channel semiconductor layers. The highly-sensitive and diffraction-limit μ-GMI becomes possible by taking advantage of the difference image sensing between at gate-on and gate-off states that are alternately biased. We successfully demonstrated that the technique is extremely useful for the microscope observations of channel charge and field distribution for studying carrier transport physics in OFETs [1,2], as well as for the rapid and collective inspection of thin-film transistor arrays [3,4].

Here we focus on the μ-GMI observations for model OFETs composed of high quality pentacene single-crystal channels that are fabricated by physical vapor transport technique and are attached on perfluorinated Cytop insulating layer coated on semi-transparent substrates. We show that anomalously large GM signals appear through the whole channel region, when the drain voltage, which is comparable to the applied gate voltage, is biased (i.e., saturation regime): The observed GM signal intensity reaches as high as ~1x10−2, which is in contrast to the much weaker GM signals (~1x10−4), as observed without the application of drain voltage. Peculiar feature is that the GM signal is considerably enhanced around the pinch-off point where the carriers should be depleted. We point out that the observation should be associated with the unexpectedly inhomogeneous distribution of positive and negative local GM signals in polycrystalline pentacene TFTs [1]. We discuss the origin of these “undefined” operating channel states in terms of the electric-field effect on charged molecules in intrinsic organic semiconductors, on the bases of further experimental results on the polarization-dependent analyses of GM spectra as well as the effect of the use of trap-free perfluorinated insulator interfaces.


The Mixed Conductivity in Highly-Ordered Polypyrrole Hybrid Materials Myung-Han Yoon, Ji Hwan Kim, Zubair Ahmad and Jaesuk Lee; Gwangju Institute of Science and Technology, Korea (the Republic of)

In this research, we report the effect of crystallinity on the mixed conductivity of highly-ordered polypyrrole film. Polypyrrol-4,4’-biphenyldisulfonic acid (poly(Py:BPDSA:Py)) hybrid was synthesized by oxidative polymerization after connecting two pyrrole monomers with various stoichiometric ratios of BPDSA in the aqueous solution. The structural and electrical/electrochemical analysis revealed that the increase in BPDSA content enlarges the crystallite size from 18.9 to 52.1 nm, the ratio of crystalline to amorphous domains by 6 times, the electrical conductivity from 174 to 406 S/cm, and the volumetric capacitance from 85 to 672 C/cm³, while the doping concentration extracted from Hall measurement and electrochemical analysis remains unchanged. On the other hand, the resultant poly(Py:BPDSA:Py)-based organic electrochemical transistors (OECTs) showed the maximum value of transconductance (0.5 mS) at the intermediate composition of BPDSA, which can be attributed to the retardation of ion movement in highly crystalline polymeric film. The repeated OECT operation revealed the stable current on-off ratio over 2 x10² without the significant loss in transconductance. All these results suggests that the mixed conductivity of poly(Py:BPDSA:Py) can be strategically modulated by engineering the crystallite size.

Gating Semiconducting Polymers with Ionic Conductors Michael L. Chabinyc; University of California, Santa Barbara, United States

Electrical doping of semiconducting polymers requires introduction of counter ions to maintain electroneutrality. These counter ions can modify electronic charge transport by changing the microstructure of the semiconductor and by electrostatic interactions between the charge carriers and their counter ion. We will discuss our recent work using single ion conducting polymers, known as polymeric ionic liquids, as the dielectric in transistors with semiconducting polymers. Polymeric ionic liquids (PILs) have tethered ionic functional groups on their backbone with an untethered counter ion leading to single ion conductivity. By appropriate molecular design of the PIL, the operation of polymer transistors can be switched from an
The electrical double layer mechanism to electrochemical doping of the bulk. The behavior of transistors with PIL gates reveals the differences in the electrical conductivity at the surface and bulk of semiconducting polymers at high charge carrier concentrations. The role of the infiltration of ions on the electronic density of states of semiconducting polymers can also be determined by measurements of the thermopower of electrochemical transistors. Our results show that electrochemical doping leads to a broadening of the DOS and helps to rationalize recent models for charge transport in semiconducting polymers at high carrier densities.

SESSION S.EL13.02/S.EL14.03: Joint Session: Frontier Devices
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL13

5:00 AM *S.EL13.02/S.EL14.03.03
Single-Layered Organic Photovoltaics with Double Cascading Charge Transport Pathways—17.78% Efficiency
Thomas P. Russell1,2, Feng Liu3, Mei Zhang4, Lei Zhu5, Guanqing Zhou6, Tianyu Hou7, Chaoqun Qiu7, Qin Hu1, Bryon Larson4, Wei Fang5, Zaiwei Ma6, Zheng Tang6, Haiming Zhu1 and Yongming Zhang7; 1University of Massachusetts Amherst, United States; 2Lawrence Berkeley National Laboratory, United States; 3Shanghai Jiao Tong University, China; 4National Renewable Energy Laboratory, United States; 5State Key Laboratory of Fluorinated Functional Membrane Materials, China; 6Donghua University, China; 7Zhejiang University, China

The chemical structure of donors (Ds) and acceptors (As) has been a limitation to the achievable power conversion efficiencies (PCEs) of bulk heterojunction (BHJ) active layers of binary D-A mixtures in organic photovoltaics. While new syntheses can be used to generate Ds and As, a holistic strategy that simultaneously improves open circuit voltage, short circuit current, and fill factor is necessary and has been pursued using different approaches in organic photovoltaics (OPVs) to PCEs. This holistic approach, though, has been elusive, due to morphological constraints and the inherent electronic structures of the components, leading to performance trade-offs. Ideally, both the morphology and electronic structure would lead to a maximization of light absorption, enhancement of exciton splitting, and ease of carrier extraction. Adding a third component has been done, resulting enhancement of either the morphology or electronic structure leading to PCE improvement, but only incremental, at best. However, using quaternary D-A blends, double cascading energy level alignment in BHJ organic photovoltaic active layers are realized, enabling efficient carrier splitting and transport, without perturbing the desired BHJ morphology. This has led to record-breaking PCEs of 17.78% where, by electronic structure and morphology optimization, simultaneous improvements of the open-circuit voltage, short-circuit current and fill factor are realized. This strategy opens numerous avenues to optimize light absorption, carrier transport, and charge transfer state energy levels by the chemical constitution of the components. The chemical structures of the Ds and As offer control over electronic structure and charge transfer state energy levels, enabling manipulation of hole-transfer rates, carrier transport, and non-radiative recombination losses.

5:30 AM *S.EL13.02/S.EL14.03.04
Interplay of Phase Diagrams, Processing and Stability of Non-Fullerene Organic Solar Cells
Harald Ade; North Carolina State University, United States

Organic solar cells (OSCs) are considered one of the most promising cost-effective options for utilizing solar energy in high energy/weight or semi-transparent applications. Recently, the OSC field has been revolutionized by the development of novel non-fullerene small molecular acceptors with efficiencies now reaching >16%. The device stability and mechanical durability of non-fullerene OPVs have received less attention and developing devices with both high performance and long-term stability remains challenging, particularly if the material choice is restricted by roll-to-roll and benign solvent processing requirements and desirable ductility requirements. Yet, morphological and mechanical stability is a prerequisite for OPV commercialization. Here, we report our current understanding of the phase behavior of OPV mixtures and the relation of phase behavior to performance, processing needs (e.g., kinetic quenches), and morphological stability via meta-stability or vitrification. Characterization methods range from SIMS and DSC measurements to delineate phase diagrams and miscibility to soft x-ray scattering and WAXS to determine critical morphology parameters and molecule packing. A large range of miscibility (from hyper-miscibility to strong hypo-miscibility) is observed, including complex temperature dependence that can be a mixture of upper- and lower critical solution temperature behavior for both the binodal and the liquidus. The
measurements presented should help to create molecular structure-function relationships that would allow some predictive guidance on how desired phase behavior and vitrification properties can be targeted by specific chemical design. They also allow to predict how unstable binary systems can be stabilized with the correct ternary compound.

6:00 AM *S.EL13.02/S.EL14.03.05
Structure, Transport and Charging in Organic Mixed Ionic/Electronic Conductors Jonathan Rivnay; Northwestern University, United States

Organic mixed ionic/electronic conductors have gained considerable interest in bioelectronics, power electronics, circuits and neuromorphic computing. These organic, often polymer-based, semiconductors rely on a combination of ionic transport, electronic transport, and high volumetric charge storage capacity. Despite recent progress and a rapidly expanding library of new materials, the understanding of stability and transport/coupling of ionic and electronic carriers remain largely unexplored. We highlight recent synthetic and processing approaches used to tailor electrochemical device properties and stability, as well as new opportunities enabled by such advances. Our understanding of critical processes in electrochemical devices further requires us to study these materials in device-relevant conditions, fully considering the effects of ions and solvent on microstructure and transport. To this end, we report on recent efforts towards structure-property relations in high performance organic mixed conductors using ex-situ, in-situ, and operando scattering and spectroscopic techniques.

6:30 AM *S.EL13.02/S.EL14.03.06
Real-Time Investigation of Crystallization Pathways of Organo-Metal-Halide Perovskites Solar by In Situ X-Ray Scattering Michael F. Toney; SLAC National Accelerator Laboratory, United States

Perovskite solar cells (PSCs) have gained tremendous attention as potential materials for photovoltaics due to their high efficiencies approaching the best silicon solar cells and their compatibility with low-cost low-temperature fabrication methods (such as solution processing). Many solution-processing approaches have been adopted to manipulate perovskite formation including anti-solvent processing, inert-gas jet treatment, and additive-assisted processing. Some of these approaches allow room-temperature processing of perovskite thin films, while other approaches require post-deposition annealing. Perovskite film formation is complex, involving the formation of intermediates and/or metastable phases that strongly affect the final perovskite film microstructure. Therefore, understanding the mechanism of perovskite formation and the crystallization pathways is key for more facile control of perovskite formation. An effective way to understand the mechanisms of perovskite formation is using real-time X-ray scattering. Here, we use time-resolved x-ray scattering to investigate the perovskite formation of MAPbI₃-based perovskites and mixed cation (Cs, FA)PbI₃ perovskites in-situ during spin coating and the subsequent post-deposition treatments with different processing approaches such as additive-assisted processing, anti-solvent processing and N₂-gas jet treatment.

Time-resolved monitoring of the perovskite thin film processing reveals the formation of intermediate phases on the route of perovskite formation, whereas perovskite formation is dominated by a sol-gel process. For MAPbI₃-based perovskites processed with the MASCN additive, we show that the nature of the intermediate precursor phases and their formation/dissociation dynamics have an impact on the extent of nucleation and growth of perovskite phase affecting the microstructure of the perovskite film. Our findings reveal that the combination of two precursors (MASCN-precursor and DMSO-precursor) with fast and slow transformation rates contributes to the formation of micron-sized perovskite crystals, through seeding nuclei combined with the slow growth of the perovskite phase. For Cs-FA-containing perovskites, we show how the competition between the non-perovskite and perovskite phases formation are affected by the processing treatments. We find that dropping anti-solvent induces immediate crystallization from the bulk wet film, whereas applying N₂-gas works by depleting volatiles from the top-surface leading to interface-induced crystallization that occurs after reaching supersaturation, while both treatments result in dominant crystallization of non-perovskite hexagonal phase with the formation of seeds of perovskite phase. When neither treatment is applied, the as-cast film is mostly amorphous with little non-perovskite phase formation. We further show how the initial structure of the as-cast precursor film impacts the perovskite formation during the subsequent annealing treatment.

Our work highlights the importance of real-time investigation of perovskite film formation which can aid in establishing processing-microstructure-functionality relationships and help to provide a fundamental understanding of the mechanisms of perovskite formation.
SESSION S.EL13.03: Thin Films and Devices
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL13

5:00 AM *S.EL13.03.01
Making Plastics Learn—High-Performance Polymer-Based Artificial Synapses are Mixed Protonic and Electronic Devices
Alberto Salleo; Stanford University, United States

The brain can perform massively parallel information processing while consuming only ~1-100 fJ per synaptic event. I will describe a novel electrochemical neuromorphic device (ENODe) that switches at record-low energy (<0.1 fJ projected, <10 pJ measured) as well as voltage (< 1mV, measured), and displays a large number of distinct, non-volatile conductance states within a ~1 V operating range. The tunable resistance behaves very linearly, allowing blind updates in a neural network when operated with the proper access device. ENODes also display outstanding endurance achieving over 10^9 switching events with very little degradation. I will describe our recent efforts at scaling and materials selection, allowing us to reach 20 ns write pulses and operation at high temperature (up to 120°C). These properties are very promising in terms of the ability to integrate with Si electronics to demonstrate online learning and inference. ENODes are electrochemical devices where gated proton drift induces changes in the electronic states of a semiconductor channel. The peculiarities of the physics of these devices will be discussed along with their consequences on device design and performance.

5:30 AM *S.EL13.03.02
Enhancement-Mode PEDOT:PSS Organic Electrochemical Transistors Using Amine-Based Molecular De-Dopants
Scott T. Keene1, Tom van der Pol2, Dante Zakhidov1, Christ Weijtens2, Rene A. Janssen2, Alberto Salleo1 and Yoeri van de Burgt2; 1Stanford University, United States; 2Technische Universiteit Eindhoven, Netherlands

The recent emphasis of point-of-care diagnostics and preventative health monitoring has led to increasing interest in electronic devices aimed at noninvasive continuous health monitoring. Organic electronic materials are well suited for bioelectronics applications because of their biocompatibility and low Young’s modulus which is comparable to that of human tissue. In particular, organic electrochemical transistors (OECTs) show promise due to their ability to convert ionic signals, which are typically found in biological systems, to electronic outputs with high gain. Furthermore, the low operating voltages (<1 V) are ideal for biological samples due to the sensitivity of cells/proteins to an applied bias. As a result, OECTs have been implemented for biosensing, ion delivery, and neural recording.

The majority of OECTs are based on the commercially available conductive polymer blend PEDOT:PSS because of its high electronic and ionic mobilities. However, PEDOT chains in PEDOT:PSS are heavily doped due to the negative charge of sulfonate anions on the PSS units, and thus OECTs must operate in depletion mode. Thus, OECTs require significant voltages (+0.8 V vs Ag/AgCl) to hold the OECT in its off state, leading to increased power consumption and device instability caused by parasitic reactions with ambient oxygen. In this work, we mitigate these inherent problems with PEDOT:PSS by introducing small molecule amine de-dopants in solution which can reduce PEDOT chains. With these additives, we effectively de-dope PEDOT:PSS to achieve electronic characteristics similar to an intrinsic semiconductor. The resulting de-doped PEDOT:PSS is used to fabricate highly stable OECTs that operate in enhancement mode while preserving the exceptional electronic and ionic transport ($\mu_h \sim 2$ cm$^2$ V$^{-1}$ s$^{-1}$, $C^* \sim 40$ F cm$^{-2}$).

This presentation describes the chemical interactions between the PEDOT:PSS and amine de-dopant molecules to understand the relationship between the film microstructure and resulting electronic structure and transport properties. We demonstrate the relationship between de-dopant concentration and OECT performance, showing a tradeoff in mobilities and transconductance with increasing de-dopant concentration. Then, we use cyclic voltammetry and ultraviolet photoemission spectroscopy to probe the electronic structure of PEDOT, showing a deeper highest-occupied molecular-orbital (HOMO) level is responsible for the shift in OECT threshold voltage. Furthermore, we investigate microstructure of the de-doped PEDOT:PSS films using grazing incidence x-ray scattering measurements (GISAXS/GIWAXS), Raman spectroscopy, and atomic force microscopy to rationalize the difference in performance across the studied amines. Finally, we develop design criteria for selecting de-doping additives to further improve the stability and performance of enhancement-mode PEDOT:PSS OECTs for low-power wearable and implantable electronic devices.

5:45 AM *S.EL13.03.04
Bio-Inspired Organic Artificial Nerves for Peripheral Nerve Emulation
Tae-Woo Lee1, Zhenan Bao2, Yeongjun Lee1, Jin...
Young Oh², Yeongin Kim², Alex Chortos², Wentao Xu¹ and Dae-Gyo Seo¹; ¹Seoul National University, Korea (the Republic of); ²Stanford University, United States

Biological nerves have evolved toward functionalities to efficiently process complex information in real-time. Unlike biological nerve system, von Neumann based computing system performs in centralized and sequential form which has difficulty in event driven and parallel operation. In this regard, there has been many efforts to adopt the superior characteristic of biological nervous system and the concept of neuromorphic electronics have emerged. As the synaptic behavior can be implemented through single artificial synaptic device, it can emulate the functions of biological sensory and motor neurons when combined with sensors and actuators. Making the artificial nervous system desirable for soft robotics and neuroprosthetics have been widely investigated.

Here, artificial nervous systems were developed by using organic electronics to emulating peripheral nervous system. Pressure sensors (artificial mechanoreceptors), organic ring oscillators (artificial nerve fibers), and synaptic transistors were integrated to emulate the biological sensory nerve system. By forming hybrid reflex arc which connects artificial sensory nerve and biological motor nerves the applicability for neural prostheses was verified and the biological motor nerves were actuated depending on external pressure information. In addition, by integrating a stretchable artificial synapse, and a polymer actuator (an artificial muscle), stretchable artificial sensorimotor nervous system was developed. The optogenetics was emulated by contracting the artificial muscle with light stimulation. In parallel, the system distinguished the alphabet Morse code which showed the potential as an optical wireless communication method for human-machine interface. Furthermore, by integrating a triboelectric sensor for an artificial auditory system, artificial auditory system was emulated.

We modulated morphology of organic semiconductors of the artificial synapses to implement the specific recover time of biological synapse facilitation. Our organic artificial nerve systems suggest promising strategy for bioinspired electronics, soft robotics, and neuroprosthetics.

6:15 AM *S.EL13.03.05
Charge Transport and Thermoelectric Properties of High Mobility Conjugated Polymers
Henning Sirringhaus; Cambridge University, United Kingdom

Over recent years several new classes of conjugated polymers have shown promise as materials for polymer field-effect transistors with high field-effect mobilities. Many of the recently discovered high mobility polymers, in particular donor-acceptor copolymers, owe their excellent charge transport properties to a low degree of energetic disorder associated with a well-defined backbone conformation with small variations in torsion angles. In this presentation we will present our current understanding of the transport physics of these materials and focus in particular on the relationship between molecular structure, thin film processing and charge transport and thermoelectric properties of these materials. We will discuss new approaches for the doping of these polymers and for understanding their thermoelectric physics.

6:45 AM S.EL13.03.06
Influence of Contact Resistance on the Thermal Operation Stability of Conjugated Polymer Transistors
Dung T. Tran, Xuyi Luo and Jianguo Mei; Purdue University, United States

The performance drop of organic field-effect transistors (OFETs) at high temperature is usually attributed to unstable and disrupted charge transport in the channel. However, the impact of charge injection process is overlooked and rarely discussed. Here, we proved that the contact resistance has a significant influence on the behavior of the OFETs at high temperature. Two different device structures with different contact resistance, bottom-contact-bottom-gate (BCBG) and top-contact-bottom-gate (TCBG), of an Isoindigo-based polymer, were characterized from room temperature to 220°C in air. The BCBG device witnessed a substantial threshold (VT) shifting, dropping on-current and unstable output curve at temperatures above 180°C. Conversely, the TCBG devices can maintain close-to-ideal VT, high mobility, stable output curves and high on/off ratio of 10⁶ at 220°C. The contact resistance of the BCBG devices, estimated using the gated-transmission line method, is much higher than that of the TCBG devices in the whole range of measured temperature. More importantly, at fixed gate voltage, the ratio of contact to channel resistance (Rc/Rch) of BCBG devices increases with increasing temperature that makes them heavily contact-limited at elevated temperature. The TCBG devices, on the other hand, show no sign of being contact-limited even at 220°C. This study indicated the importance of charge injection and device architecture on designing thermal resistant OFETs as well as fundamental understanding of the charge transport in conjugated polymers in extreme conditions.

7:00 AM *S.EL13.03.08
Ultraflexible Organic Single Crystal Electronics through Cooperative Structural Transitions
Ying Diao; University of Illinois at Urbana-Champaign, United States
Electronic materials require flexibility in order to accomplish conformal integration on nonplanar dynamic surfaces such as skins, internal organs, and textiles for wearable and implantable devices. Mechanical flexibility of electronic materials has been achieved by geometrical engineering of hard materials or by molecular design of intrinsically deformable π-conjugated polymers. The latter approach is further amenable to large-scale, low-cost solution processing. However, high intrinsic deformability of π-conjugated polymers is attained at the expense of reduced crystallinity and/or conjugation length, either by the synthetic approach to introduce dynamic bonds or through nanoconfinement to enhance chain dynamics. On the other hand, exceptional molecular ordering is the primary requirement for disorder-free charge transport. Towards this end, single crystals or long-range ordered crystalline films of organic semiconductors have been pursued, achieving charge carrier mobility above 10 cm²V⁻¹s⁻¹ for both small molecules and polymers. Despite their promising performances, single crystals or crystalline films are not tolerant to mechanical deformation. It has been revealed that strain allows a shift toward non-equilibrium packing within the elastic deformation regime (the strain window limited up to about ±2%); strain above this limit leads to brittle fractures.

How to render molecular crystals highly deformable to reconcile the conflict of mechanical flexibility and exceptional molecular ordering? An intriguing strategy offered by biological systems is the contractile tail of bacteriophage T4 virus—its tail is comprised of a protein crystal capable of undergoing strain-induced cooperative structural transition to reach a staggering 60% contraction, thereby injecting DNA into the bacteria host. A similar strategy has been applied to synthetic materials, whose atomic/molecular cooperativity enables strain accommodation mechanisms such as shape memory effect (recovery of mechanically deformed shape by thermally induced phase transition), superelasticity (mechanically induced reversible shape change through stable-to-metastable phase transition) and ferroelasticity (mechanical shape reconfiguration through deformation twinning and detwinning). On the contrary, mechanically deformable molecular crystals realized through cooperative structural transition are rare and has not been reported for electronic materials and applications.

We discover that mechanically-induced cooperative structural transitions can serve as a stress-releasing mechanism when mechanical deformation surpasses the intrinsic elastic limit. Upon mechanical shearing or bending, synchronized molecular rotation and/or displacement give rise to cooperative structural transitions, i.e. superelastic polymorph transition and ferroelastic deformation twinning in organic semiconductor single crystals. Through this mechanism, organic semiconductor single crystals can tolerate an unprecedented 13% strain while maintaining >70% of the unstrained charge carrier mobility. Moreover, thermomechanical cooperative structural transitions further enable shape memory effect, paving ways to designing ultraflexible single crystal electronic devices that can memorize shape and function at once.

7:30 AM S.EL13.03.09
Capturing the Stress-strain Behavior of Polymer Thin Films and Using the Knowledge Gained to Achieve High-Performance Stretchable Electronics
Runqiao Song1, Nrup Balar1, Salma Siddika1, Harry Schrickx1, Jeromy James Rech2, Wei You2 and Brendan T. O’Connor4; 1North Carolina State University, United States; 2University of North Carolina at Chapel Hill, United States

Polymer semiconductors are promising materials for stretchable electronics owing to the opportunity to achieve intrinsically stretchable films. In stretchable devices, the films are expected to repeatedly deform under cyclic strain while being operationally stable. While there have been a number of successful demonstrations, the physical origin of the deformation behavior remains elusive. This is in part due to the difficulty in probing the stress-strain behavior of the semiconductor film owing to its thin nature and in-plane cyclic loading. Here, we employ a novel method to probe the stress-strain behavior of polymer semiconductor films under large cyclic strains. This is achieved by laminating the films onto a thin elastomer substrate and testing the composite behavior in a dynamic mechanical analyzer (DMA). The elastomer provides support to handle the film but is thin enough that the semiconductor of interest can be probed. The DMA provides a highly sensitive tool to extract detailed mechanical behavior of the composite with fine control of the sample temperature and strain rate. We use this film laminated on elastomer (FLOTE) method to study a range of conjugated polymers and compare the results to the thermomechanical relaxation of the polymers. We find that the viscoelastic characteristics of the polymer not only impact film deformation in tension but also contraction upon strain removal. We find that many DA polymers have stress-strain behavior characteristic of cold-drawing at room temperature and are unstable under cyclic strain loading. However, we show that stretchability can be improved by varying the molecular structure of the polymer to modify viscoelastic behavior, demonstrated by exploring structural variants of PBNdDT-FTAZ. Furthermore, we show that the polymer semiconductor elastomer composites have features consistent with Mullins’ effect that is commonly observed in elastomer composites. These features include strain-softening after the first strain cycle, stress-strain behavior that tracks with a virgin sample upon greater extensions, and a permanent set that changes with applied strain. This behavior is exploited to demonstrate high-performance stretchable field-effect transistors that are stable over a 40% cyclic strain.
Semiconducting polymers are attractive materials for flexible and stretchable electronics owing to favorable mechanical properties. These properties are afforded by the viscoelastic nature of the polymers, which directly impact the mechanical and thermodynamic stability of the film. Recently, dynamic mechanical analysis (DMA) have been shown to be a sensitive probe to capture thermal relaxations in conjugated polymers. This is particularly useful to study recently developed donor-acceptor (DA) type copolymers that have been shown to have complex thermomechanical characteristics without a clear glass transition. In addition, DMA probes thermal transitions under the effect of direct mechanical loads, thus, provides a complete picture of thermomechanical properties of the polymer including thermal relaxations, storage and loss moduli, stress relaxation, etc. In this talk, we report on the origin of the thermal relaxations in the representative DA polymer PbnDT-FTAZ. This is done through an analysis of the DA polymer with systematic changes to the molecular structure. We then extend this analysis to a broad set of high performance DA polymers showing the common origin of the relaxation behavior associated with side-chains, localized backbone motion, and chain slippage. We then show that these transitions have a significant impact on film toughness demonstrating that localized relaxation largely associated with polymer side-chains dictate the ductile to brittle transition of the film. Finally, we take the information gained by the thermomechanical behavior of the polymers to demonstrate high performance stretchable organic field effect transistors, and morphologically stable high efficiency organic solar cells.

Influence of Acceptor Type and Polymer Molecular Weight on the Mechanical Properties of Polymer Solar Cells Bumjoon Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The mechanical robustness of polymer solar cells (PSCs) is of great importance to ensure the long-term stability and enable their use as power-generators in flexible and stretchable electronics. Here, we present a comparative study of the mechanical properties of small-molecule acceptor (SMA)-based, polymer acceptors (PA)-based, and fullerene-based PSCs. We chose ITIC, P(NDI2OD-T2), and PCBM as three representative acceptor materials and blended them with the same polymer donor. To understand the difference between the mechanical properties of SMA-based and PA-based PSCs, we control the number-average molecular weight ($M_n$) of P(NDI2OD-T2) from 15 to 163 kg mol$^{-1}$ in all-PSCs. The high $M_n$ PA-based-PSCs exhibited a high strain at fracture of 31.1%, which is 9- and 28-fold higher than those of SMA-PSCs and PCBM-PSCs, respectively. The superior mechanical robustness of all-PSCs is attributed to using a PA above the critical molecular weight ($M_c$), which produces tie molecules and polymer entanglements that dissipate substantial mechanical strain energy with large plastic deformation. The connectivity between the crystalline domains generated by PA tie chains leads to high charge mobilities and photovoltaics performances of all-PSCs. Also, this feature explains very high donor:acceptor composition tolerance of all-PSCs in the photovoltaic and mechanical performances. Therefore, our work highlights the importance of incorporating high $M_n$ PAs above the $M_c$ for producing the PSCs with excellent mechanical robustness and device performance.

High-Performance Solution-Processed Two-Dimensional p- and n-Type Organic Single-Crystal Transistors and CMOS Circuits Jun Takeya; The University of Tokyo, Japan

Electronic devices in the future sustainable societies require maximum function with minimum amount of constituent materials and energy cost for production. Electronic functions are often originated from two-dimensional material properties so that device components of large area and small thickness saves material consumption. The fundamental electronic functions such as switching “zero” and “one” in the digit of information are governed only by a nanometer-scale thin layer at the very surface of the semiconductor material due to the very short penetration length of electric field. Future ten-meter scale large-area display also needs to be more “two-dimensional” to save materials and save energies to carry and equip on billboards. This presentation focuses on recently developed ultrathin organic semiconductor single crystalline films that is suitable for large-area production with low energy consumption; the films is easily formed to large area from solution at relatively low temperature at 80 degrees centigrade. Extremely thin crystal films are controllably grown to a few molecular layers with the thickness of only 10 nm, so that material cost can be only 0.01 Euro per cm2. The talk begins with material chemistry of
designing the semiconductor molecules that causes very high carrier mobility more than 10 cm²/Vs for p-type and 3-5 cm²/Vs for n-type organic single-crystal transistors. Furthermore, Recent development of key technologies for printed integrated circuits which can provide future low-cost platforms for RFID tags and sensing circuitries. Finally, a technology for large-area light-weight display sheets will be demonstrated.

Such prospect bears increasing reality because of recent research innovations in the field of material chemistry, charge transport physics, and solution processes of printable organic semiconductors. With excellent chemical and thermal stability in recently developed new materials, we are developing simple integrated devices based on CMOS using p-type and n-type printed organic FETs. Particularly important are new processing technologies for continuous growth of the organic single-crystalline semiconductor “wafers” from solution and for lithographical patterning of semiconductors and metal electrodes. Successful rectification and identification are demonstrated at 13.56 MHz with printed organic CMOS circuits.

SESSION S.EL13.04: Materials Processing
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL13

5:00 AM S.EL13.04.02
Interfacial Drawing—Roll-to-Roll Coating of Semiconducting Polymer and Barrier Films onto Plastic Foils and Textiles Rory Runser¹, Samuel E. Root²,Derick Ober¹, Kartik Choudhary¹, Alexander Chen¹, Charles Dhong³, Armando D. Urbina¹ and Darren J. Lipomi¹; ¹University of California, San Diego, United States; ²Harvard University, United States; ³University of Delaware, United States

This paper demonstrates that a thin polymeric film (10-80 nm) can be continuously drawn from the meniscus of a nonpolar polymer solution at an air-water-fluoropolymer interface using a roll-to-roll process: “interfacial drawing.” With this process, it is possible to control the thickness of the film by manipulating the concentration of the solution, along with the drawing velocity of the receiving substrate. We demonstrate the formation of thin films >1 m in length, and 1000 cm² in area, using our custom-designed apparatus. Interfacial drawing has three characteristics which compare favorably to other methods of forming and depositing polymeric thin films. First, the films are solidified prior to deposition, which means that they can be used to uniformly coat nonplanar, rough, or porous substrates. Second, these films can be stacked into multilayered architectures without risk of redissolving the layer beneath. Third, for some materials, the process yields films with superior mechanical compliance for applications such as wearable or flexible devices, compared to films produced by spin-coating. We demonstrate the utility of interfacial drawing by forming thin films of various semiconducting polymers, including the active layers of all-polymer bulk heterojunction solar cells as well as barrier coatings. As part of these demonstrations, we show how floating polymeric films can be transferred easily to diverse substrates, including those with rough and irregular surfaces, such as textiles and fabrics.

5:15 AM S.EL13.04.03
Modelling Grain Development in Crystalline Thin Films Produced by Meniscus-Guided Coating Ke Zhang, Tomasz Marszalek, Wojciech Pisula and Jasper Michels; Max Planck Institute, Germany

Meniscus-guided coating (MGC) represents a range of scalable methods for controlled solution-deposition of functional materials, such as organic semiconductors, polymers, perovskites and metal-organic frameworks. MGC is of special interest to the fabrication of thin film devices that rely on an active layer with a high unidirectional charge carrier mobility. During MGC a substrate is translated under a coating head, slot or blade which deposits the solution from a steady-state liquid meniscus. The thickness of the dry film may decrease or increase with the coating speed, depending on whether deposition takes place in a, respectively, evaporation-controlled or hydrodynamic (Landau-Levich) regime. The occurrence of these regimes has been reproduced and explained by models based on lubrication theory. In contrast to film thickness, so far little theoretical attention has been given to the effect of process parameters on the actual thin-film crystalline morphology, which is of critical influence to device performance. In this contribution we present our first effort to accounts for this. We develop a model that explains how substrate translation and solvent evaporation determine crystalline morphology in terms of the size, dispersity and shape anisotropy of spherulitic domains. The model reproduces the experimentally observed transition from macroscopically aligned structures, via stretched grains to isotropically impinged domains upon increasing the coating speed. Our calculations provide a framework that relates morphological characteristics to the deposition regime in MGC.
Patterning Organic and Hybrid Semiconductor Microstructures for Electronics and Optoelectronics  
Aram Amassian; North Carolina State University, United States

The transport properties and device performance of organic semiconductors is determined by the microstructure and morphology of polycrystalline thin films, including grain size, domain orientation and grain boundaries. For device applications, such as field-effect transistors, controlling the domain orientation and grain boundaries is particularly important as this mediates charge transport in the channel of the device. More generally, the opportunity to fabricate single crystal domains to match the device architecture would be a very promising pathway to unlock the intrinsic properties of organic and hybrid semiconductors. This presentation will discuss recent efforts to reduce and even eliminate grain boundaries in solution-processed organic and hybrid semiconductor films, with such applications as high performance field-effect transistors, photodetectors and light emitting devices envisioned. Approaches based on patterning the microstructure of thin films post-deposition or in situ will be discussed, as well as additive manufacturing-based coating and printing methods of delivering materials with single crystal-like properties at designated locations.

Quantifying Effects of Molecular Interfaces on Device Dynamics via Resonant Soft X-Rays  
Brian A. Collins; Washington State University, United States

With printable single-junction organic solar cell efficiencies reaching 16%, the economic viability of a >20% efficient, printable, and non-toxic panel is more achievable than ever before. To realize such a device near its limiting performance, however, a much more quantitative and granular model of how molecular ordering affects charge generation is required. The development of resonant soft X-ray scattering (RSoXS) has considerably aided nanostructure characterization yet is still rather undeveloped. I will discuss using new analytical models of RSoXS going beyond the simplistic 2-phase assumptions and that quantify the device donor-acceptor interfaces toward characterizing interfacial molecular orientation. We have, furthermore, developed an in-situ photophysical measurement suite, including time-delayed collection field. This suite and new device analysis quantifies the full excited state population dynamics on the exact same devices within which we measure the nanostructure. This has resulted in unprecedentedly quantitative structure-property relationships in model systems that reveal the effect of the mixed amorphous interface. With this new capability, functional relationships that dictate device performance from interfacial aggregation, mixing, and molecular orientation can be used to tailor molecular architecture and device processing that achieves the promise of truly competitive large scale solar harvesting.

Hybrid Materials Design for Wearables, Prosthetics and Robotics Systems  
Benjamin C. Tee; National University of Singapore, Singapore

We are increasingly living in a hyper-connected environment where humans, smart devices and robots live in synergy together. The continued development of soft organic devices\(^1\) for bio-integrable and even neuro-integrable sensory systems will augment human abilities and drive new applications as health diagnostics, surgery and predictive analytics. In my talk, I will discuss materials design and strain engineering techniques to develop electronic intelligent materials with stretchability, sensitivity and robust mechanical properties, such as self-healing\(^2,3\). In addition, I will also discuss our recent progress in developing new scalable electronic skin platform technologies\(^4\) for systems capable of far greater perception and intelligence. It is envisioned that such electronic skins can be useful in future distributed conformable electronic skins\(^5\), neuro-prosthetic devices and wearable exo-suits in the increasingly digital and augmented human era.


6:00 AM *S.EL13.05.04
**Nanocrystalline Organic Semiconductor Photocatalysts—A Dominance of Oxygen Reduction Reactions** Eric D. Glowacki1,2; 1Linkoping University, Sweden; 2Warsaw University of Technology, Poland

Semiconductor-based catalysts can convert solar energy into chemical fuels such as hydrogen, hydrogen peroxide, or hydrocarbons produced via carbon dioxide reduction. Long overlooked due to stability concerns, some organic semiconductors have recently emerged as promising electrocatalysts and photocatalysts for operation in aqueous environments. Our attention has focused on nanocrystalline pigment-type organic semiconductors, which stand out due to stability and performance. Generally, we have found a high selectivity of organic semiconductors for oxygen reduction reactions, by both one-electron and two-electron pathways. The products of these reactions are superoxide or hydrogen peroxide. We find this occurs on numerous organic semiconductors and conducting polymers in a pH range from 1 to 12. The large pH stability window is remarkable when compared with inorganic counterparts. We have found that while photogenerated electrons reduce oxygen, the fate of the holes represents a complex picture. When the nanocrystalline semiconductor is used as a photocathode and efficient p-type transport is available, photogenerated holes can easily be extracted to an external circuit. If this is not possible or inefficient, the hole will either oxidize electron-donors in solution or precipitate autooxidation reactions of the semiconductor itself. The factors affecting this photocorrosion effect will be discussed, as well as principles leading to stabilization of the semiconductor catalyst. The possibilities of solar energy conversion into the high-energy molecule H2O2 enabling carbon-neutral energy storage in liquid form, in contrast to gaseous H2, will be covered. Organic semiconductors have potential to become a powerful class of intrinsic catalysts, tunable by molecular design.

6:30 AM *S.EL13.05.05
**Structure-Property Relationships for Mixed Conductors in Organic Bioelectronics** Sahika Inal; King Abdullah University of Science and Technology, Saudi Arabia

In this talk, I will present an electronic platform based on an n-type conjugated polymer for detecting glucose as well as generating power from bodily fluids. We employ the n-type semiconducting material in an accumulation mode organic electrochemical transistor (OECT). The polymer is engineered to have specific interactions with the enzyme. This micron-scale device detects glucose without the need of a mediator and shows excellent sensitivity and selectivity over five orders of magnitude wide detection range. When integrated into an enzymatic biofuel cell, the same polymer serves as the anode, converting the glucose metabolism in an aqueous medium into power. The mediator-free glucose-oxygen fuel cell outperforms other reported systems at physiological glucose concentrations. This is the first-time use of n-type polymer in an energy generation device with the capability to operate in human fluids. Such polymers open up an avenue for the development of self-powered microscale sensors that run on metabolites produced by the body. These devices can be fabricated on flexible substrates, paving the way for implantable self-powered metabolite sensing.

SESSION S.EL13.06: Miscellaneous
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

5:00 AM *S.EL13.06.01
**Plasticizing Small Molecule and Polymeric Semiconductors by Molecular Design** Antonio Facchetti1,2; 1Northwestern University, United States; 2Flexterra Inc., United States

In this presentation we report the development of novel semiconductors for mechanically flexible and more ductile transistors and circuits. Particularly, we show that “ultra-soft” polymers comprising naphthalenediimides (NDI) units co-polymerized with “rigid” and “flexible” organic units can change how charge transport is affected by mechanical stress, demonstrating
that polymer backbone composition is more important than film degree of texturing. This strategy enables to reduce the elastic modulus of the semiconducting film by >2-4x while retaining charge transport characteristics. In addition, new polycrystalline molecular semiconductor films based on perylenediimide molecules are plasticized by using an innovative polymer additive design strategy enabling polymer localization at the fragile grain boundaries. This approach preserves charge transport characteristics in a TFT architecture as well as greatly enhances film bendability and charge transport stability upon multiple bending (> 1000 x vs < 10 for the pristine molecular film).

SESSION S.EL13.07: Poster Session: Processing, Microstructure and Multifunctioning of Organic Semiconductors
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
5:00 AM - 8:00 AM
S-EL13

S.EL13.07.03
Understanding the Processing Variables under Meniscus-Line-Guided Coating Ming Chen and Paddy K. L. Chan; University of Hong Kong, Hong Kong

Solution processable meniscus-line-guided (MGC) coating is an excellent candidate to realize highly crystallized organic semiconductor thin films in the fabrication of organic field effect transistors (OFETs). The basic processing parameters, including shearing speed ($v$), concentration ($c$), solvent boiling point ($T_b$) and deposition temperature ($T$), are pivotal to achieve fine control over the crystallinity of the deposited organic thin films and therefore, understanding of the interconnections between these parameters are highly desired. Here, we examine the effects of different fabrication factors on the crystal deposition rate systematically under MGC approach. The active layer material in current study is the 2,7-Dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT) organic semiconductor. It is verified that $v$ and $c$ are connected to crystal deposition rate by means of mass conservation. The crystal deposition rate is further related to $T$ and latent heat ($L$, proportional to $T_b$) in the Arrhenius form. Furthermore, the optimum organic thin film (roughness $R_q < 0.25$ nm and average mobility $\mu_{ave} = 5.88$ cm$^2$ V$^{-1}$ s$^{-1}$) is achieved under a mass transfer rate of $6 \times 10^{-11}$ kg s$^{-1}$ to $15 \times 10^{-11}$ kg s$^{-1}$. Our findings provide valuable information in understanding the crystal growth under the MGC method, which is believed to be one of the highest potential approaches for the mass production of OFETs.

S.EL13.07.05
The Fabrication of the Organic Field-Effect Transistor Device at the Atomic Force Microscopy Probe Shui Hong Siddhartha Dai and Paddy K. L. Chan; The University of Hong Kong, Hong Kong

Sample surface potential measurement is one of the important topics for material research. The state-of-art surface measure technologies are Kelvin Probe Force Microscope (KPFM) and Electrostatic Force Microscope (EFM). Although those technologies can measure the surface of the sample in nanoscale, the equipment, in general, is sensitive to the environment due to the measurement noise and require extra amplifiers to improve the signal-to-noise ratio. This research aims at functionalizing the AFM probes by integrating an OFET onto the tip for localized electrical signal amplification. The OFET-AFM tip structure includes the source, drain, organic semiconductor and dielectric coating. The patterning of the source and drain electrodes are developed by the Focused Ion Beam (FIB). The meniscus-guided solution-processing method is employed to grow ultrathin (~30 nm) C10-DNTT crystal which will be transferred to the electrodes by the FIB milling method. We believe the ultrathin organic semiconductor crystal allows the contact resistance between electrodes and semiconductors to be low enough (< 100 Ωcm) for decent transistor operation. Furthermore, the FIB milling can minimize the thermal damage, which is caused by the thermal evaporation of metal to the organic semiconductor during the fabrication process. As a result, building up a small scale (channel length less than 2 micrometer) OFET device at the AFM tip becomes possible. The Parylene coating (~500 nm) serves as the dielectric layer of the OFET and allows the OFET-AFM probe to measure the voltage signal from the sample surface. The surface potential of the probe will act as the gate bias of the OFET, thus to control the channel current of the device. We believe the OFET-AFM probe can open up a new direction in small scale biomedical applications.

S.EL13.07.06
Phototransistors Based on a Lightly Doped P3HT Thomas H. Debesay and Sam-Shajing Sun; Norfolk State University, United States

2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
Organic/Polymeric Semiconductor (OSC) based devices have been under extensive study for the past three decades due to their intrinsic potential advantages such as lightweight, flexible, biocompatible, low toxicity, abundant material availability, low cost of processing, etc. A phototransistor incorporates the properties and functions of a transistor and photodetector. In this study, a phototransistor based on a donor/acceptor (D/A) pair (photo-doping) was studied and demonstrated. Unlike in organic photovoltaics (OPV) where 1:1 proportion by mass of the donor:acceptor is typically utilized to make up the active layer, that ratio appears to be too high for phototransistor applications. It has been reported that the D/A 1:1 concentration leads to a low overall phototransistor device performance, lack of I-V curve saturation (kink effect), and other undesired bipolar transistor behaviors. By systematically adjusting the materials doping concentrations and ratios, as well as device fabrication techniques, we were able to demonstrate a much-improved performance of a p-type phototransistor. Specifically, a high-performance OFET phototransistor was achieved via a very small amount of Phenyl-C71-butyric acid methyl ester (PCBM) doped into a Poly(3-hexylthiophene) (P3HT) host. With this work, a greater understanding behind the optimization of D/A based phototransistors is advanced.

S.EL13.07.07
Application of Fluorescent Molecules as Non-Invasive Sensors for Opto-Electronic Characterization on Nanometer Length Scales

Thomas Ferschke1, Alexander Hofmann2, Wolfgang Brütting2 and Jens Pflaum1,†; 1University of Würzburg, Germany; 2University of Augsburg, Germany; †Bavarian Center for Applied Energy Research (ZAE Bayern), Germany

The non-invasive, in operando characterization of opto-electronic properties of organic semiconductors is of special interest as it enables information on microscopic processes governing the performance of a device and sheds light on its real lifecycle.

In this contribution we present a new approach to cope with this challenge by utilizing fluorescent Tetraphenyldibenzo[1]periflanthene (DBP) molecules as optically addressable sensors, deterministically positioned at very low concentration within archetypical N,N’-di-(1-naphthyl)-N,N’-diphenyl-(1,1’-biphenyl)-4,4’-diamo/Tris(8-hydroxyquinolato)aluminium (NPB/Alq3) organic light-emitting diodes (OLEDs) as model system.

Observing variations in fluorescence intensity of the optically excited DBP sensor molecules during device operation allows for a correlation with the charge carrier distribution within a dynamic range of four orders of magnitude in current density ($10^{-4}$ – $10^{0}$ mA/cm²) under forward bias [1]. Due to the deliberate incorporation of the molecular probes at a well-defined depth within the OLED stack as well as utilization of a μ-photoluminescence technique this information is gathered with nanometer length scale resolution. The resolution is determined by opto-electronic processes like Langevin capture of injected charge carriers and Förster type resonant energy transfer and can be estimated to around 15 nm. Under reverse bias condition the molecular sensing method proves sensitive to uncompensated dipoles at the NPB/Alq3 heterointerface, which results from the preferential orientation of the molecular Alq3 dipoles during layer deposition [2]. The optical data is substantiated by complementary macroscopic impedance measurements performed on identical devices. In conjunction with the impedance measurement, drift-diffusion simulations [3] of the OLED stack characteristics are carried out to further corroborate the correlation between the observed photoluminescence changes and the opto-electronic device properties. The broad variety of molecular host-guest systems, renders this approach a universal tool for analyzing not only opto-electronic phenomena in many different organic electronic device structures but, for example, also in biological soft matter systems.


S.EL13.07.10
Ultra-Thin Laminated Organic Field-Effect Transistors (OFETs) Based Flexible Devices

Zhenfei He and Paddy K. L. Chan; The University of Hong Kong, Hong Kong

Organic field-effect transistors (OFETs) based flexible electronic devices are the key players of the next generation wearable electronics. The conventional fabrication processes of flexible OFETs usually require layer by layer deposition which requires thermal and chemical compatibility among different layers. Fabrication errors induced in each layer will accumulate and eventually affect the overall performance of device. Here, we introduce a lamination method to fabricate ultra-thin flexible OFETs from separately prepared layers. Compared with the vacuum sublimated method where thin film Dinaphtho[2,3-b:2’,3’-f]thieno[3,2-b]thiophene (DNTT) is directly deposited onto the PEN substrate, the proposed method allows us to modify the growth mode of the DNTT by regulating the surface energy of the substrate, thus high crystallinity DNTT can be potentially obtained. Furthermore, the transferred gold electrodes onto the PMMA which can not only avoid
the thermal damage of the organic semiconductors, but also serve as the encapsulation layer for the OFET operation. We will show how to align the DNTT layer with the electrodes and top gate vertically under the microscope by lamination. Another major advantage of our lamination method is one can repeatedly using them onto different devices by delamination. The ultimate effective mobility of the flexible OFETs is targeting at 1.5 cm$^2$V$^{-1}$s$^{-1}$. Last but not least, the proposed method allows us to fabricate individual layers at the same time which in principle would also boost up the production efficiency. The ultra-flexible OFETs can achieve a bending radius of 2 mm or less without significant degradation in electrical performance.

S.EL13.07.09
Epitaxial Growth of Vertical Organic Single-Crystalline Heterojunctions on Graphene
Zixuan Guo, Enrique D. Gomez and Alejandro L. Brisenõ; The Pennsylvania State University, United States

Model heterojunctions have the potential to elucidate fundamental mechanisms for charge transfer at these interfaces. We demonstrate the epitaxial growth of single-crystalline p-n junctions on a graphene substrate using two organic small molecules: Zinc phthalocyanine (ZnPc) as a donor-type material (p-type), and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) as an acceptor-type material (n-type). The morphology of a p-n junction was demonstrated to vary upon deposition sequence, as an epitaxial PTCDA layer grown on top of ZnPc exhibits a nanopillar structure, while a ZnPc layer grown on PTCDA shows a bulk, island-like structure. The epitaxy mechanism follows a “point-on-line” rule where organic crystalline layers grow on top of each other by sensing and registering the spacings and periodicities of the lattice plane it grows on, which leads to different molecular packing motifs and resultant different morphologies. Preliminary grazing incidence wide-angle X-ray scattering (GIWAX) and high-resolution TEM studies show that both types of p-n junctions are highly orientated and molecules have a preferred face-on packing motif. This work together with conducting AFM results that show diode characteristics of p-n junctions in the dark suggest that graphene-templated p-n junctions can favor vertical charge carrier transport, and thus be suitable for use in organic photovoltaics (OPV). From this study, we can better understand the packing/orientation of molecules in vertically aligned nanostructures and how the geometrical arrangement, and resultant morphology, will affect the electronic properties and photovoltaic device design.

S.EL13.07.15
Electron and Hole Mobility in Graphene and Glassy Carbon-Based Transistors
Trevor Hunt and Sammuel Kassegne; San Diego State University, United States

Transistors have many uses for electrical systems including acting as a gate switch and enhancing signals. However most transistors are not compatible with biological systems due to the metallic materials they are made up of. For these instances, organic transistors made with carbon based materials are used. For my research I have been working on a similar carbon based FET (field effect transistor) using Glassy Carbon (GC) and Graphene (GR). With these two materials I hope to fabricate a transistor that will be compatible in biological systems as well as have high thermal and electrical properties as compared to conventional FET transistors. This type of transistor could be used to enhance electrochemical signals in vivo to act as a highly sensitive biosensor.

To test the properties of these combined materials, the electron mobility and resistivity was experimentally determined using the Hall Effect method along with Hall Bar type devices. Three devices were tested for the electron mobility; one fabricated with Graphene on top of Glassy Carbon and the other two were made with just a single layer of Glassy Carbon or Graphene respectively. A device made of gold was also tested as an experimental control. The transistors are characterized by determining the Transconductance, this is an electrical characteristic of transistors relating an output current with a given source voltage through the device. In order to determine the Transconductance of the transistor devices, numerous designs will be fabricated to test different sizes and design types. This will also be done with different material types (GR/GC, GC, and GR) similar to the mobility testing to have comparable results. Preliminary results from the Hall Experiments showed that the Graphene had the highest mobility and Glassy Carbon the lowest. The combination device (GR/GC) had a measured mobility between the two controls. These results show that the stacked material (GR/GC) has properties that lie between the two, which is typical of compound materials.

S.EL13.07.27
Novel A-D-A Type Compatibilizer for Thermally Stable Blend Morphology of Organic Solar Cells
Seungjin Lee¹, Geonu Kim¹, Nguyen Thanh Luan², Han Young Woo² and Bumjoon Kim¹; ¹KAIST, Korea (the Republic of); ²Korea University, Korea (the Republic of)

One of the biggest issues within BHJ light-harvesting films is macro-phase separation in domains of the donor and acceptor materials leading to severe PCE drop. To alleviate this problem, incorporating compatibilizer has been one solution by increasing adhesion between the phases, reducing the interfacial tension, and stabilizing morphology. In this study, a novel
acceptor–donor–acceptor (A−D−A) triad type small molecule (SM), 5TRh-PCBM, which has an oligothiophene segment as the central core and fullerene-derivatives as the end groups, was synthesized. 5TRh-PCBM was added and evaluated into traditional fullerene-based blend (P3HT:PCBM), and high-efficiency blend system (PTB7-Th:PCBM) and (PBDB-T:PCBM), respectively. Interestingly, with incorporating of 5TRh-PCBM, PCEs of PTB7-Th:PCBM;5TRh-PCBM blends were 9.37%(1:1.5:0), 10.09%(1:1.5:0.125), and 9.72%(1:1.5:0.25). Furthermore, thermal stability of PTB7-Th:PCBM;5TRh-PCBM (1:1.5:0.25) blend was improved retaining approximately 85% of its initial PCE at the annealing condition of 80°C for 120 hrs. Blend morphology was investigated through OM, GIWAXS, and RSoXS varying compatibilizer content ratio and annealing time. When 5TRh-PCBM was incorporated into each blend system, there were no apparent morphological transitions and macro-phase separation after thermal annealing. This thermally stable tolerance is likely due to the fullerene derivative end groups of 5TRh-PCBM as a binder which can prevent thermal diffusion of PCBM or PCBM and suppress its aggregation within each of the BHJ films. This compatibilization strategy demonstrated the useful guidelines of molecular engineering to achieve highly efficient and stable OSCs through controlling and stabilizing blend morphology.

S.EL13.07.25
Incorporating Nitrogen Atoms in Naphthalenediimide-Based Polymers for the Efficient Charge Generation, Device Performance and High Stability of All-Polymer Solar Cells Jin Su Park1, Sang Woo Kim1, Yang Wang2, Hoseon You1, Wonho Lee3, Tsuyoshi Michinobu2 and Bumjoon J. Kim1; 1Korea Advanced Institute of Science and Technology, Korea (the Republic of); 2Tokyo Institute of Technology, Japan; 3Kumoh National Institute of Technology, Korea (the Republic of)

Substitution of C atoms in a polymer backbone by N atoms allows for the facile tuning of the energy levels as well as the backbone conformation and packing structures of conjugated polymers. Herein, we report a series of three polymer acceptors (PAs) with N atoms introduced at different positions of the backbone, and investigate how these N atoms affect the device performances of all-polymer solar cells (all-PSCs). The three PAs, namely, P(NDI2DT-BTT), P(NDI2DT-PTT), and P(NDI2DT-BTTz), are composed of naphthalenediimide (NDI) and benzothiadiazole (BT)-based derivative (dithiophene-BT (BT), dithiophene-thiadiazolepyridine (PTT), and dithiazole-BT (BTzz)) units. The PTT and BTzz units are synthesized by replacing the C atoms in BT and thiophene, respectively, with N atoms, which effectively tune the optical, electrochemical, and charge-transporting properties of the corresponding PAs. The all-PSCs using PBDB-T as a polymer donor and P(NDI2DT-PTT) as the PA exhibit a significantly enhanced power conversion efficiency (PCE) of 6.95%, whereas the all-PSCs based on the other PAs show relatively lower PCEs (6.02% for PBDB-T:P(NDI2DT-BTT) and 1.43% for PBDB-T:P(NDI2DT-BTTz)). The high PCE of the PBDB-T:P(NDI2DT-PTT) device is due to superior charge transfer and charge dissociation, resulting from the closely-matched energy levels between PBDB-T and P(NDI2DT-PTT), as well as the more favorable BHJ morphology with improved miscibility. Importantly, the P(NDI2DT-PTT)-based all-PSC device shows improved air stability compared to the P(NDI2DT-BTT)-based device, which is most likely due to a decreased lowest unoccupied molecular orbital level of the PA. Our findings suggest that incorporation of N atoms into the PAs is an effective strategy for improving the efficiency and stability of all-PSCs.

S.EL13.07.23
Morphology Dependence of the Triplet Excited State in Platinum Containing Polyfluorene Copolymers Nikol Lambeva1, Moritz Riede1 and Donal D. Bradley2,1; 1University of Oxford, United Kingdom; 2King Abdullah University of Science and Technology, Saudi Arabia

Understanding the structure-property relationship of organic semiconducting polymers is critical for their future development for technological applications. To this end, studying suitable model systems is needed to expand our knowledge of how to modify the chemical structure of materials to get the desirable performance necessary for commercialization. The triplet states play a vital role in the optoelectronic properties of organic semiconductors with direct consequences for their use in devices. It is, thus, vital to have a deep understanding of the formation, transport and harvesting of triplet excitons in such materials. We report a photophysical study of a series of copolymers containing the light emitting polymer 9,9-diocetylfluorene (PFO). These comprise varying amounts (0.5, 1, 2.5 and 5%) of cyclometalated PyTPAP(acac) complex or the corresponding organic PyTPA ligand embedded into the backbone of the PFO. Interest in such compounds stems from the large enhancement in spin-orbit coupling induced by the heavy platinum atoms making triplet emission partially allowed. Additionally, the morphological diversity of PFO allows to study the effect of film morphology on the photophysics. We investigate the temperature dependence of the photoluminescence in the range between 5K and 300K as well as the room temperature electroluminescence. Strong emission quenching with increasing platinum content is observed in both the glassy and β phases of the fluorene moiety with phosphorescence only observed at low temperature. The phosphorescence is ascribed to fluorene triplet emission from its energy and linewidth. We explore how trapping at defects and bimolecular recombination affect the emission efficiency. Analysis of photoluminescence measurements at different
excitation intensities indicates triplet-triplet annihilation leading to emission losses while phosphorescence temperature
dependent intensity measurements demonstrate a
distribution of trap sites for the triplet excited state. Finally, at higher platinum contents triplet emission from both the planar
β phase and disordered glassy phase of PFO is observed despite fluorescence arising only from the β phase. We explore this
phenomenon in the context of energy transfer between the different excited state energy levels.

S.EL.13.07.21
Chain Conformation Control of a Polyfluorene-Based Copolymer for Improved OLED Performance Bingjun Wang1,
Moritz Riede1 and Donal D. Bradley1,2; 1University of Oxford, United Kingdom; 2King Abdullah University of Science and
Technology, Saudi Arabia

Poly(9,9-di-n-octyfluorenyl-2,7-diy), also known as PFO, is one of the most well-studied light emission polymers which
can exhibit different microstructures depending on processing methods and conditions. One microstructure that attracts much
attention is β-phase, in which the intermonomer torsion angle is ~180°, resulting in a planar-zigzag chain conformation.
Researchers have shown that with a very small amount of β-phase in PFO (~1.3%), the luminance and external quantum
efficiency (EQE) of OLEDs can triple[1]. In this work, we report on the generation of β-phase in a 10% benzothiadiazole-
containing PFO-based copolymer, poly[(9,9-di-n-octyfluorenyl-2,7-diy)-co-(1,4-benzo-{2,1’,3’}-thiadiazole)] (ADS233YE),
and the improvements in OLED performance that ensue.

The β-phase was induced into ADS233YE thin films by either solvent vapour annealing or dipping the sample in a
solvent/non-solvent mixture. The existence of β-phase was confirmed by absorption spectra, and both photoluminescence
(PL) spectra and photoluminescence quantum efficiencies (PLQE) of pristine and β-phase-containing samples were measured
and compared. ADS233YE OLEDs with β-phase were found to perform better than without, including luminance (at 10 V,
5000 cd m⁻² to 5700 cd m⁻², i.e. 14% increase), EQE (peak value, 1.09% to 1.93%, i.e. 77% increase), luminance efficiency
(peak value, 3.96 cd A⁻¹ to 6.26 cd A⁻¹, i.e. 58% increase), and luminous power efficiency (peak value, 2.20 lm W⁻¹ to 3.69
lm W⁻¹, i.e. 68% increase). Possible reasons for these enhancements include a lower ionisation potential in β-phase-
containing samples due to an extension of the conjugation length, more balanced hole and electron mobility caused by the
self-doping effect of β-phase chain segments, and more efficient energy transfer from fluorene to benzothiadiazole moieties,
mediated by the β-phase, all of which are currently being investigated.

Our study shows that controlling chain conformation by inducing β-phase into a PFO-based copolymer can be a simple but
effective way to boost OLED performance. It will be interesting to see if this approach can be generalised to other PFO-
derivatives and even other polymer families, providing us with new options to optimise OLED devices.

Reference:

S.EL.13.07.31
Impact of Non-Halogenated Solvent Additives and Slot-Die Coating Processing on Perylene Diimide Based Active
Layers Morphology Francesco Tintori, Audrey Laventure and Gregory C. Welch; University of Calgary, Canada

Perylene diimide (PDI) derivatives are organic semiconductor that, among others, have been identified as one of the best
classes of non-fullerene acceptors (NFAs) for organic photovoltaic (OPV) devices, with the best power conversion efficiency
surpassing 10%.[1] Recently, our group has developed a series of N-annulated PDI dimers, that have demonstrated excellent
processability from all types of solvents, including environmentally friendly 2-Me-THF and 2-Me-anisole, and can achieve
respectable performances in OPV devices.[2-4] The synthetic methods required to produce some of these have proven to be
scalable and efficient, making them excellent candidates for the up-scaling of green printed electronic devices. We had
previously identified one of said PDI dimers, with ethyl-hexyl side chains on the pyrrolic position, to be a suitable NFA for
green solvent and air processed OPV.[3]

This presentation will first discuss the rather unique self-assembly properties of this specific PDI NFA under the influence of
processing solvent additives such as 1,8-diiodooctane (DIO), which can cause the crystallization of the molecular material in
a polymeric matrix. This phenomenon was studied, and the aggregation effect was controlled under specific conditions using
the benchmark polymer P3HT.[4] To further investigate these findings and probe the phenomenon impact on a higher
performing, and potentially scalable system, we identified a suitable medium band-gap benzothiophene-quinoxaline
polymer. The presentation will then focus on our effort to understand this system and translate it to scalable processing. First,
diphenyl ether (DPE) was selected as a non-halogenated counterpart to DIO to make our system completely halogen-free, and
effect of DPE on the PDI molecular material was studied. Then, a comparison of spin-coated and slot-die coated active layer films was made looking at film properties, morphology evolution and OPV device performance. We identified dependencies between these parameters and the selected coating method and worked with slot-die coating to obtain superior OPV results. The results obtained demonstrated that solvent additives might play an additional beneficial role in the device fabrication of printed organic active layers, highlighting the need of further exploration of additives with dual or even multiple functions to optimize the processing involved in green printed electronics.[5]


S.E13.07.33
Scalable Fabrication of High Mobility Monolayer OFETs Using Floating Film Transfer Thomas M. Steckmann, Masrur Morshed Nahid, Abay Gadisa and Harald Ade; North Carolina State University, United States

Traditionally, the fabrication of ultrathin organic field-effect transistors (OFETs) is limited by both poor electrical performance in devices with fewer than 2-5 molecular layers and poor scalability of these methods. Here, we employ a floating film transfer method which uses the spontaneous spreading of polymer solutions over the surface of a green solvent to fabricate floating large area, highly uniform monolayer films which can be transferred to an arbitrary substrate for use in organic electronic devices. This method enables achieving high charge carrier mobility in material-efficient ultrathin films, which is comparable with values achieved in spin-cast thick film.

S.E13.07.36
Screening of Organic Solar Cell Materials Using Contactless Photoconductivity Measurements Supriya Pillai1, Chao Wang2, Chris McNeill2, Mats Anderson2 and Nikos Kopidakis1; 1Macquarie University, Australia; 2Monash University, Australia; 3Flinders University, Australia

Introduction: The photovoltaic market is growing and although Silicon solar cells is considered to be the dominant technology, there is significant interest in research and development of other low-cost novel technologies. Organic Solar Cells (OSCs) has a niche market that require lightweight and flexible structures however their application is still limited because of low efficiencies and stability issues when compared to their inorganic counterparts. OSCs can clearly be a low cost technology, but to be able to take it to commercialisation, there is a need to develop new and efficient materials that are both stable and scalable. One of the great advantages of organic solar cells is the myriad of combinations of polymer materials that can be easily synthesised to form donor-acceptor blends, but the key is the performance in a device architecture.

Background: Currently, the organic blends need to be tested through trial and error and by fabricating the full devices which needs time and effort. In this work, we use the contactless technique of Time resolved microwave conductivity (TRMC) that can be used as a powerful diagnostic characterisation tool to screen and select the most promising materials and organic blend ratio before it goes into the device fabrication stage. It uses a pump-probe technique to measure the transient change in the microwave reflectivity of a sample inside a microwave cavity in the dark and when pumped with light, usually a laser pulse. The relative change in the absorbed microwave power from the dark signal to the excited signal is directly proportional to the photoconductance. Apart from being a contactless technique, it is also a non-intrusive photo-conductivity measurement technique that can measure dynamics of charge carrier generation and recombination and also study post-bleaching behaviour.

Method: To validate the TRMC as a screening tool, we identify a few blend materials from literature with known efficiencies and compare the TRMC figure of merit with the device efficiency results. The donor-acceptor blend samples for the TRMC are prepared by spin coating or blade coating on quartz substrates. To investigate the material properties better, photoconductivity decay analysis is also performed and photocarrier lifetimes are extracted. The ‘figure of merit’ for TRMC measurements used to evaluate the quality of the absorber material will be discussed and some preliminary results of screening a few polymer blends will be presented.
Conclusion: Our results so far show that there is a clear correlation between material quality and TRMC figure of merit and its extracted parameters. Hence TRMC characterisation can be used as a fast and high throughput technique to screen new polymer blends and predict device performance.

SESSION S.LP02.06: Live Poster Session: Electronics and Photonics (S.EL13 and S.EL14)
Session Chairs: Brian Collins and Xiaodan Gu
Monday Afternoon, November 30, 2020
7:30 PM - 9:30 PM
S.EL13

S.EL13.07.03
Understanding the Processing Variables under Meniscus-Line-Guided Coating Ming Chen and Paddy K. L. Chan; University of Hong Kong, Hong Kong

Solution processable meniscus-line-guided (MGC) coating is an excellent candidate to realize highly crystallized organic semiconductor thin films in the fabrication of organic field effect transistors (OFETs). The basic processing parameters, including shearing speed ($v$), concentration ($c$), solvent boiling point ($T_b$) and deposition temperature ($T$), are pivotal to achieve fine control over the crystallinity of the deposited organic thin films and therefore, understanding of the interconnections between these parameters are highly desired. Here, we examine the effects of different fabrication factors on the crystal deposition rate systematically under MGC approach. The active layer material in current study is the 2,7-Diocytl[1]benzothieno[3,2-b][1]benzothiophene (C$_8$-BTBT) organic semiconductor. It is verified that $v$ and $c$ are connected to crystal deposition rate by means of mass conservation. The crystal deposition rate is further related to $T$ and latent heat ($L$, proportional to $T_b$) in the Arrhenius form. Furthermore, the optimum organic thin film (roughness $R_q < 0.25$ nm and average mobility $\mu_{ave} = 5.88$ cm$^2$ V$^{-1}$ s$^{-1}$) is achieved under a mass transfer rate of $6 \times 10^{-11}$ kg s$^{-1}$ to $15 \times 10^{-11}$ kg s$^{-1}$. Our findings provide valuable information in understanding the crystal growth under the MGC method, which is believed to be one of the highest potential approaches for the mass production of OFETs.

S.EL13.07.05
The Fabrication of the Organic Field-Effect Transistor Device at the Atomic Force Microscopy Probe Shui Hong Siddhartha Dai and Paddy K. L. Chan; The University of Hong Kong, Hong Kong

Sample surface potential measurement is one of the important topics for material research. The state-of-art surface measure technologies are Kelvin Probe Force Microscope (KPFM) and Electrostatic Force Microscope (EFM). Although those technologies can measure the surface of the sample in nanoscale, the equipment, in general, is sensitive to the environment due to the measurement noise and require extra amplifiers to improve the signal-to-noise ratio. This research aims at functionalizing the AFM probes by integrating an OFET onto the tip for localized electrical signal amplification. The OFET-AFM tip structure includes the source, drain, organic semiconductor and dielectric coating. The patterning of the source and drain electrodes are developed by the Focused Ion Beam (FIB). The meniscus-guided solution-processing method is employed to grow ultrathin (~30 nm) C$_{10}$-DNTT crystal which will be transferred to the electrodes by the FIB milling method. We believe the ultrathin organic semiconductor crystal allows the contact resistance between electrodes and semiconductors to be low enough (< 100 $\Omega$cm) for decent transistor operation. Furthermore, the FIB milling can minimize the thermal damage, which is caused by the thermal evaporation of metal to the organic semiconductor during the fabrication process. As a result, building up a small scale (channel length less than 2 micrometer) OFET device at the AFM tip becomes possible. The Parylene coating (~500 nm) serves as the dielectric layer of the OFET and allows the OFET-AFM probe to measure the voltage signal from the sample surface. The surface potential of the probe will act as the gate bias of the OFET, thus to control the channel current of the device. We believe the OFET-AFM probe can open up a new direction in small scale biomedical applications.

S.EL13.07.06
Phototransistors Based on a Lightly Doped P3HT Thomas H. Debesay and Sam-Shajing Sun; Norfolk State University, United States

Organic/Polymeric Semiconductor (OSC) based devices have been under extensive study for the past three decades due to their intrinsic potential advantages such as lightweight, flexible, biocompatible, low toxicity, abundant material availability,
The non-invasive, in operando characterization of opto-electronic properties of organic semiconductors is of special interest as it enables information on microscopic processes governing the performance of a device and sheds light on its real lifecycle.

In this contribution we present a new approach to cope with this challenge by utilizing fluorescent Tetraphenyl dibenzoperiflanthene (DBP) molecules as optically addressable sensors, deterministically positioned at very low concentration within archetypical N,N-di-(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine/Tris(8-hydroxyquinolato)aluminium (NPB/Alq3) organic light-emitting diodes (OLEDs) as model system.

Observing variations in fluorescence intensity of the optically excited DBP sensor molecules during device operation allows for a correlation with the charge carrier distribution within a dynamic range of four orders of magnitude in current density (10^-4 – 10^6 mA/cm²) under forward bias [1]. Due to the deliberate incorporation of the molecular probes at a well-defined depth within the OLED stack as well as utilization of a µ-photoluminescence technique this information is gathered with nanometer length scale resolution. The resolution is determined by opto-electronic processes like Langevin capture of injected charge carriers and Förster type resonant energy transfer and can be estimated to around 15 nm. Under reverse bias condition the molecular sensing method proves sensitive to uncompensated dipoles at the NPB/Alq3 heterointerface, which results from the preferential orientation of the molecular Alq3 dipoles during layer deposition [2]. The optical data is substantiated by complementary macroscopic impedance measurements performed on identical devices. In conjunction with the impedance measurement, drift-diffusion simulations [3] of the OLED stack characteristics are carried out to further corroborate the correlation between the observed photoluminescence changes and the opto-electronic device properties.

The broad variety of molecular host-guest systems, renders this approach a universal tool for analyzing not only opto-electronic phenomena in many different organic electronic device structures but, for example, also in biological soft matter systems.


S.EL13.07.09 Epitaxial Growth of Vertical Organic Single-Crystalline Heterojunctions on Graphene Zixuan Guo, Enrique D. Gomez and Alejandro L. Briseno; The Pennsylvania State University, United States

Model heterojunctions have the potential to elucidate fundamental mechanisms for charge transfer at these interfaces. We demonstrate the epitaxial growth of single-crystalline p-n junctions on a graphene substrate using two organic small molecules: Zinc phthalocyanine (ZnPc) as a donor-type material (p-type), and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) as an acceptor-type material (n-type). The morphology of a p-n junction was demonstrated to vary upon deposition sequence, as an epitaxial PTCDA layer grown on top of ZnPc exhibits a nanopillar structure, while a ZnPc layer grown on PTCDA shows a bulk, island-like structure. The epitaxy mechanism follows a “point-on-line” rule where organic crystalline layers grow on top of each other by sensing and registering the spacings and periodicities of the lattice plane it grows on, which leads to different molecular packing motifs and resultant different morphologies. Preliminary grazing incidence wide-angle X-ray scattering (GIWAX) and high-resolution TEM studies show that both types of p-n junctions are highly orientated and molecules have a preferred face-on packing motif. This work together with conducting AFM results that show diode characteristics of p-n junctions in the dark suggest that graphene-templated p-n junctions can favor vertical charge carrier

2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
Researchers have shown that with a very small amount of attention is efficiency (EQE) of OLEDs can triple[1]. In this work, we report on the generation of Moritz Riede1 and Donal D. Bradley1,2; 1University of Oxford, United Kingdom; 2King Abdullah University of Science and Technology, Saudi Arabia.

Ultra-Thin Laminated Organic Field-Effect Transistors (OFETs) Based Flexible Devices Zhenfei He and Paddy K. L. Chan; The University of Hong Kong, Hong Kong

Organic field-effect transistors (OFETs) based flexible electronic devices are the key players of the next generation wearable electronics. The conventional fabrication processes of flexible OFETs usually require layer by layer deposition which requires thermal and chemical compatibility among different layers. Fabrication errors induced in each layer will accumulate and eventually affect the overall the performance of device. Here, we introduce a lamination method to fabricate ultra-thin flexible OFETs from separately prepared layers. Compared with the vacuum sublimated method where thin film Dinaphtho[2,3-b:2¢,3¢-f]thieno[3,2-b]thiophene (DNTT) is directly deposited onto the PEN substrate, the proposed method allows us to modify the growth mode of the DNTT by regulating the surface energy of the substrate, thus high crystallinity DNTT can be potentially obtained. Furthermore, the transferred gold electrodes onto the PMMA which can not only avoid the thermal damage of the organic semiconductors, but also serve as the encapsulation layer for the OFET operation. We will show how to align the DNTT layer with the electrodes and top gate vertically under the microscope by lamination. Another major advantage of our lamination method is one can repeatedly using them onto different devices by delamination. The ultimate effective mobility of the flexible OFETs is targeting at 1.5 cm²V⁻¹s⁻¹. Last but not least, the proposed method allows us to fabricate individual layers at the same time which in principle would also boost up the production efficiency. The ultra-flexible OFETs can achieve a bending radius of 2 mm or less without significant degradation in electrical performance.

Electron and Hole Mobility in Graphene and Glassy Carbon-Based Transistors Trevor Hunt and Sammuel Kassegne; San Diego State University, United States

Transistors have many uses for electrical systems including acting as a gate switch and enhancing signals. However most transistors are not compatible with biological systems due to the metallic materials they are made up of. For these instances, organic transistors made with carbon based materials are used. For my research I have been working on a similar carbon based FET (field effect transistor) using Glassy Carbon (GC) and Graphene (GR). With these two materials I hope to fabricate a transistor that will be compatible in biological systems as well as have high thermal and electrical properties as compared to conventional FET transistors. This type of transistor could be used to enhance electrochemical signals in vivo to act as a highly sensitive biosensor.

To test the properties of these combined materials, the electron mobility and resistivity was experimentally determined using the Hall Effect method along with Hall Bar type devices. Three devices were tested for the electron mobility; one fabricated with Graphene on top of Glassy Carbon and the other two were made with just a single layer of Glassy Carbon or Graphene respectively. A device made of gold was also tested as an experimental control. The transistors are characterized by determining the Transconductance, this is an electrical characteristic of transistors relating an output current with a given source voltage through the device. In order to determine the Transconductance of the transistor devices, numerous designs will be fabricated to test different sizes and design types. This will also be done with different material types (GR/GC, GC, and GR) similar to the mobility testing to have comparable results. Preliminary results from the Hall Experiments showed that the Graphene had the highest mobility and Glassy Carbon the lowest. The combination device (GR/GC) had a measured mobility between the two controls. These results show that the stacked material (GR/GC) has properties that lie between the two, which is typical of compound materials.

Chain Conformation Control of a Polyfluorene-Based Copolymer for Improved OLED Performance Bingjun Wang1, Moritz Riede1 and Donal D. Bradley1,2; 1University of Oxford, United Kingdom; 2King Abdullah University of Science and Technology, Saudi Arabia

Poly(9,9-di-octylfluorenyl-2,7-diyl), also known as PFO, is one of the most well-studied light emission polymers which can exhibit different microstructures depending on processing methods and conditions. One microstructure that attracts much attention is β-phase, in which the intermonomer torsion angle is ~180°, resulting in a planar-zigzag chain conformation. Researchers have shown that with a very small amount of β-phase in PFO (~1.3%), the luminance and external quantum efficiency (EQE) of OLEDs can triple[1]. In this work, we report on the generation of β-phase in a 10% benzothiadiazole-containing PFO-based copolymer, poly[(9,9-di-octylfluorenyl-2,7-diyl)-co-(1,4-benzo-2,1’,3’-thiadiazole)] (ADS233YE),...
and the improvements in OLED performance that ensue.

The β-phase was induced into ADS233YE thin films by either solvent vapour annealing or dipping the sample in a solvent/non-solvent mixture. The existence of β-phase was confirmed by absorption spectra, and both photoluminescence (PL) spectra and photoluminescence quantum efficiencies (PLQE) of pristine and β-phase-containing samples were measured and compared. ADS233YE OLEDs with β-phase were found to perform better than without, including luminance (at 10 V, 5000 cd m⁻² to 5700 cd m⁻², i.e. 14% increase), EQE (peak value, 1.09% to 1.93%, i.e. 77% increase), luminance efficiency (peak value, 3.96 cd A⁻¹ to 6.26 cd A⁻¹, i.e. 58% increase), and luminous power efficiency (peak value, 2.20 lm W⁻¹ to 3.69 lm W⁻¹, i.e. 68% increase). Possible reasons for these enhancements include a lower ionisation potential in β-phase-containing samples due to an extension of the conjugation length, more balanced hole and electron mobility caused by the self-doping effect of β-phase chain segments, and more efficient energy transfer from fluorene to benzothiadiazole moieties, mediated by the β-phase, all of which are currently being investigated.

Our study shows that controlling chain conformation by inducing β-phase into a PFO-based copolymer can be a simple but effective way to boost OLED performance. It will be interesting to see if this approach can be generalised to other PFO-derivatives and even other polymer families, providing us with new options to optimise OLED devices.

Reference:

S.EL13.07.23
Morphology Dependence of the Triplet Excited State in Platinum Containing Polyfluorene Copolymers Nikol Lambeva¹, Moritz Riedel¹ and Donal D. Bradley²,¹; ¹University of Oxford, United Kingdom; ²King Abdullah University of Science and Technology, Saudi Arabia

Understanding the structure-property relationship of organic semiconducting polymers is critical for their future development for technological applications. To this end, studying suitable model systems is needed to expand our knowledge of how to modify the chemical structure of materials to get the desirable performance necessary for commercialization. The triplet states play a vital role in the optoelectronic properties of organic semiconductors with direct consequences for their use in devices. It is, thus, vital to have a deep understanding of the formation, transport and harvesting of triplet excitons in such materials. We report a photophysical study of a series of copolymers containing the light emitting polymer 9,9-diocetylfluorene (PFO). These comprise varying amounts (0.5, 1, 2.5 and 5%) of cyclometalated PyTPA Pt(acac) complex or the corresponding organic PyTPA ligand embedded into the backbone of the PFO. Interest in such compounds stems from the large enhancement in spin-orbit coupling induced by the heavy platinum atoms making triplet emission partially allowed. Additionally, the morphological diversity of PFO allows to study the effect of film morphology on the photophysics. We investigate the temperature dependence of the photoluminescence in the range between 5K and 300K as well as the room temperature electroluminescence. Strong emission quenching with increasing platinum content is observed in both the glassy and β phases of the fluorene moiety with phosphorescence only observed at low temperature. The phosphorescence is ascribed to fluorene triplet emission from its energy and linewidth. We explore how trapping at defects and bimolecular recombination affect the emission efficiency. Analysis of photoluminescence measurements at different excitation intensities indicates triplet-triplet annihilation leading to emission losses while phosphorescence temperature dependent intensity measurements demonstrate a distribution of trap sites for the triplet excited state. Finally, at higher platinum contents triplet emission from both the planar β phase and disordered glassy phase of PFO is observed despite fluorescence arising only from the β phase. We explore this phenomenon in the context of energy transfer between the different excited state energy levels.

S.EL13.07.25
Incorporating Nitrogen Atoms in Naphthalenediimide-Based Polymers for the Efficient Charge Generation, Device Performance and High Stability of All-Polymer Solar Cells Jin Su Park¹, Sang Woo Kim¹, Yang Wang², Hoseon You¹, Wonho Lee³, Tsuyoshi Michinobu² and Bumjoon J. Kim¹; ¹Korea Advanced Institute of Science and Technology, Korea (the Republic of); ²Tokyo Institute of Technology, Japan; ³Kumoh National Institute of Technology, Korea (the Republic of)

Substitution of C atoms in a polymer backbone by N atoms allows for the facile tuning of the energy levels as well as the backbone conformation and packing structures of conjugated polymers. Herein, we report a series of three polymer acceptors (P₃S₈) with N atoms introduced at different positions of the backbone, and investigate how these N atoms affect the device performances of all-polymer solar cells (all-PSCs). The three P₃S₈, namely, P(NDI2DT-BT), P(NDI2DT-PTT), and P(NDI2DT-BTTz), are composed of naphthalenediimide (NDI) and benzothiadiazole (BT)-based derivative (dithiophene-BT...
films was made looking at film properties, morphology evolution and OPV device performance. We identified dependencies on the effect of DPE on the PDI molecular material was studied. Then, a comparison of spin-coated and slot-die coated active layer between these parameters and the selected coating method and worked with slot-die coating to obtain superior OPV results. Likely due to the fullerene derivative end groups of 5TRh-PCBM as a binder which can prevent thermal diffusion of PC61BM and apparent morphological transitions and macro-phase separation after thermal annealing. This thermally stable tolerance is compatibilizer content ratio and annealing time. When 5TRh-PCBM was incorporated into each blend system, there were no respectable performances in OPV devices.[2-4] The synthetic methods required to produce some of these have proven to be performing, and potentially scalable system, we identified a suitable medium band-gap benzodithiophene-quinoxaline polymer. The presentation will then focus on our effort to understand this system and translate it to scalable processing. First, the benchmark polymer P3HT.[4] To further investigate these findings and probe the phenomenon impact on a higher processing solvent additives such as 1,8-diiodooctane (DIO), which can cause the crystallization of the molecular material in P(NDI2DT-BTT), dithiophene-thiazolepyridine (PTT), and dithiazole-BT (BTTz) units. The PTT and BTTz units are synthesized by replacing the C atoms in BT and thiophene, respectively, with N atoms, which effectively tune the optical, electrochemical, and charge-transporting properties of the corresponding PAs. The all-PSCs using PBDB-T as a polymer donor and P(NDI2DT-PTT) as the PA exhibit a significantly enhanced power conversion efficiency (PCE) of 6.95%, whereas the all-PSCs based on the other PAs show relatively lower PCEs (6.02% for PBDB-T:P(NDI2DT-BTT) and 1.43% for PBDB-T:P(NDI2DT-BTTz)). The high PCE of the PBDB-T:P(NDI2DT-PTT) device is due to superior charge transfer and charge dissociation, resulting from the closely-matched energy levels between PBDB-T and P(NDI2DT-PTT), as well as the more favorable BHJ morphology with improved miscibility. Importantly, the P(NDI2DT-PTT)-based all-PSC device shows improved air stability compared to the P(NDI2DT-BTT)-based device, which is most likely due to a decreased lowest unoccupied molecular orbital level of the PA. Our findings suggest that incorporation of N atoms into the PAs is an effective strategy for improving the efficiency and stability of all-PSCs.

S.EL13.07.27
Novel A-D-A Type Compatibilizer for Thermally Stable Blend Morphology of Organic Solar Cells Seungjin Lee1, Geonu Kim1, Nguyen Thanh Luan2, Han Young Woo2 and Bumjoon Kim1; 1KAIST, Korea (the Republic of); 2Korea University, Korea (the Republic of)

One of the biggest issues within BHJ light-harvesting films is macro-phase separation in domains of the donor and acceptor materials leading to severe PCE drop. To alleviate this problem, incorporating compatibilizer has been one solution by increasing adhesion between the phases, reducing the interfacial tension, and stabilizing morphology. In this study, a novel acceptor–donor–acceptor (A–D–A) triad type small molecule (SM), 5TRh-PCBM, which has an oligothiophene segment as the central core and fullerene-derivatives as the end groups, was synthesized. 5TRh-PCBM was added and evaluated into traditional fullerene-based blend (P3HT:PC61BM), and high-efficiency blend system (PTB7-Th:PC71BM) and (PBDB-T:PC71BM), respectively. Interestingly, with incorporating of 5TRh-PCBM, PCEs of PTB7-Th:PC71BM:5TRh-PCBM blends were 9.37%(1:1.5:0), 10.09%(1:1.5:0.125), and 9.72%(1:1.5:0.25). Furthermore, thermal stability of PTB7-Th:PC71BM:5TRh-PCBM blend was improved retaining approximately 85% of its initial PCE at the annealing condition of 80°C for 120 hrs. Blend morphology was investigated through OM, GIWAXS, and RSoXS varying compatibilizer content ratio and annealing time. When 5TRh-PCBM was incorporated into each blend system, there were no apparent morphological transitions and macro-phase separation after thermal annealing. This thermally stable tolerance is likely due to the fullerene derivative end groups of 5TRh-PCBM as a binder which can prevent thermal diffusion of PC61BM (or PC71BM) and suppress its aggregation within each of the BHJ films. This compatibilization strategy demonstrated the useful guidelines of molecular engineering to achieve highly efficient and stable OSCs through controlling and stabilizing blend morphology.

S.EL13.07.31
Impact of Non-Halogenated Solvent Additives and Slot-Die Coating Processing on Perylene Diimide Based Active Layers Morphology Francesco Tintori, Audrey Laventure and Gregory C. Welch; University of Calgary, Canada

Perylene diimide (PDI) derivatives are organic semiconductor that, among others, have been identified as one of the best classes of non-fullerene acceptors (NFAs) for organic photovoltaic (OPV) devices, with the best power conversion efficiency surpassing 10%.[1] Recently, our group has developed a series of N-annulated PDI dimers, that have demonstrated excellent processability from all types of solvents, including environmentally friendly 2-Me-THF and 2-Me-anisole, and can achieve respectable performances in OPV devices.[2-4] The synthetic methods required to produce some of these have proven to be scalable and efficient, making them excellent candidates for the up-scaling of green printed electronic devices. We had previously identified one of said PDI dimers, with ethyl-hexyl side chains on the pyrrolic position, to be a suitable NFA for green solvent and air processed OPV.[3]

This presentation will first discuss the rather unique self-assembly properties of this specific PDI NFA under the influence of processing solvent additives such as 1,8-diiodooctane (DIO), which can cause the crystallization of the molecular material in a polymeric matrix. This phenomenon was studied, and the aggregation effect was controlled under specific conditions using the benchmark polymer P3HT.[4] To further investigate these findings and probe the phenomenon impact on a higher performing, and potentially scalable system, we identified a suitable medium band-gap benzodithiophene-quinoxaline polymer. The presentation will then focus on our effort to understand this system and translate it to scalable processing. First, diphenyl ether (DPE) was selected as a non-halogenated counterpart to DIO to make our system completely halogen-free, and effect of DPE on the PDI molecular material was studied. Then, a comparison of spin-coated and slot-die coated active layer films was made looking at film properties, morphology evolution and OPV device performance. We identified dependencies between these parameters and the selected coating method and worked with slot-die coating to obtain superior OPV results.
The results obtained demonstrated that solvent additives might play an additional beneficial role in the device fabrication of printed organic active layers, highlighting the need of further exploration of additives with dual or even multiple functions to optimize the processing involved in green printed electronics.[5]


S.EL13.07.33
Scalable Fabrication of High Mobility Monolayer OFETs Using Floating Film Transfer Thomas M. Steckmann, Masrur Morshed Nahid, Abay Gadisa and Harald Ade; North Carolina State University, United States

Traditionally, the fabrication of ultrathin organic field-effect transistors (OFETs) is limited by both poor electrical performance in devices with fewer than 2-5 molecular layers and poor scalability of these methods. Here, we employ a floating film transfer method which uses the spontaneous spreading of polymer solutions over the surface of a green solvent to fabricate floating large area, highly uniform monolayer films which can be transferred to an arbitrary substrate for use in organic electronic devices. This method enables achieving high charge carrier mobility in material-efficient ultrathin films, which is comparable with values achieved in spin-cast thick film.

S.EL13.07.36
Screening of Organic Solar Cell Materials Using Contactless Photoconductivity Measurements Supriya Pillai¹, Chao Wang², Chris McNeill², Mats Anderson¹ and Nikos Kopidakis¹; ¹Macquarie University, Australia; ²Monash University, Australia; ³Flinders University, Australia

Introduction: The photovoltaic market is growing and although Silicon solar cells is considered to be the dominant technology, there is significant interest in research and development of other low-cost novel technologies. Organic Solar Cells (OSCs) has a niche market that require lightweight and flexible structures however their application is still limited because of low efficiencies and stability issues when compared to their inorganic counterparts. OSCs can clearly be a low cost technology, but to be able to take it to commercialisation, there is a need to develop new and efficient materials that are both stable and scalable. One of the great advantages of organic solar cells is the myriad of combinations of polymer materials that can be easily synthesised to form donor-acceptor blends, but the key is the performance in a device architecture.

Background: Currently, the organic blends need to be tested through trial and error and by fabricating the full devices which needs time and effort. In this work, we use the contactless technique of Time resolved microwave conductivity (TRMC) that can be used as a powerful diagnostic characterisation tool to screen and select the most promising materials and organic blend ratio before it goes into the device fabrication stage. It uses a pump-probe technique to measure the transient change in the microwave reflectivity of a sample inside a microwave cavity in the dark and when pumped with light, usually a laser pulse. The relative change in the absorbed microwave power from the dark signal to the excited signal is directly proportional to the photoconductance. Apart from being a contactless technique, it is also a non-intrusive photo-conductivity measurement technique that can measure dynamics of charge carrier generation and recombination and also study post-bleaching behaviour.

Method: To validate the TRMC as a screening tool, we identify a few blend materials from literature with known efficiencies and compare the TRMC figure of merit with the device efficiency results. The donor-acceptor blend samples for the TRMC are prepared by spin coating or blade coating on quartz substrates. To investigate the material properties better, photoconductivity decay analysis is also performed and photocarrier lifetimes are extracted. The ‘figure of merit’ for TRMC measurements used to evaluate the quality of the absorber material will be discussed and some preliminary results of screening a few polymer blends will be presented.

Conclusion: Our results so far show that there is a clear correlation between material quality and TRMC figure of merit and its extracted parameters. Hence TRMC characterisation can be used as a fast and high throughput technique to screen new polymer blends and predict device performance.
S.EL14.07.03
Exploring Additive Effects on Charge Generation in a PM6:Y6 Organic Solar Cells
Awwad N. Alotaibi1, Xaiobo Zhou2, Brian A. Collins1,2 and Ma Wei2; 1Washington State University, United States; 2Xi’an Jiaotong University, China

Organic solar cells (OSCs) are promising as an alternative solar energy technology and their efficiencies are continuously increasing, with record power conversion efficiency at ~ 17%. The processes involved in charge generation and recombination in the bulk heterojunction active layer govern device performance. However, these processes are all entangled and hard to measure quantitatively, which limits progress in optimizing the ultimate performance. We use time delay collection field (TDCF) to disentangle and fully quantify each process occurring in the current record OSC system PM6:Y6 as a function of processing co-solvent, chloronapthalene, concentration. TDCF is an advanced charge extraction technique that can separate charge generation and recombination processes. We use this to measure generation current, recombination current, and extraction current all at the operating condition of the OSC devices, fully quantifying each loss process. A field dependence of charge generation indicates geminate recombination and our measurements show that the additive eliminates this loss process in PM6:Y6. We additionally vary the excitation wavelength to selectively excite the accepter and the donor molecules. Our initial result suggests that the excited Y6 acceptor generates relatively less charge than the PM6 donor. This new understanding of charge generation and recombination processes will help in design of new materials and optimization of device fabrication for high-performance, economical, and massively scalable solar power.

S.EL14.07.04
Towards In Situ Measurement of Nanostructure Dynamics During Ion Transport within a Conducting Polymer
Tamanna T. Khan1, Terry McAfee1,2, Thomas Ferron1 and Brian A. Collins1; 1Washington State University, United States; 2Lawrence Berkeley National Laboratory, United States

Ion transport in organic materials is attracting tremendous attention due to the possibilities in applications such as electrochemical transistors, bioelectronics, sensors, soft robotics, and printed electronics. Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) shows promise as an ion transport material and has been integrated into biomedical applications while the nano-structure that enables this property is still unknown. Our previous study utilized Resonant Soft X-ray Scattering (RSoXS) which affords orders of magnitude higher contrast at an elemental absorption edge than electron or nonresonant X-ray techniques. There we showed the morphology consists of PEDOT-rich gel particles embedded within a PSS matrix and upon the addition of a co-solvent (Ethylene glycol) the PEDOT domains swell which was found to correlate with a reduction in ion flow. However, the measured nanostructures were dry and undoped, which do not directly demonstrate which domain facilitates ion flow. Here we will present our progress toward an in-situ RSoXS investigation of a PEDOT:PSS electrochemical transistor during ion transport. We will utilize an in-vacuum, microfluidic sample environment that is compatible with the newly developed RSoXS liquid-chamber at the Advanced Light Source. To achieve this goal, we modified the electrochemical device architecture and replaced the insulating ion barrier with no appreciable reduction in ion transport capabilities. Additionally, the fabrication of a miniaturized device on a micro-electromechanical system (MEMS) chip is under development. Understanding how the ions interact with the nano-structure to transduce an electric signal will enable these devices to potentially use in next generation medical devices.

S.EL14.07.05
Imaging the Spatial Distribution of Molecular Dopants in Organic Semiconductors at High Spatial Resolution Using Electron Microscopy
Gustav Persson, Sepideh Zokaei, Renée Kroon, Christian Muller and Eva M. Olsson; Chalmers University of Technology, Sweden

Electronic devices based on organic semiconductors have great potential for future applications in devices for energy harvesting and electronics due to low costs, mechanical flexibility and tunable properties. Molecular doping of organic semiconductors is fundamental in order to optimize their electronic properties in high performance devices such as photovoltaic cells, thermoelectrics or light emitting diodes. However, the spatial distribution of these dopants is not completely controlled.[1] Previous studies have shown how density, distribution and diffusion of dopants can significantly affect electronic properties, disrupt the microstructure[2] and decrease long term stability of the host polymer.[3] Electron microscopy has been used successfully in multiple studies characterizing organic semiconductor materials and extracting information with high spatial resolution. However, crucial information about the distribution of dopants and its
dependence of the structure of the surrounding material still remains to be investigated with high spatial resolution. This work addresses the fine scale distribution of molecular dopants in a polar polythiophene with oligoethylene glycol side chains. The microstructure of the system and the distribution of dopants will be correlated to electronic properties at different doping concentrations. Concepts on how to control the distribution of the dopants will be presented.


S.EL14.07.07

**Key Factors Study in Amphiphilic Block Copolymer-Oriented Porous SnO₂ Synthesis Process** Shanshan Yin¹, Peter Muller-Buschbaum¹,² and Stephan V. Roth¹,⁴; ¹Technische Universität München, Germany; ²Heinz Maier-Leibnitz Zentrum, Germany; ³KTH Royal Institute of Technology, Sweden; ⁴Deutsches Elektronen-Synchrotron DESY, Germany

SnO₂, as a crucial material in the field of energy storage, has always been the focus of scientific research. For organic-inorganic halide perovskite solar cells (PSCs) or dye-sensitized solar cells (DSSCs), SnO₂ affords high electron mobility and superior chemical stability amongst the various metal oxides. Moreover, as an alternative anode material for lithium-ion battery, it possesses a decent theoretical specific capacity of 1494 mAhg⁻¹. Compared with conventional bulk materials, mesoporous SnO₂ with high specific surface area affords more advantages when applied on either solar cells or lithium-ion batteries. By introducing the mesoporous structure, the recombination of injected electrons within the electron transport layer of the solar cell can be effectively inhibited. Furthermore, with this unique mesoporous structure, the structural collapse of lithium-ion battery anode provoked by significant volume expansion can also be effectively alleviated during the cycling process. In the present work, a novel amphiphilic block copolymer assisted sol-gel chemistry is used for the synthesis of porous SnO₂ nanostructure. Different kinds of solvent are used as a good solvent for both PS and PEO polymer chains, HCl is a selective poor solvent for PS chains and catalyst for the hydrolytic condensation reaction of SnO₂ precursor. With the progressive addition of HCl, the stretch of the hydrophobic PS chains is significantly restricted. As a result, different micelle structures of the block polymer are formed in the sol-gel solution, and the simultaneously hydrolysed SnO₂ nano-dot array is specifically confined in the PEO domains by hydrogen-bond interaction. With the evaporation of the solvent during spin-coating and annealing process, a distinct phase-separated SnO₂/PS-b-PEO composite thin film is obtained on the silicon substrate. For removing the organic polymer template, the composite thin film is calcined at 500 °C for two hours under ambient condition. The obtained nanostructure is visualized by scanning electron microscope (SEM). Crystallinity is characterized by X-ray diffraction (XRD). The buried structure within the thin film is investigated with grazing-incidence small-angle X-ray scattering (GISAXS) measurement.

S.EL14.07.08

**Near-IR Dual Luminescent Single Layer OLEDs** Sebastian Hammer¹, Thomas Ferschke¹, Gabriel Freiherr von Eyb¹ and Jens Pflaum¹,²; ¹Julius-Maximillian-University Würzburg, Germany; ²The Bavarian Center for Applied Energy Research, Germany

Multi-color organic light emitting diodes (OLEDs) comprising just one active electro-optical material define the next vital step in the fast-developing field of photonic devices for optical data communication. Taking into account the spectral range of relevant transmission windows as well as the feasibility of coupling light to plasmonic nanostructures, an OLED device emitting at different wavelengths in the near infra-red (NIR) would be highly desirable. In this contribution we cope with these challenges by demonstrating a stable, dual luminescent OLED based on just one electro-optical active zinc phthalocyanine (ZnPc) layer [1]. ZnPc turns out to be a promising candidate for such single layer devices due to its different polymorphs [2] combined with specific emission characteristics, its photo-stability as well as luminescence in the long wavelength range between 800 and 900 nm which allows for efficient coupling to plasmonic excitations in metallic nanostructures [3]. Performing photoluminescence (PL) studies on ZnPc thin films over the full course of the phase transition between α- and β-polymorph, we are able to optically monitor the thermally induced structural changes and their impact on the respective emission over time. The Johnson-Mehl-Kolmogorov-Avrami model [4] can consistently describe the observed behavior of the transition kinetics derived by the distinct emission features of the involved α- and β-polymorphs. In combination with complementary structural studies and temperature dependent PL measurements from 4 K - 360 K this enables us to provide a comprehensive picture of the excited state emission and its correlation to the crystalline packing on molecular length.
scales. Vice versa, we exploit these morphology dependent emission characteristics to demonstrate a prototypical dual luminescent OLED comprising just one active layer of ZnPc. As will be shown, the emission properties can be spectrally tuned on demand between the excimer emission of the α-phase at 930 nm and the Frenkel emission of the β-phase at 780 nm by a suited thermal treatment. Considering the long-term stability of the adjusted spectral intensity distribution of the devices our work presents an approach towards simple organic photonic devices being of interest for future optical information technology.


S.EL14.07.10
Time Resolved GIWAXS of PEDOT:PSS During Electrolyte Gating Bryan D. Paulsen1, Ruiheng Wu1, Christopher J. Takacs2, Joseph Strzalka3, Qingteng Zhang4 and Jonathan Rivnay1; 1Northwestern University, United States; 2Stanford Synchrotron Radiation Lightsource, United States; 3Argonne National Laboratory, United States

Electrochemical control of electronic charge (electrolyte gating) has opened a broad array of applications for organic electronic materials including printed electronics, biosensors, neuromorphics, electrochromics, supercapacitors, and actuators to name a few. Structure-property relationships are critical for the advancement of these materials across application. Because electrolyte gating necessarily requires dynamic ion and solvent intercalation and expulsion during device operation, static structural measurements, including steady-state in situ and operando measurements, are critically limited. Understanding electrolyte gated organic materials requires understanding their dynamic structure, which in turn requires time-resolved in situ or operando techniques. Grazing incident wide angle X-ray scattering is a powerful tool to for accessing the microstructure of organic electronic materials. In particular, PEDOT:PSS is ubiquitous in organic electrolyte gated devices. Here the dynamic time-resolved operando GIWAXS of acid crystallized PEDOT:PSS films during aqueous electrolyte gating is reported. The majority of the structural transformation occurs over a narrow range of potential and the doping-dedoping structure dynamics are not symmetric, displaying very different time dependences. Coupling the time-resolved operando GIWAXS with time-resolved UV-vis-NIR reveals that the PEDOT:PSS structure depends not on the absolute charge density, but on the relative population dynamics of neutral, polaronic, and bipolaronic species. Even after the relative populations of charge species equilibrates, time-resolved GIWAXS shows continued long-lived structural relaxations. This complicated phenomena, which is inaccessible with steady-state ex situ, in situ, or operando methods, gives a concrete physical origin of the commonly observed asymmetry of electrolyte gated transistor turn on and turn off. Further it identifies the structural origin of the rate limiting physical processes to be targeted for rational materials design. Finally, this work represents the first report time-resolved X-ray scattering of an organic electronic material during electrochemical gating.

SYMPOSIUM S.EL14

New Materials Design for Organic Semiconductors Through Multimodel Characterization and Computational Techniques
November 21 - November 29, 2020

Symposium Organizers
Aram Amassian, North Carolina State University
Brian Collins, Washington State University
Xiaodan Gu, University of Southern Mississippi
Eva Herzig, Universität Bayreuth

* Invited Paper
Session Chairs: Brian Collins and Eva Herzig
Saturday Afternoon, November 28, 2020
S.EL14

12:30 PM *S.EL14.03/S.EL13.02.03
Single-Layered Organic Photovoltaics with Double Cascading Charge Transport Pathways—17.78%
Efficiencies

Thomas P. Russell1,2, Feng Liu3, Mei Zhang3, Lei Zhu3, Guanqing Zhou3, Tianyu Hou3, Chaqun Qiu3, Qin Hu1, Bryon Larson4, Wei Fang2, Zaifei Ma2, Zheng Tang2, Haiming Zhu1 and Yongming Zhang3; 1University of Massachusetts Amherst, United States; 2Lawrence Berkeley National Laboratory, United States; 3Shanghai Jiao Tong University, China; 4National Renewable Energy Laboratory, United States; 5State Key Laboratory of Fluorinated Functional Membrane Materials, China; 6Donghua University, China; 7Zhejiang University, China

The chemical structure of donors (Ds) and acceptors (As) has been a limitation to the achievable power conversion efficiencies (PCEs) of bulk heterojunction (BHJ) active layers of binary D-A mixtures in organic photovoltaics. While new synthesizes can be used to generate Ds and As, a holistic strategy that simultaneously improves open circuit voltage, short circuit current, and fill factor is necessary and has been pursued using different approaches in organic photovoltaics (OPVs) to PCEs. This holistic approach, though, has been elusive, due to morphological constraints and the inherent electronic structures of the components, leading to performance trade-offs. Ideally, both the morphology and electronic structure would lead to a maximization of light absorption, enhancement of exciton splitting, and ease of carrier extraction. Adding a third component has been done, resulting enhancement of either the morphology or electronic structure leading to PCE improvement, but only incremental, at best. However, using quarternary D-A blends, double cascading energy level alignment in BHJ organic photovoltaic active layers are realized, enabling efficient carrier splitting and transport, without perturbing the desired BHJ morphology. This has led to record-breaking PCEs of 17.78% where, by electronic structure and morphology optimization, simultaneous improvements of the open-circuit voltage, short-circuit current and fill factor are realized. This strategy opens numerous avenues to optimize light absorption, carrier transport, and charge transfer state energy levels by the chemical constitution of the components. The chemical structures of the Ds and As offer control over electronic structure and charge transfer state energy levels, enabling manipulation of hole-transfer rates, carrier transport, and non-radiative recombination losses.

12:54 PM *S.EL14.03/S.EL13.02.04
Interplay of Phase Diagrams, Processing and Stability of Non-Fullerene Organic Solar Cells

Harald Ade; North Carolina State University, United States

Organic solar cells (OSCs) are considered one of the most promising cost-effective options for utilizing solar energy in high energy/weight or semi-transparent applications. Recently, the OSC field has been revolutionized by the development of novel non-fullerene small molecular acceptors with efficiencies now reaching >16%. The device stability and mechanical durability of non-fullerene OPVs have received less attention and developing devices with both high performance and long-term stability remains challenging, particularly if the material choice is restricted by roll-to-roll and benign solvent processing requirements and desirable ductility requirements. Yet, morphological and mechanical stability is a prerequisite for OPV commercialization. Here, we report our current understanding of the phase behavior of OPV mixtures and the relation of phase behavior to performance, processing needs (e.g., kinetic quenches), and morphological stability via meta-stability or vitrification. Characterization methods range from SIMS and DSC measurements to delineate phase diagrams and miscibility to soft x-ray scattering and WAXS to determine critical morphology parameters and molecule packing. A large range of miscibility (from hyper-miscibility to strong hypo-miscibility) is observed, including complex temperature dependence that can be a mixture of upper- and lower critical solution temperature behavior for both the binodal and the liquidus. The measurements presented should help to create molecular structure-function relationships that would allow some predictive guidance on how desired phase behavior and vitrification properties can be targeted by specific chemical design. They also allow to predict how unstable binary systems can be stabilized with the correct ternary compound.

1:18 PM *S.EL14.01.04
In-situ Multimodal Measurements of Structure Formation in Solution Processed Semiconductors

Lee Richter; National Institute of Standards and Technology, United States
Solution processing of electrically active layers is a promising route to sustainable manufacturing of functional components on diverse substrates such as flexible foils and textiles. Typically, solution processing does not result in the thermodynamic equilibrium form; instead metastable, kinetically trapped structures dominate. This allows great flexibility in the ability to tailor film structure (and performance) by processing details. In general, ink formulation (solvent, additives), processing conditions (casting temperature), and post processing (thermal and solvent annealing) are empirically optimized. The transition to rational process design requires in-situ measurements to determine the complex trajectory of the system through phase separation and domain refinement. Photon-based techniques are ideally suited to this problem, yet no single measurement provides the required knowledge of composition, nano- and meso- scale structure. Lab-scale techniques, such as UV-vis or IR spectroscopy, ellipsometry, and photoluminescence are easily implemented and rapid, yet rely on phenomenological relationships between observable and structure. Synchrotron based grazing incidence X-ray scattering techniques (both wide angle diffraction and small angle scattering) are more rigorous in interpretation but can be limited in contrast. By performing multiple measurements on a single system, either simultaneously, or separately, detailed models for the kinetic evolution of film structure can be developed. Results will be presented from a number of studies of solution processing of organic semiconducting layers for both photovoltaic and transistor applications. Studies of both ink deposition, via blade coating and post processing (thermal and solvent vapor annealing) will highlight insights into phase separation, liquid-liquid vs liquid-solid, and kinetics, nucleation and vitrification, afforded by multimodal analysis for each highlighted system. The role of fundamental material properties: semi-crystallinity, liquid crystallinity, glass transition temperature, etc. as guides to ink processing will be developed.

1:42 PM *S.EL14.01.10
In Situ and In Operando Scattering Studies on Polymer Based Organic Solar Cells Peter Muller-Buschbaum; TU Munich, Germany

Organic solar cells are an interesting alternative to conventional silicon based solar cells as the feature new possibilities introduced by using a different class of materials namely polymers. Instead of expensive ultra-high vacuum technologies, fabrication can be done at room temperature, using wet chemical processing, and thereby enabling usage of methods such as roll-to-roll printing. As a consequence, the production of organic solar cells has the potential to become very cheap and easy. With in-situ grazing incidence small and wide angle X-ray scattering (GISAXS and GIWAXS) studies, we gain information on the kinetics of morphology formation of electrodes, blocking layers and active layers of the solar cells during processing. In terms of large scale usability, one of the major challenges for organic solar cells is to overcome their relatively short lifetime, as compared to their inorganic counterparts. To gain a deeper understanding of organic solar cell degradation with respect to changes in the active layer nano-morphology, we present an in-situ study on model polymer-fullerene solar cells during the first hours of operation. The in-operando study reveals information on both, its evolving current-voltage characteristics and active layer nano-morphology. For that purpose, GISAXS / GIWAXS measurements and current-voltage (IV) tracking of an operating solar cell are performed simultaneously to gain fundamental understanding. Starting from an optimized morphology of the active layers in terms of highest efficiencies for organic solar cells, depending on the system, a mixing or demixing process are identified to cause changes of the morphology. The altered morphology is less optimal for charge transport through the active layer due to poor percolation in a too fine morphology or poor splitting of excitons in a too coarse morphology.

2:06 PM *S.EL14.03/S.EL13.02.06
Real-Time Investigation of Crystallization Pathways of Organo-Metal-Halide Perovskites Solar by In Situ X-Ray Scattering Michael F. Toney; SLAC National Accelerator Laboratory, United States

Perovskite solar cells (PSCs) have gained tremendous attention as potential materials for photovoltaics due to their high efficiencies approaching the best silicon solar cells and their compatibility with low-cost low-temperature fabrication methods (such as solution processing). Many solution-processing approaches have been adopted to manipulate perovskite formation including anti-solvent processing, inert-gas jet treatment, and additive-assisted processing. Some of these approaches allow room-temperature processing of perovskite thin films, while other approaches require post-deposition annealing. Perovskite film formation is complex, involving the formation of intermediates and/or metastable phases that strongly affect the final perovskite film microstructure. Therefore, understanding the mechanism of perovskite formation and the crystallization pathways is key for more facile control of perovskite formation. An effective way to understand the mechanisms of perovskite formation is using real-time X-ray scattering. Here, we use time-resolved x-ray scattering to investigate the perovskite formation of MAPbI$_3$-based perovskites and mixed cation (Cs, FA)PbI$_3$ perovskites in-situ during spin coating and the subsequent post-deposition treatments with different processing approaches such as additive-assisted processing, anti-solvent processing and N$_2$-gas jet treatment.
Time-resolved monitoring of the perovskite thin film processing reveals the formation of intermediate phases on the route of perovskite formation, whereas perovskite formation is dominated by a sol-gel process. For MAPbI$_3$-based perovskites processed with the MASCN additive, we show that the nature of the intermediate precursor phases and their formation/dissociation dynamics have an impact on the extent of nucleation and growth of perovskite phase affecting the microstructure of the perovskite film. Our findings reveal that the combination of two precursors (MASCN-precursor and DMSO-precursor) with fast and slow transformation rates contributes to the formation of micron-sized perovskite crystals, through seeding nuclei combined with the slow growth of the perovskite phase. For Cs-FA-containing perovskites, we show how the competition between the non-perovskite and perovskite phases formation are affected by the processing treatments. We find that dropping anti-solvent induces immediate crystallization from the bulk wet film, whereas applying N$_2$-gas works by depleting volatiles from the top-surface leading to interface-induced crystallization that occurs after reaching supersaturation, while both treatments result in dominant crystallization of non-perovskite hexagonal phase with the formation of seeds of perovskite phase. When neither treatment is applied, the as-cast film is mostly amorphous with little non-perovskite phase formation. We further show how the initial structure of the as-cast precursor film impacts the perovskite formation during the subsequent annealing treatment.

Our work highlights the importance of real-time investigation of perovskite film formation which can aid in establishing processing-microstructure-functionality relationships and help to provide a fundamental understanding of the mechanisms of perovskite formation.

Session Chairs: Aram Amassian and Xiaodan Gu
Sunday Morning, November 29, 2020
S.EL14

8:00 AM *S.EL14.06.01
Advances in the Theoretical Description of Nonfullerene-Based Organic Solar Cells Jean-Luc Bredas1,2; 1Georgia Institute of Technology, United States; 2The University of Arizona, United States

The field of organic photovoltaics is currently enjoying a major resurgence thanks to the development of increasingly performant combinations of polymer donors and nonfullerene-based acceptors. Power conversation efficiencies now approach the 18% mark in single-junction devices.

In this contribution, we will provide a theoretical description of of the factors that have enabled such advances, including:
- hybridization of the strongly absorbing local-exciton electronic states with the charge-transfer electronic states appearing at the donor-acceptor interfaces [1-2];
- minimization of the voltage losses through reduction of the nonradiative recombination pathways [3]; and
- extent of order in the nonfullerene acceptor domains [4-5].

This work is supported by the Office of Naval Research.

**8:24 AM *S.EL14.04.04**

Pushing the Resolution Limits of Transmission Electron Microscopy for Imaging of Conjugated Polymers with Sub 4 Angstrom Resolution

Brooke Kuei, Ryan Fair and Enrique D. Gomez; The Pennsylvania State University, United States

Despite significant advances in transmission electron microscopes, the resolution limit of polymers remains limited by the electron dose the sample can handle. We thus propose that revealing the mechanisms for radiation damage can yield new methods for imaging at length scales not previously achievable. We have characterized the effect of beam damage on various conjugated polymers, including poly(3-hexylthiophene-2,5-diyl) (P3HT), poly(3-docetylthiophene-2,5-diyl) (P3DDT), poly[N-9’-heptadecanyl-2,7-carbazole-alt-5,5-(4’,-7’-di-2-thienyl-2’,1’,3’-benzo thiadiazole)] (PCDTBT), and poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl]and poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3’’’-di(2-octyldecyl)-2,2”;5”;2”;5”’;2”’-quaterthiophene-5,5”’-diyl)] (PffBT4T-2OD), via electron diffraction and low-loss electron energy-loss spectroscopy (EELS). We find that the critical dose for damage depends on dose rate, temperature and beam size. Altogether, our results suggest that a significant mechanism for beam damage in conjugated polymers is diffusion of secondary reactive species, such as free radicals. These new concepts in beam damage reveal strategies to push the resolution in the TEM, allowing us to image 3.6 Å π-π stacking in PffBT4T-2OD with high-resolution TEM (HRTEM) at cryogenic conditions, 4D STEM again at cryo temperatures, and HRTEM at room temperature using antioxidants to limit damage. We use high resolution information to reveal pathways for charge conduction, including the type of grain boundaries present, as well as the effect of liquid crystallinity on promoting orientational correlations between domains. Together with our work on predicting liquid crystalline order in conjugated polymers, we use microscopy to develop strategies for designing new molecules with long-range order and strong orientational correlations that lead to enhancement of macroscopic charge transport.

**8:48 AM *S.EL14.06.04**

In Situ Transient Absorption Spectroscopy During the Formation of Organic Thin Films

Cathy Y. Wong; University of Oregon, United States

The electronic structure and exciton dynamics of the molecules and polymers that form the active layer in organic electronic devices can change dramatically during solution deposition. As solvent vaporizes, molecules aggregate and become electronically coupled, sometimes dramatically changing the exciton dynamics and thus the suitability of the material for electronic devices. The exciton dynamics of molecules in solution and in films of aggregates can be measured using transient absorption spectroscopy. However, the progression of exciton dynamics during film formation is unknown since measurements typically cannot be performed quickly enough to collect accurate transient absorption spectra of these species. The exciton dynamics of evolving material systems can be measured by increasing the speed of data collection. A novel implementation of transient absorption spectroscopy is introduced that can measure transient spectra with up to a 60 ps pump-probe time delay in one shot. The exciton dynamics of intermediate aggregation states are revealed during the formation of an organic film. The information gained using this technique can be used to modify environmental parameters during the film formation process to kinetically trap aggregates with exciton dynamics tailored for particular types of electronic devices.

**9:12 AM *S.EL14.01.03**

Developing Models to Determine the Impacts of Synthetic Design and Processing on Organic Semiconductors

Chad Risko; University of Kentucky, United States

The potential to modulate material (opto)electronic properties through well-established synthetic chemistry methods has made organic semiconductors (OSC) a scientific playground. Limited knowledge among the relationships that connect chemical composition and molecular architecture, materials processing, and the solid-state packing arrangements that define the underlying physicochemical processes that determine OSC performance, however, renders OSC design to be highly Edisian. We seek to address these connections to facilitate OSC design and deployment through the development and application of multiscale, theoretical materials chemistry approaches that build upon principles from organic and physical chemistry, condensed matter physics, and materials and polymer science. In this presentation, we will demonstrate how such approaches can reveal the striking influence that seemingly modest changes in chemical structure can have on the dynamics and solid-state packing of OSC active layers and resulting materials characteristics.

**9:36 AM *S.EL14.04.05**

Machine Learning for Characterization Techniques

Alexander Hexemer; Lawrence Berkeley National Lab, United States
The materials discovery cycle contains many different components, including synthesis, characterization and data analysis and interpretation. In the past few decades, automatic synthesis pipelines have been established for many chemistry and materials systems. For characterization, many advanced techniques, such as X-ray scattering and NMR crystallography, have enabled the structure identification of various chemical, biological and materials systems, including polymers, inorganic materials, and proteins. These techniques have been developed and improved substantially over the past few decades, which brings high-throughput experimental discovery into reach. Meanwhile, these breakthroughs produce enormous data amounts. However, the process of understanding the structural features from data is still very labor-intensive. It requires many man-hours of work by highly specialized and trained scientific staff to interpret the data and identify the structure correctly. Recently, machine learning, a branch of artificial intelligence, has demonstrated the potential to tackle and accelerate the analysis of common techniques such as tomography, scattering, and spectroscopy.

SESSION S.EL14.01: *In-Situ* Characterization

On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

S-EL14

5:00 AM S.EL14.01.01

**Investigating MAPbI₃ Thin-Film Formation During Spin Coating by *In Situ* Absorption and Photoluminescence Spectroscopy** Mihirsinh Chauhan¹, Yu Zhong¹, Konstantin Schötz¹, Brijesh Trpati², Sven Huetter¹, Anna Kohler¹ and Fabian Panzer¹; ¹University of Bayreuth, Germany; ²Pandit Deendayal Petroleum University, India

Until today, the two-step processing method represents an attractive route for the thin film formation of halide perovskites. However, a fundamental understanding about the film formation dynamics in case of spin coating methylammonium iodide (MAI) on PbI₂ has not been established yet. Here we apply in-situ optical spectroscopy during the two-step film formation of the model halide perovskite MAPbI₃ via spin coating. We identify and analyze in detail the optical features that occur in photoluminescence and corresponding absorption spectra during processing. We find that the film formation takes place in five consecutive steps, including the formation of a MAPbI₃ capping layer via an interface crystallization and the occurrence of an intense dissolution-recrystallization process. Consideration of confinement and self-absorption effects in the PL spectra, together with consideration of the corresponding absorption spectra allows to quantify the growth rate of the initial interface crystallization to be 12 nm/s. We find the main dissolution recrystallization process to happen with a rate of 445 nm/s, emphasizing its importance to the overall processing.

5:15 AM S.EL14.01.02

**In-Situ Characterization of Organic Colloidal Composite Nanoparticles** Anderson M. de Campos and Tayebeh Ameri; University of Munich (LMU), Germany

The use of aqueous / alcohol-based nanoparticulate dispersions in printable optoelectronics offers a promising approach to control the donor: acceptor morphology on the nanoscale with the benefit of environmentally-friendly, solution-based fabrication. Appropriate nanoscale morphology of the donor: acceptor composite nanoparticles (NPs), such as Janus structure, is the prerequisite for a well-suited mesoscale morphology formation to ensure an efficient charge transport. The final nanostructure of a composite NP is determined by the competition between thermodynamics and kinetics during the particle formation. However, fine tuning and control of these variables require prior observations and *in-situ* measurements. In this presentation, we will discuss our achieved results on the in-situ analysis of the size growth and morphology evolution of the colloidal organic composite NPs by employing a stopped-flow apparatus equipped with various optical spectroscopic methods.

5:30 AM S.EL14.01.03

**Developing Models to Determine the Impacts of Synthetic Design and Processing on Organic Semiconductors** Chad Risko; University of Kentucky, United States

The potential to modulate material (opto)electronic properties through well-established synthetic chemistry methods has made organic semiconductors (OSC) a scientific playground. Limited knowledge among the relationships that connect chemical composition and molecular architecture, materials processing, and the solid-state packing arrangements that define
the underlying physicochemical processes that determine OSC performance, however, renders OSC design to be highly Edisonian. We seek to address these connections to facilitate OSC design and deployment through the development and application of multiscale, theoretical materials chemistry approaches that build upon principles from organic and physical chemistry, condensed matter physics, and materials and polymer science. In this presentation, we will demonstrate how such approaches can reveal the striking influence that seemingly modest changes in chemical structure can have on the dynamics and solid-state packing of OSC active layers and resulting materials characteristics.

6:00 AM *S.EL14.01.04
In-situ Multimodal Measurements of Structure Formation in Solution Processed Semiconductors Lee Richter; National Institute of Standards and Technology, United States

Solution processing of electrically active layers is a promising route to sustainable manufacturing of functional components on diverse substrates such as flexible foils and textiles. Typically, solution processing does not result in the thermodynamic equilibrium form; instead metastable, kinetically trapped structures dominate. This allows great flexibility in the ability to tailor film structure (and performance) by processing details. In general, ink formulation (solvent, additives), processing conditions (casting temperature), and post processing (thermal and solvent annealing) are empirically optimized. The transition to rational process design requires in-situ measurements to determine the complex trajectory of the system through phase separation and domain refinement. Photon-based techniques are ideally suited to this problem, yet no single measurement provides the required knowledge of composition, nano- and meso- scale structure. Lab-scale techniques, such as UV-vis or IR spectroscopy, ellipsometry, and photoluminescence are easily implemented and rapid, yet rely on phenomenological relationships between observable and structure. Synchrotron based grazing incidence X-ray scattering techniques (both wide angle diffraction and small angle scattering) are more rigorous in interpretation but can be limited in contrast. By performing multiple measurements on a single system, either simultaneously, or separately, detailed models for the kinetic evolution of film structure can be developed. Results will be presented from a number of studies of solution processing of organic semiconducting layers for both photovoltaic and transistor applications. Studies of both ink deposition, via blade coating and post processing (thermal and solvent vapor annealing) will highlight insights into phase separation, liquid-liquid vs liquid-solid, and kinetics, nucleation and vitrification, afforded by multimodal analysis for each highlighted system. The role of fundamental material properties: semi-crystallinity, liquid crystallinity, glass transition temperature, etc. as guides to ink processing will be developed.

6:30 AM S.EL14.01.05
Resolving Structure Formation in Printed Thin Films Oliver Filonik1, Michael Buchhorn2, Christopher Greve2,1, Stephan Pröller1, Fabian Eller2, Adrian Ebert2 and Eva M. Herzig2; 1Technische Universität München, Germany; 2Universität Bayreuth, Germany

Structure formation is a complex interplay of physical interactions between the molecules of a system. In thin films structure formation can be triggered e.g. by the evaporation of the solvent or by heat treatments and is further influenced by a multitude of external parameters. Such external parameters can influence the nanostructure significantly and therefore alter the function of the involved materials. For some external parameters already small changes are sufficient to alter the final nanostructure within the thin film. If these are unidentified this results in poor reproducibility of the final thin film structure. For other external parameters the processing is rather stable. Often it is unclear what the physical reason for the sensitivity or stability towards the external parameters is. We want to show that time-resolved measurements, ideally on multi-length scales and with complementary methods will help to resolve fundamental structure formation processes in thin films. Comparing different material systems from printed organic photovoltaics to hybrid perovskite solar cells, I will point out the opportunities we have in interfering with the structure formation process to tune the material properties by external processing parameters.

6:45 AM S.EL14.01.06
In Situ Investigation of Sputter Deposition Electrodes on Different Layers of Non-Fullerene Organic Solar Cells Xinyu Jiang1, Simon J. Schaper1, Matthias Schwartzkopf2, Stephan V. Roth2,3 and Peter Muller-Buschbaum1,4; 1Technische Universität München, Germany; 2Deutsches Elektronen-Synchrotron DESY, Germany; 3KTH Royal Institute of Technology, Sweden; 4Heinz Maier-Leibnitz Zentrum, Germany

Bulk heterojunction (BHJ) polymer solar cells have gained significant improvements via both novel organic synthesis and easy fabrication methods. Especially the fabrication through solution allows for large scale deposition processes such as roll to roll printing. Furthermore, the application of conjugated polymers as functional layers makes organic solar cells an
attractive approach for a cost-effective solution to the current energy-shortage issue. Recently, the efficiencies of non-fullerene organic solar cells (OSCs) with small molecule acceptors rapidly increased to over 16%, which makes OSCs competitive to commercial available solid-state solar cells [1]. However, to make OPVs commercial competitive in the long term, overcoming degradation and achieving long device lifetime is of significant interest. The peeling-off of the electrode from the contact layer surface caused by aging stresses lead to an intrinsic degradation, which is one of the main reasons for the performance loss of OSCs [2]. Although thermal evaporation is a common method of fabricating the electrode due to its low cost, this technique brings several problems for the device such as soft contact between electrode and function layer interface. Another disadvantage is the inevitable high temperature during the fabrication process. Magnetron sputtering technique is a promising technique to solve these issues.

For understanding the mechanism of the metal cluster growth on the thin films with various morphologies, we introduce in-situ grazing incidence small angle X-ray scattering (GISAXS) is a technique to observe the morphology change during sputter process. In-situ GISAXS measurements during sputter deposition of Al nanolayers are conducted at the beamline P03 of DESY in Hamburg via using a DC magnetron sputter chamber. Active layers contain a PfdT4T-2OD donor with a small molecule accepter EH-IDTBR blender dissolved in 1,2,4-trimethyl benzene and chlorobenzene respectively to obtain different morphology. Then 10 nm MoO3 blocking layers were deposited on their top surface, which usually acts as the electron blocking layer for the invert solar cell device. A 20 nm Al layer deposited on these four different layers through the sputtering technique. The morphology evolution during Al nanolayers growth observed in the out-of-plane cuts. The plane referred to is defined by the sample’s surface normal and the wave vector of the incident X-ray beam. All peaks of different thin films appear at lower effective thickness value. These peaks can be assigned to Al particles and clusters appearing during the sputtering process. It should be noted that the formation of Al layers with one layer MoO3 deposited on the active layer is slower than the active layer without deposition of MoO3. In Addition, SEM and AFM images indicate that the morphology impact on Al growth significantly.


7:00 AM *S.EL14.01.07
Understanding and Controlling Aggregate Formation During Spin-Coating Anna Kohler, Fabian Panzer, Konstantin Schötz and Markus Reichenberger; University of Bayreuth, Germany

In this presentation, I shall discuss what we can learn from comparatively simple spectroscopic measurements regarding the formation of aggregates in polymers and oligomers when spin-coating. I will demonstrate that the aggregation process is preceded by a planarization of the polymer backbone, and that it can be described like a coil-globule transitions [1]. In particular, the nature of the resulting aggregates can be controlled through the substrate temperature [2,3] which changes the nucleation process. This is illustrated for a range of widely used polymers such as P3HT, PFO, PCPDTBT, PCE11 and others.


7:30 AM S.EL14.01.09
The Critical Role of Materials’ Interaction in Realizing Organic Field-Effect Transistors via High-Dilution Blending with Insulating Polymers Indunil Angunawela, Masrur Morshed Nahid, Masoud Ghasemi, Aram Amassian, Harald Ade and Abay Gadisa; North Carolina State University, United States

A detailed understanding of the molecular and mesoscopic structure of a solution-processed organic, semiconducting thin film is still lacking, mostly due to the complicated film morphology. Recent progress, however, demonstrated the possibility of tuning the electronic properties of either short or long-range local molecular aggregates in films where high-performing semiconductor polymers are dispersed in a majority insulator and utilized in organic field effect transistors. Such a diluted blend matrix offers opportunities not only to reduce the cost associated with the semiconducting polymer significantly but also to systematically explore the fundamental molecular structure-function relationships. Herein, basic thermodynamic material interaction principles, in conjunction with detailed morphological studies, are invoked to understand the mesoscale
structures leading to more efficient charge transport in the ultrathin films applicable for transparent and flexible electronic applications. Exploring two high-performing polymers, PDPP3T and N2200, we report a drastic variance in the change in charge transport properties of these two polymers when dispersed in an insulator matrix, due to the large difference in thermodynamics, resulting differences in molecular interaction and dimension of their fibrillar morphology. This basic finding provides design guidelines for semiconductor: insulator blends to achieve long-range ordered polymers by selecting compatible blends, and hence, high mobility in organic transparent ultrathin films.

7:45 AM *S.EL14.01.10
In Situ and In Operando Scattering Studies on Polymer Based Organic Solar Cells Peter Muller-Buschbaum; TU Munich, Germany

Organic solar cells are an interesting alternative to conventional silicon based solar cells as the feature new possibilities introduced by using a different class of materials namely polymers. Instead of expensive ultra-high vacuum technologies, fabrication can be done at room temperature, using wet chemical processing, and thereby enabling usage of methods such as roll-to-roll printing. As a consequence, the production of organic solar cells has the potential to become very cheap and easy. With in-situ grazing incidence small and wide angle X-ray scattering (GISAXS and GIWAXS) studies, we gain information on the kinetics of morphology formation of electrodes, blocking layers and active layers of the solar cells during processing. In terms of large scale usability, one of the major challenges for organic solar cells is to overcome their relatively short lifetime, as compared to their inorganic counterparts. To gain a deeper understanding of organic solar cell degradation with respect to changes in the active layer nano-morphology, we present an in-situ study on model polymer-fullerene solar cells during the first hours of operation. Their in operando study reveals information on both, its evolving current-voltage characteristics and active layer nano-morphology. For that purpose, GISAXS / GIWAXS measurements and current-voltage (IV) tracking of an operating solar cell are performed simultaneously to gain fundamental understanding. Starting from an optimized morphology of the active layers in terms of highest efficiencies for organic solar cells, depending on the system, a mixing or demixing process are identified to cause changes of the morphology. The altered morphology is less optimal for charge transport through the active layer due to poor percolation in a too fine morphology or poor splitting of excitons in a too coarse morphology.

SESSION S.EL14.02: Novel Engineering Strategies

5:00 AM S.EL14.02.01
Microfluidic Printing of Two-Phase Polymer Semiconductor Systems for Enhanced Charge Transport and Solar Efficiency Antonio Facchetti1,2, 1Northwestern University, United States; 2Flexterra Inc., United States

The rational design of phase purity for two-phase conjugated polymer systems is challenging but crucial for organic/printed electronics. In this presentation we report a ‘mixed-flow design’ concept for printing two-phase conjugated polymer systems promoting phase purity for application in both bulk-heterojunction solar cells and thin-film transistors. The key aspect of this work lies in the mixed-flow design concept with the integration of both laminar and extensional flows using a unique designed microstructured shear blade. The fluid simulation is utilized as a tool for the flow pattern design to induce the shear, stretch and push-out effects to achieve optimal polymer chain conformation for phase purity. Experimentally, this mixed-flow strategy enhances semiconductor blend thin film crystallinity and increases phase purity with proper percolation. The improved morphology leads to higher short-circuit currents, enhanced fill factors, and significantly improved power conversion efficiency (PCE, enhanced by ~50% compared with conventional blade coating method) for printed all-polymer solar cells. In addition, this printing technique also enhances the performance of all-semiconductor polymer ambipolar transistors (mobility = + ~70%) as well as unipolar semiconductor polymer-insulating polymer transistors (mobility = + ~ 100%), suggesting the versatility of this methodology for various two-phase conjugated polymer systems.

5:15 AM S.EL14.02.03
Uncovering the Roles of the Donor-Acceptor Oligomer Chemistry and Solution Environment on the Conformation and Aggregation of Oligomers in Solution Chamikara D. Karunasena, Shi Li and Chad Risko; University of Kentucky, United States
The extrinsic properties of organic semiconductors (OSC) are deeply interconnected to their thin-film morphologies. To implement high performance and reproducible device fabrication guidelines and for synthetic regulation of the thin film morphologies, a rich understanding of the structure–processing–function relationships needs to be established. However, there currently exists limited insight to elucidate the physicochemical mechanisms that determine aggregation and self-assembly of OSC. Through molecular dynamics (MD) simulations, we aim to systematically understand how molecular design and processing chemistry impact the behavior of donor–acceptor (D–A) type oligomers in solution. In particular, we isolate the roles of the oligomer chemistry, oligomer concentration, and host solvent. Variations in these factors lead to a variety of rotational isomer preferences that, in turn, impacts the capacity of the oligomers to aggregate in solution. In total, the results provide molecular-scale foundations to allow for kinetic and thermodynamic control of OSC morphology development through solvent optimization.

5:00 AM *S.E14.03/S.E13.02.03
Single-Layered Organic Photovoltaics with Double Cascading Charge Transport Pathways—17.78% Efficiencies
Thomas P. Russell1,2, Feng Liu3, Mei Zhang4, Lei Zhu1, Guanqing Zhou1, Tianyu Hou1, Chaoqun Qiu1, Qin Hu1, Bryon Larson4, Wei Fang5, Zaiwei Ma6, Zheng Tang6, Haiming Zhu1 and Yongming Zhang1; 1University of Massachusetts Amherst, United States; 2Lawrence Berkeley National Laboratory, United States; 3Shanghai Jiao Tong University, China; 4National Renewable Energy Laboratory, United States; 5State Key Laboratory of Fluorinated Functional Membrane Materials, China; 6Donghua University, China
The chemical structure of donors (Ds) and acceptors (As) has been a limitation to the achievable power conversion efficiencies (PCEs) of bulk heterojunction (BHJ) active layers of binary D-A mixtures in organic photovoltaics. While new syntheses can be used to generate Ds and As, a holistic strategy that simultaneously improves open circuit voltage, short circuit current, and fill factor is necessary and has been pursued using different approaches in organic photovoltaics (OPVs) to PCEs. This holistic approach, though, has been elusive, due to morphological constraints and the inherent electronic structures of the components, leading to performance trade-offs. Ideally, both the morphology and electronic structure would lead to a maximization of light absorption, enhancement of exciton splitting, and ease of carrier extraction. Adding a third component has been done, resulting enhancement of either the morphology or electronic structure leading to PCE improvement, but only incremental, at best. However, using quarternary D-A blends, double cascading energy level alignment in BHJ organic photovoltaic active layers are realized, enabling efficient carrier splitting and transport, without perturbing the desired BHJ morphology. This has led to record-breaking PCEs of 17.78% where, by electronic structure and morphology optimization, simultaneous improvements of the open-circuit voltage, short-circuit current and fill factor are realized. This strategy opens numerous avenues to optimize light absorption, carrier transport, and charge transfer state energy levels by the chemical constitution of the components. The chemical structures of the Ds and As offer control over electronic structure and charge transfer state energy levels, enabling manipulation of hole-transfer rates, carrier transport, and non-radiative recombination losses.

5:30 AM *S.E14.03/S.E13.02.04
Interplay of Phase Diagrams, Processing and Stability of Non-Fullerene Organic Solar Cells Harald Ade; North Carolina State University, United States
Organic solar cells (OSCs) are considered one of the most promising cost-effective options for utilizing solar energy in high energy/weight or semi-transparent applications. Recently, the OSC field has been revolutionized by the development of novel non-fullerene small molecular acceptors with efficiencies now reaching >16%. The device stability and mechanical durability of non-fullerene OPVs have received less attention and developing devices with both high performance and long-term stability remains challenging, particularly if the material choice is restricted by roll-to-roll and benign solvent processing requirements and desirable ductility requirements. Yet, morphological and mechanical stability is a prerequisite for OPV
commercialization. Here, we report our current understanding of the phase behavior of OPV mixtures and the relation of phase behavior to performance, processing needs (e.g., kinetic quenches), and morphological stability via meta-stability or vitrification. Characterization methods range from SIMS and DSC measurements to delineate phase diagrams and miscibility to soft x-ray scattering and WAXS to determine critical morphology parameters and molecule packing. A large range of miscibility (from hyper-miscibility to strong hypo-miscibility) is observed, including complex temperature dependence that can be a mixture of upper- and lower critical solution temperature behavior for both the binodal and the liquidus. The measurements presented should help to create molecular structure-function relationships that would allow some predictive guidance on how desired phase behavior and vitrification properties can be targeted by specific chemical design. They also allow to predict how unstable binary systems can be stabilized with the correct ternary compound.

6:00 AM *S.EL14.03/S.EL13.02.05
Structure, Transport and Charging in Organic Mixed Ionic/Electronic Conductors Jonathan Rivnay; Northwestern University, United States

Organic mixed ionic/electronic conductors have gained considerable interest in bioelectronics, power electronics, circuits and neuromorphic computing. These organic, often polymer-based, semiconductors rely on a combination of ionic transport, electronic transport, and high volumetric charge storage capacity. Despite recent progress and a rapidly expanding library of new materials, the understanding of stability and transport/coupling of ionic and electronic carriers remain largely unexplored. We highlight recent synthetic and processing approaches used to tailor electrochemical device properties and stability, as well as new opportunities enabled by such advances. Our understanding of critical processes in electrochemical devices further requires us to study these materials in device-relevant conditions, fully considering the effects of ions and solvent on microstructure and transport. To this end, we report on recent efforts towards structure-property relations in high performance organic mixed conductors using ex-situ, in-situ, and operando scattering and spectroscopic techniques.

6:30 AM *S.EL14.03/S.EL13.02.06
Real-Time Investigation of Crystallization Pathways of Organo-Metal-Halide Perovskites Solar by In Situ X-Ray Scattering Michael F. Toney; SLAC National Accelerator Laboratory, United States

Perovskite solar cells (PSCs) have gained tremendous attention as potential materials for photovoltaics due to their high efficiencies approaching the best silicon solar cells and their compatibility with low-cost low-temperature fabrication methods (such as solution processing). Many solution-processing approaches have been adopted to manipulate perovskite formation including anti-solvent processing, inert-gas jet treatment, and additive-assisted processing. Some of these approaches allow room-temperature processing of perovskite thin films, while other approaches require post-deposition annealing. Perovskite film formation is complex, involving the formation of intermediates and/or metastable phases that strongly affect the final perovskite film microstructure. Therefore, understanding the mechanism of perovskite formation and the crystallization pathways is key for more facile control of perovskite formation. An effective way to understand the mechanisms of perovskite formation is using real-time X-ray scattering. Here, we use time-resolved x-ray scattering to investigate the perovskite formation of MAPbI₃-based perovskites and mixed cation (Cs, FA)PbI₃ perovskites in-situ during spin coating and the subsequent post-deposition treatments with different processing approaches such as additive-assisted processing, anti-solvent processing and N₂-gas jet treatment.

Time-resolved monitoring of the perovskite thin film processing reveals the formation of intermediate phases on the route of perovskite formation, whereas perovskite formation is dominated by a sol-gel process. For MAPbI₃-based perovskites processed with the MASCN additive, we show that the nature of the intermediate precursor phases and their formation/dissociation dynamics have an impact on the extent of nucleation and growth of perovskite phase affecting the microstructure of the perovskite film. Our findings reveal that the combination of two precursors (MASCN-precursor and DMSO-precursor) with fast and slow transformation rates contributes to the formation of micron-sized perovskite crystals, through seeding nuclei combined with the slow growth of the perovskite phase. For Cs-FA-containing perovskites, we show how the competition between the non-perovskite and perovskite phases formation are affected by the processing treatments. We find that dropping anti-solvent induces immediate crystallization from the bulk wet film, whereas applying N₂-gas works by depleting volatiles from the top-surface leading to interface-induced crystallization that occurs after reaching supersaturation, while both treatments result in dominant crystallization of non-perovskite hexagonal phase with the formation of seeds of perovskite phase. When neither treatment is applied, the as-cast film is mostly amorphous with little non-perovskite phase formation. We further show how the initial structure of the as-cast precursor film impacts the perovskite formation during the subsequent annealing treatment.

Our work highlights the importance of real-time investigation of perovskite film formation which can aid in establishing
processing-microstructure-functionality relationships and help to provide a fundamental understanding of the mechanisms of perovskite formation.

SESSION S.EL14.04: Multimodal Characterization

On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL14

5:00 AM S.EL14.04.01
Multimodal Measurements for Organic Semiconductors—Comparing Real Space and Reciprocal Space Dean M. DeLongchamp, Subhrangsu Mukherjee and Andrew Herzing; National Institute of Standards and Technology, United States

Resonant soft X-ray scattering (RSoXS) has proven to be a powerful technique to measure the structure of organic semiconductor systems. A particularly common application is found in the determination of relative domain purity in organic solar cells (OSC). In polymer-fullerene systems, RSoXS has shown that higher average domain purity is generally correlated to OSC device performance. A simple interpretation of RSoXS purity measurements is complicated by the consideration that real morphologies may be composed of three or more phases, with mixed amorphous regions in addition to relatively pure, aggregated donor and acceptor domains. Scattering originating from orientational contrast is convoluted with phase purity information in OSC systems, further complicating analysis. A complete model that includes both molecular orientation and composition fluctuations is required.

Phase information is lost in RSoXS pattern collection, as it is in most radiation scattering experiments, and algorithmic reconstruction of the reciprocal-space pattern into a real-space model is not straightforward. Model development and forward pattern simulation with iterative comparison to experimentally collected data is the most common interpretation method. In RSoXS analysis these approaches are greatly accelerated by multimodal measurements that directly provide a real-space model of composition fluctuations. By applying atomic force microscopy (AFM) and transmission electron microscopy (TEM), we can construct real-space models for RSoXS interpretation that allow for the extraction of information that the RSoXS technique uniquely provides: the nanoscale molecular orientation. A mathematical and computational framework for forward-simulating RSoXS patterns from these real-space models will be demonstrated. Results from these approaches explain trends in device performance for both OSC and organic transistor devices.

5:30 AM S.EL14.04.02
Revealing Strain-Induced Conjugated Polymer Behaviors Using Soft X-Ray Scattering and Spectroscopy Wenkai Zhong1, Gregory Su1, Feng Liu2, Wanli Yang1 and Cheng Wang1; 1Lawrence Berkeley National Laboratory, United States; 2Shanghai Jiao Tong University, China

Conjugated polymers have generated great interest due to their potential in the fabrication of deformable logic circuits that can be integrated into portable/wearable electronics. Here, we developed a beamline setup that can be capable of probing the bulk- and surface-sensitive data of polymer thin films during tensile test using soft x-ray. The combination of experimental and simulated x-ray spectroscopies assists to uncover the fingerprint of molecular behaviors under strain-stress measurement. Furthermore, to establish the relationship of the molecular evolution and device performances, the charge transport properties of the static strained thin film are also evaluated. We expect this work can contribute to understand the molecular origins of mechanical behaviors associated with the resulting device performances.

5:45 AM S.EL14.04.03
Sharp Interfaces and Pure Domains Allow for Efficient Thick Organic Solar Cells for Roll-to-roll Production Obaid Alqahtani1,2, Victor Murcia1, Thomas Ferron1, Terry McAfee1,3, Safa Shoae4, Ardalan Armin4 and Brian A. Collins5; 1Washington State University, United States; 2Prince Sattam bin Abdulaziz University, Saudi Arabia; 3Advanced Light Source, Lawrence Berkeley National Laboratory, United States; 4University of Potsdam, Germany; 5Swansea University, United Kingdom

Organic solar cells (OSCs) shows continued progress as an alternative photovoltaic technology, now with power conversion efficiency record ~ 17% and rising. For successful industrialization of OSCs, a few challenges need to be overcome such as high performance with thick active layers. Intense research has shown that active-layer nanostructure governs performance in
bulk-heterojunction (BHJ) photovoltaics and uncovered some guidelines to optimum nanostructure. Unfortunately, many of those guidelines only apply to specific organic systems, are not quantitative, and do not target donor-acceptor (DA) interfaces.

Here, we present quantitative studies of active-layer domains and DA interfaces in multiple classes of organic photovoltaic systems, thus establishing universal structure-performance relationships. We utilize soft x-ray techniques (spectroscopy, microscopy, and scattering) to quantify domain size and composition, crystallinity, and mixing of donor-acceptor interfaces. We find that these parameters, specifically sharpness of DA interfaces have strong impacts on charge generation and recombination in both small-molecule and polymer based OSCs. In particular, our study shed light on a recent novel system that has high efficiency (>10%) with suitable BHJ thickness (~1 μm) for large-scale production. Our established structure-performance relationships will help in guiding molecular design and device engineering for industrial production of solar power.

6:00 AM *S.EL14.04.04
Pushing the Resolution Limits of Transmission Electron Microscopy for Imaging of Conjugated Polymers with Sub 4 Angstrom Resolution Brooke Kuei, Ryan Fair and Enrique D. Gomez; The Pennsylvania State University, United States

Despite significant advances in transmission electron microscopes, the resolution limit of polymers remains limited by the electron dose the sample can handle. We thus propose that revealing the mechanisms for radiation damage can yield new methods for imaging at length scales not previously achievable. We have characterized the effect of beam damage on various conjugated polymers, including poly(3-hexylthiophene-2,5-diyl) (P3HT), poly(3-dodecylthiophene-2,5-diyl) (P3DDT), poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT), and poly[[9-(1-octylthiophenyI)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl]-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl]and poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3’’’’-di(2-octyldodecyl)-2,2’,5’,2’’,5’’,2’’’’-quaterthiophene-5,5’’’’-diyl)] (PffBT4T-2OD), via electron diffraction and low-loss electron energy-loss spectroscopy (EELS). We find that the critical dose for damage depends on dose rate, temperature and beam size. Altogether, our results suggest that a significant mechanism for beam damage in conjugated polymers is diffusion of secondary reactive species, such as free radicals. These new concepts in beam damage reveal strategies to push the resolution in the TEM, allowing us to image 3.6 Å π-π stacking in PffBT4T-2OD with high-resolution TEM (HRTEM) at cryogenic conditions, 4D STEM again at cryo temperatures, and HRTEM at room temperature using antioxidants to limit damage. We use high resolution information to reveal pathways for charge conduction, including the type of grain boundaries present, as well as the effect of liquid crystallinity on promoting orientational correlations between domains. Together with our work on predicting liquid crystalline order in conjugated polymers, we use microscopy to develop strategies for designing new molecules with long-range order and strong orientational correlations that lead to enhancement of macroscopic charge transport.

6:30 AM *S.EL14.04.05
Machine Learning for Characterization Techniques Alexander Hexemer; Lawrence Berkeley National Lab, United States

The materials discovery cycle contains many different components, including synthesis, characterization and data analysis and interpretation. In the past few decades, automatic synthesis pipelines have been established for many chemistry and materials systems. For characterization, many advanced techniques, such as X-ray scattering and NMR crystallography, have enabled the structure identification of various chemical, biological and materials systems, including polymers, inorganic materials, and proteins. These techniques have been developed and improved substantially over the past few decades, which brings high-throughput experimental discovery into reach. Meanwhile, these breakthroughs produce enormous data amounts. However, the process of understanding the structural features from data is still very labor-intensive. It requires many man-hours of work by highly specialized and trained scientific staff to interpret the data and identify the structure correctly. Recently, machine learning, a branch of artificial intelligence, has demonstrated the potential to tackle and accelerate the analysis of common techniques such as tomography, scattering, and spectroscopy.

7:00 AM S.EL14.04.06
Machine Learning for Predicting Charge Transfer Integrals in Organic Thin Films Alessio Gagliardi and Michael Rinderle; Technical University Munich, Germany

Getting accurate performance predictions of organic semiconductors is crucial for the development of organic devices. Existing multi-scale analysis often relies on computationally expensive quantum-chemical calculations [1]. Machine learning approaches have been proposed to efficiently predict quantum-chemical quantities [2]. In this project, we present a multi-scale simulation for charge transport in an amorphous organic thin film of pentacene. The molecular structure of the pentacene film is obtained by Molecular Dynamics simulations. The transfer integrals between molecules are calculated with
Density Functional Theory (DFT) methods and passed to a kinetic Monte Carlo simulation to calculate charge carrier mobility. Since DFT simulations for every possible molecule orientation are not feasible we use machine learning using kernel ridge regression to predict the transfer integrals [3]. Critical steps to obtain a well trained, highly predictive model is the feature design, the prior information embedding and the structure of the training dataset. Several techniques will be discussed involving these three aspects of Machine Learning applied to organic semiconductor properties.


SESSION S.EL14.05: Materials Discovery
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL14

5:00 AM *S.EL14.05.04
Finding the Right Bricks for Molecular Legos—Data Mining Approaches to Organic Semiconductor Design Karsten Reuter, Christian Kunkel and Harald Oberhofer; Technische Universität München, Germany

Reflecting the general data revolution, knowledge-based methods are now also entering theoretical catalysis and energy related research with full might. Automated workflows and the training of machine learning approaches with first-principles data generate predictive-quality insight into elementary processes and process energetics at undreamed-of pace. Computational screening and data mining allows to explore these data bases for promising materials and extract correlations like structure-property relationships. In this talk I will illustrate this general development on the basis of an in-house database of >64,000 organic molecular crystals for which charge-transport descriptors have been calculated from first principles [1]. Suitable clustering of this data leads for instance to engineered molecular crystals, in which promising scaffolds are functionalized with favorable side groups [2]. At the same time, smart visualization techniques like chemical space networks identify scaffolds with most room for optimization in hitherto least explored parts of materials space [3].


5:30 AM S.EL14.05.06
Quantum-Mechanical Investigation of Structure-Property Relationships in Organic Emitters for Efficient Thermally Activated Delayed Fluorescence Seyhan Salman1 and Veaceslav Coropceanu2; 1Clark Atlanta University, United States; 2Georgia Institute of Technology, United States

Thermally Activated Delayed Fluorescence (TADF) is one of the most promising mechanisms to realize high efficiency Organic Light Emitting Diodes (OLEDs) without the use of heavy transition metals and offers flexibility to fine-tune the electronic and optical properties of purely organic molecules. In TADF, nonemissive triplet excitons are harvested through a designed molecular emitter that undergoes efficient thermally activated reverse intersystem crossing (RISC) to a singlet manifold, which is followed by a radiative relaxation to the ground state. The rate of the RISC depends on the singlet-triplet energy gap, deltaE(ST), which needs to be minimized for an efficient TADF process. To minimize deltaE(ST), organic molecules with electron donor (D) and acceptor (A) groups are utilized, such that, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are localized on the donor and acceptor, respectively, giving spatially separated HOMOs and LUMOs, giving in a small deltaE(ST). While D-A molecules were the first examples of effective TADF materials, how this efficiency is achieved in devices is not understood. We use multiscale quantum-chemical methods to characterize the (opto)electronic properties of carbazole-based TADF emitters with known D-A groups. We benchmark our calculations with these systems. We will develop: (1) a comprehensive description, at the molecular level, of the fundamental photophysical processes of TADF emitters; (2) a modelling protocol that can accurately describe the electronic structure of such emitters; (3) structure-property relationships; and provide theoretical guidelines for the design of new materials and/or selection of existing materials with well-defined properties leading to devices with improved performances.
Improving Solution Processability of Benzodithiophene-Based Donor Polymer via Side Group Halogenation for Highly Efficient Organic Photovoltaics

Jin Su Park, Geonu Kim and Bumjoon J. Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

For the last few decades, bulk heterojunction (BHJ) organic photovoltaics (OPVs) have been considered as strong candidates for next generation power source for portable or wearable electronic devices with their versatile properties such as low-cost, large-area solution based fabrication, light weight, and flexibility. For general binary blend based OPVs, rational design of polymer donor for optimization of its physical and chemical properties is probably the most decisive step to improve the efficiency. In this sense, introduction of halogen atoms like fluorine and chlorine to either backbone or side chain of conjugated polymer is one of the most favored strategies. Halogen atoms have strong electronegativity values so that fluorinated or chlorinated polymers have downshifted HOMO and LUMO energy levels. This is particularly beneficial for donor polymers since downshifted HOMO can contribute to increase in open circuit voltage (VOC). Furthermore, small size fluorine atoms can induce molecular planarity to enhance the long-range ordering in the blend morphology, while large size chlorine atoms can reduce the unnecessary molecular aggregation. In other words, we can precisely control the blend morphology with fluorine and chlorine atoms. Herein, we demonstrated the positive effects of halogenation strategy to the OPV performance with three polymer donor series PBDT-X (X=H, F, and Cl). We could successfully achieve simultaneous control in the HOMO energy level and aggregation behavior of BDT-based polymer via introducing fluorine and chlorine atoms to side thienyl groups. Interestingly, PBDT-Cl showed a much enhanced processability and we could prepare super high $M_n$ of PBDT-Cl for device fabrication. The PCEs dramatically increased from 9.03% for PBDT-H:Y6 to 12.68% for PBDT-F:Y6 and 15.11% PBDT-Cl:Y6 based OPV devices. To our best knowledge, the PCE over 15% is comparably high with state-of-the-art highly efficient binary OPVs.

SESSION S.EL14.06: Advanced Characterization for Excited States

On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

5:00 AM *S.EL14.06.01

Advances in the Theoretical Description of Nonfullerene-Based Organic Solar Cells

Jean-Luc Bredas1,2; 1Georgia Institute of Technology, United States; 2The University of Arizona, United States

The field of organic photovoltaics is currently enjoying a major resurgence thanks to the development of increasingly performant combinations of polymer donors and nonfullerene-based acceptors. Power conversion efficiencies now approach the 18% mark in single-junction devices.

In this contribution, we will provide a theoretical description of of the factors that have enabled such advances, including:
- hybridization of the strongly absorbing local-exciton electronic states with the charge-transfer electronic states appearing at the donor-acceptor interfaces [1-2];
- minimization of the voltage losses through reduction of the nonradiative recombination pathways [3]; and
- extent of order in the nonfullerene acceptor domains [4-5].

This work is supported by the Office of Naval Research.

In Situ Transient Absorption Spectroscopy During the Formation of Organic Thin Films

Cathy Y. Wong; University of Oregon, United States

The electronic structure and exciton dynamics of the molecules and polymers that form the active layer in organic electronic devices can change dramatically during solution deposition. As solvent vaporizes, molecules aggregate and become electronically coupled, sometimes dramatically changing the exciton dynamics and thus the suitability of the material for electronic devices. The exciton dynamics of molecules in solution and in films of aggregates can be measured using transient absorption spectroscopy. However, the progression of exciton dynamics during film formation is unknown since measurements typically cannot be performed quickly enough to collect accurate transient absorption spectra of these species. The exciton dynamics of evolving material systems can be measured by increasing the speed of data collection. A novel implementation of transient absorption spectroscopy is introduced that can measure transient spectra with up to a 60 ps pump-probe time delay in one shot. The exciton dynamics of intermediate aggregation states are revealed during the formation of an organic film. The information gained using this technique can be used to modify environmental parameters during the film formation process to kinetically trap aggregates with exciton dynamics tailored for particular types of electronic devices.

Probing Self-Assembly of Intra-Molecular Singlet-Fission Materials

David J. Jones; University of Melbourne, Australia

Multiple exciton generation (MEG) through singlet fission (SF) is a spin allowed process whereby a singlet excited state is split into two triplet excitons. Inclusion of SF chromophores into solar cells raises the maximum theoretical efficiency of a solar cell from the Shockley-Queisser limit of 33% to around 45% by effectively harvesting the energy from high energy photons. We have been examining self-assembly of intra-molecular singlet fission materials as a pathway to control local energy landscapes and assist the dephasing of the correlated triplet pair [1,2]. Decoupling “isolated” triplet generation from the initially generated correlated triplet pair remains a significant issue as long lived “dephased” triplets allow for a higher chance of exciton harvesting. We have demonstrated high solid-state SF yield (170%) in solution processed intra-molecular SF materials, with isolated triplet lifetimes in the microseconds [2], using pi-pi-stacking to generate hexagonal columnar structures with the diketopyrrolopyrrole (TDPP) triplet host chromophores on the outside of the stacks. New transient EPR measurements indicate support for a \( S_1 \rightarrow \Sigma^+(TT) \rightarrow \Sigma^+(T-T) \rightarrow T_3^+T_3 \) mechanism, that is a pathway to the quintet coupled triplet pair, then to the isolated triplets from the initially generated correlated triplet pair.

In this presentation we will discuss the recent results from our structure property studies in the impact of self-assembly on SF yield and triplet lifetimes.


SESSION S.EL14.07: Poster Session: Organic Electronics
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
5:00 AM - 8:00 AM
S-EL14

S.EL14.07.03
Exploring Additive Effects on Charge Generation in a PM6:Y6 Organic Solar Cells Awwad N. Alotaibi1, Xaiobo Zhou2, Brian A. Collins1,2 and Ma Wei2; 1Washington State University, United States; 2Xi'an Jiaotong University, China

Organic solar cells (OSCs) are promising as an alternative solar energy technology and their efficiencies are continuously increasing, with record power conversion efficiency at ~ 17%. The processes involved in charge generation and recombination in the bulk heterojunction active layer govern device performance. However, these processes are all entangled and hard to measure quantitatively, which limits progress in optimizing the ultimate performance. We use time delay collection field (TDCF) to disentangle and fully quantify each process occurring in the current record OSC system PM6:Y6 as a function of processing co-solvent, chloronaphthalene, concentration. TDCF is an advanced charge extraction technique that can separate charge generation and recombination processes. We use this to measure generation current, recombination current, and extraction current all at the operating condition of the OSC devices, fully quantifying each loss process. A field dependence of charge generation indicates geminate recombination and our measurements show that the additive eliminates this loss process in PM6:Y6. We additionally vary the excitation wavelength to selectively excite the accepter and the donor molecules. Our initial result suggests that the excited Y6 acceptor generates relatively less charge than the PM6 donor. This new understanding of charge generation and recombination processes will help in design of new materials and optimization of device fabrication for high-performance, economical, and massively scalable solar power.

Towards In Situ Measurement of Nanostructure Dynamics During Ion Transport within a Conducting Polymer Tamanna T. Khan1, Terry McAfee1,2, Thomas Ferron1 and Brian A. Collins1; 1Washington State University, United States; 2Lawrence Berkeley National Laboratory, United States

Ion transport in organic materials is attracting tremendous attention due to the possibilities in applications such as electrochemical transistors, bioelectronics, sensors, soft robotics, and printed electronics. Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) shows promise as an ion transport material and has been integrated into biomedical applications while the nano-structure that enables this property is still unknown. Our previous study utilized Resonant Soft X-ray Scattering (RSoXS) which affords orders of magnitude higher contrast at an elemental absorption edge than electron or nonresonant X-ray techniques. There we showed the morphology consists of PEDOT-rich gel particles embedded within a PSS matrix and upon the addition of a co-solvent (Ethylene glycol) the PEDOT domains swell which was found to correlate with a reduction in ion flow. However, the measured nanostructures were dry and undoped, which do not directly demonstrate which domain facilitates ion flow. Here we will present our progress toward an in-situ RSoXS investigation of a PEDOT:PSS electrochemical transistor during ion transport. We will utilize an in-vacuum, microfluidic sample environment that is compatible with the newly developed RSoXS liquid-chamber at the Advanced Light Source. To achieve this goal, we modified the electrochemical device architecture and replaced the insulating ion barrier with no appreciable reduction in ion transport capabilities. Additionally, the fabrication of a miniaturized device on a micro-electromechanical system (MEMS) chip is under development. Understanding how the ions interact with the nano-structure to transduce an electric signal will enable these devices to potentially use in next generation medical devices.

Imaging the Spatial Distribution of Molecular Dopants in Organic Semiconductors at High Spatial Resolution Using Electron Microscopy Gustav Persson, Sepideh Zokaei, Renée Kroon, Christian Muller and Eva M. Olsson; Chalmers University of Technology, Sweden

Electronic devices based on organic semiconductors have great potential for future applications in devices for energy harvesting and electronics due to low costs, mechanical flexibility and tunable properties. Molecular doping of organic semiconductors is fundamental in order to optimize their electronic properties in high performance devices such as photovoltaic cells, thermoelectrics or light emitting diodes. However, the spatial distribution of these dopants is not completely controlled.[1] Previous studies have shown how density, distribution and diffusion of dopants can significantly affect electronic properties, disrupt the microstructure[2] and decrease long term stability of the host polymer.[3]

Electron microscopy has been used successfully in multiple studies characterizing organic semiconducting materials and extracting information with high spatial resolution. However, crucial information about the distribution of dopants and its dependence of the structure of the surrounding material still remains to be investigated with high spatial resolution. This work addresses the fine scale distribution of molecular dopants in a polar polythiophene with oligoethylene glycol side
The microstructure of the system and the distribution of dopants will be correlated to electronic properties at different doping concentrations. Concepts on how to control the distribution of the dopants will be presented.


**S.EL14.07.07**

**Key Factors Study in Amphiphilic Block Copolymer-Oriented Porous SnO2 Synthesis Process** Shanshan Yin¹, Peter Muller-Buschbaum¹,² and Stephan V. Roth¹,⁴; ¹Technische Universität München, Germany; ²Heinz Maier-Leibnitz Zentrum, Germany; ³KTH Royal Institute of Technology, Sweden; ⁴Deutsches Elektronen-Synchrotron DESY, Germany

SnO₂, as a crucial material in the field of energy storage, has always been the focus of scientific research. For organic-inorganic halide perovskite solar cells (PSCs) or dye-sensitized solar cells (DSSCs), SnO₂ affords high electron mobility and superior chemical stability amongst the various metal oxides. Moreover, as an alternative anode material for lithium-ion battery, it possesses a decent theoretical specific capacity of 1494 mAhg⁻¹. Compared with conventional bulk materials, mesoporous SnO₂ with high specific surface area affords more advantages when applied on either solar cells or lithium-ion batteries. By introducing the mesoporous structure, the recombination of injected electrons within the electron transport layer of the solar cell can be effectively inhibited. Furthermore, with this unique mesoporous structure, the structural collapse of lithium-ion battery anode provoked by significant volume expansion can also be effectively alleviated during the cycling process. In the present work, a novel amphiphilic block copolymer assisted sol-gel chemistry is used for the synthesis of porous SnO₂ nanostructure. Different kinds of solvent are used as a good solvent for both PS and PEO polymer chains, HCl is a selective poor solvent for PS chains and catalyst for the hydrolytic condensation reaction of SnO₂ precursor. With the progressive addition of HCl, the stretch of the hydrophobic PS chains is significantly restricted. As a result, different micelle structures of the block polymer are formed in the sol-gel solution, and the simultaneously hydrolysed SnO₂ nano-dot array is specifically confined in the PEO domains by hydrogen-bond interaction. With the evaporation of the solvent during spin-coating and annealing process, a distinct phase-separated SnO₂/PS-b-PEO composite thin film is obtained on the silicon substrate. For removing the organic polymer template, the composite thin film is calcined at 500 °C for two hours under ambient condition. The obtained nanostructure is visualized by scanning electron microscope (SEM). Crystallinity is characterized by X-ray diffraction (XRD). The buried structure within the thin film is investigated with grazing-incidence small-angle X-ray scattering (GISAXS) measurement.

**S.EL14.07.08**

**Near-IR Dual Luminescent Single Layer OLEDs** Sebastian Hammer¹, Thomas Ferschke¹, Gabriel Freiherr von Eyb¹ and Jens Pflaum¹,²; ¹Julius-Maximillian-University Würzburg, Germany; ²The Bavarian Center for Applied Energy Research, Germany

Multi-color organic light emitting diodes (OLEDs) comprising just one active electro-optical material define the next vital step in the fast-developing field of photonic devices for optical data communication. Taking into account the spectral range of relevant transmission windows as well as the feasibility of coupling light to plasmonic nanostructures, an OLED device emitting at different wavelengths in the near infra-red (NIR) would be highly desirable. In this contribution we cope with these challenges by demonstrating a stable, dual luminescent OLED based on just one electro-optical active zinc phthalocyanine (ZnPc) layer [1]. ZnPc turns out to be a promising candidate for such single layer devices due to its different polymorphs [2] combined with specific emission characteristics, its photo-stability as well as luminescence in the long wavelength range between 800 and 900 nm which allows for efficient coupling to plasmonic excitations in metallic nanostructures [3]. Performing photoluminescence (PL) studies on ZnPc thin films over the full course of the phase transition between α- and β-polymorph, we are able to optically monitor the thermally induced structural changes and their impact on the respective emission over time. The Johnson-Mehl-Kolmogorov-Avrami model [4] can consistently describe the observed behavior of the transition kinetics derived by the distinct emission features of the involved α- and β-polymorphs. In combination with complementary structural studies and temperature dependent PL measurements from 4 K - 360 K this enables us to provide a comprehensive picture of the excited state emission and its correlation to the crystalline packing on molecular length scales. *Vice versa*, we exploit these morphology dependent emission characteristics to demonstrate a prototypical dual luminescent OLED comprising just one active layer of ZnPc. As will be shown, the emission properties can be spectrally
tuned on demand between the excimer emission of the α-phase at 930 nm and the Frenkel emission of the β-phase at 780 nm by a suited thermal treatment. Considering the long-term stability of the adjusted spectral intensity distribution of the devices our work presents an approach towards simple organic photonic devices being of interest for future optical information technology.


S.EL14.07.10
Time Resolved GIWAXS of PEDOT:PSS During Electrolyte Gating
Bryan D. Paulsen1, Ruiheng Wu1, Christopher J. Takaes2, Joseph Strzaika3, Qingteng Zhang4 and Jonathan Rivnay1; 1Northwestern University, United States; 2Stanford Synchrotron Radiation Lightsource, United States; 3Argonne National Laboratory, United States

Electrochemical control of electronic charge (electrolyte gating) has opened a broad array of applications for organic electronic materials including printed electronics, biosensors, neuromorphics, electrochromics, supercapacitors, and actuators to name a few. Structure-property relationships are critical for the advancement of these materials across application. Because electrolyte gating necessarily requires dynamic ion and solvent intercalation and expulsion during device operation, static structural measurements, including steady-state in situ and operando measurements, are critically limited. Understanding electrolyte gated organic materials requires understanding their dynamic structure, which in turn requires time-resolved in situ or operando techniques. Grazing incident wide angle X-ray scattering is a powerful tool to for accessing the microstructure of organic electronic materials. In particular, PEDOT:PSS is ubiquitous in organic electrolyte gated devices. Here the dynamic time-resolved operando GIWAXS of acid crystallized PEDOT:PSS films during aqueous electrolyte gating is reported. The majority of the structural transformation occurs over a narrow range of potential and the doping-dedoping structure dynamics are not symmetric, displaying very different time dependences. Coupling the time-resolved operando GIWAXS with time-resolved UV-vis-NIR reveals that the PEDOT:PSS structure depends not on the absolute charge density, but on the relative population dynamics of neutral, polaronic, and bipolaronic species. Even after the relative populations of charge species equilibrates, time-resolved GIWAXS shows continued long-lived structural relaxations. This complicated phenomena, which is inaccessible with steady-state ex situ, in situ, or operando methods, gives a concrete physical origin of the commonly observed asymmetry of electrolyte gated transistor turn on and turn off. Further it identifies the structural origin of the rate limiting physical processes to be targeted for rational materials design. Finally, this work represents the first report time-resolved X-ray scattering of an organic electronic material during electrochemical gating.
SESSION S.EL15.09: Live Keynote I: Ultra-Wide Bandgap Materials, Devices and Systems

Session Chairs: Robert Nemanich and Hongping Zhao
Sunday Morning, November 29, 2020
S.EL15

10:15 AM WELCOME

10:25 AM *S.EL15.01.01
Toward Fundamental Limits of Ga2O3 Power Devices Huili G. Xing, Wenshen Li and Debdeep Jena; Cornell University, United States

Ga2O3, as a very wide bandgap semiconductor, promises a very high critical breakdown field. The theoretically estimated breakdown field is about 8 MV/cm, and the experimentally observed values are as high as 5.4 to 5.9 MV/cm to date. To take full advantage of the bandgap of Ga2O3, it is necessary to manage the electric field distribution in a Ga2O3 device to be as slow-changing as possible. In this talk, I will review various strategies and their underlying physical principles to manage the field distribution. With these strategies, record high figure-of-merits BV^2/Ron have been demonstrated in Ga2O3 Schottky barrier diodes and fin-transistors [1,2].


10:55 AM *S.EL15.04.01
Ultra-Wide Bandgap 2D Materials—Challenges and New Approaches Joan M. Redwing1, Anushka Bansal1 and Zakaria Al Balushi2; 1The Pennsylvania State University, United States; 2University of California, Berkeley, United States

There is growing interest in wide and ultra-wide bandgap 2D materials such as hexagonal boron nitride (hBN) to serve as dielectric encapsulation layers for 2D heterostructures, as a host matrix for single photon emitters and as an integral part of III-nitride heterostructure devices. In the case of hBN, flakes and films have been formed by exfoliation of bulk crystals and CVD growth on metal substrates, respectively, but further advances are needed to realize wafer-scale single crystal films and expand the available range of wide bandgap 2D materials.

Our studies have focused on epitaxial growth of hBN and other 2D nitride layers by metalorganic chemical vapor deposition (MOCVD). High temperature epitaxial growth of hBN on c-plane sapphire was investigated using B2H6 and NH3 precursors to achieve high purity films. Gas phase pre-reactions between B2H6 and NH3 result in a significantly reduced growth rate for hBN at 1350°C and 50 Torr in a H2 carrier gas. Sequential precursor pulsing was used to minimize gas phase mixing and enable the growth of films with controlled thicknesses ranging from 5-100 nm. The hBN films on sapphire were subsequently used as templates for epitaxial growth of 2D transitional metal dichalcogenides such as MoS2 and WSe2. We have also investigated novel methods to stabilize 2D forms of conventional III-nitride materials such as GaN. This process uses controlled intercalation and reaction of group III and V precursors within the interfacial region of quasi-free standing epitaxial graphene formed on SiC to form stable ultrathin GaNx films. The graphene capping layer provides thermodynamic stabilization of a unique R3m structure as identified by aberration-corrected scanning transmission electron microscopy. Density functional theory predicts a bandgap energy in the range of 4.79-4.89 eV for this structure which correlates well with experimental results from UV-visible reflectance and absorption measurements. The realization of few layer films of group III-nitrides would broaden the range of accessible bandgap energies of 2D materials providing new avenues for scientific exploration and electronic/optoelectronic device development.

11:25 AM *S.EL15.05.01
Dependence of Critical Electric Field on Semiconductor Bandgap—An Analytical Study Mark A. Hollis1, Oleksiy Slobodyan2, Jack Flicker2, Jeremy Dickerson2, Andrew Binder2, Trevor Smith2 and Robert J. Kaplar2; 1MIT Lincoln Laboratory, United States; 2Sandia National Laboratories, United States
An accurate understanding of the critical electric breakdown field ($E_{\text{crit}}$) characterizing semiconductor materials is necessary for the design of power switches, power diodes, and RF power transistors. It is particularly important to understand the dependence of $E_{\text{crit}}$ on bandgap ($E_g$) as new ultrawide-bandgap materials are developed. Unfortunately, the reported dependencies of $E_{\text{crit}}$ on $E_g$ cover a surprisingly wide range in the literature. Moreover, while $E_{\text{crit}}$ is often assumed to be constant for a given material, it is more accurately a function of the device depletion-region width and doping. Further, there are wide discrepancies in the literature where $E_{\text{crit}}$ values for punch-through and non-punch-through structures are compared without regard for these differences. We report a new normalization procedure that enables an equivalent comparison of $E_{\text{crit}}$ values across materials, doping, and punch-through/non-punch-through device types. An extensive examination of many experimental avalanche-breakdown and ionization references reveals that the dependence $E_{\text{crit}} \sim E_g^{1.86}$ best fits the most reliable and newest data for both direct and indirect semiconductors over the range from $E_g = 0.66$ to 5.5 eV (comprising Ge, Si, InP, GaAs, 4H-SiC, GaN, and diamond). It may therefore be reasonable to use this $E_{\text{crit}} \sim E_g^{1.86}$ dependence as an approximate rule of thumb for predicting the critical electric fields of novel ultrawide-bandgap materials until precise measurements are made. Based on the $E_{\text{crit}} \sim E_g^{1.86}$ dependence, the relationship between specific on-resistance ($R_{\text{ON,sp}}$), breakdown voltage ($V_{\text{BD}}$), and $E_g$ for power switches over this bandgap range is best described by $R_{\text{ON,sp}} \sim V_{\text{BD}}^{-3} E_g^{5.58}$ for both direct- and indirect-gap semiconductors.

**11:55 AM OPEN Q&A**

SESSION S.EL15.10: Live Panel Discussion: Ultra-Wide Bandgap Materials, Devices and Systems  
Session Chairs: Masataka Higashiwaki and David Moran  
Monday Morning, November 30, 2020  
S.EL15

9:00 AM WELCOME

9:10 AM PANEL DISCUSSION

10:00 AM MARK HOLLIS, PANELIST

10:00 AM ROBERT KAPLAR, PANELIST

10:00 AM ROBERT NEMANICH, PANELIST

10:00 AM MASATAKA HIGASHIWAKI, PANELIST

10:00 AM HUILI XING, PANELIST

SESSION S.EL15.11: Live Keynote II: Ultra-Wide Bandgap Materials, Devices and Systems  
Session Chairs: Masataka Higashiwaki and Hongping Zhao  
Tuesday Afternoon, December 1, 2020  
S.EL15

7:30 PM WELCOME

7:40 PM *S.EL15.07.01  
Ultra-Wide Bandgap Oxide Semiconductors for Power Electronics and Deep-UV Optics Shizuo Fujita¹, Kentaro Kaneko¹ and Takayoshi Onuma²; ¹Kyoto University, Japan; ²Kogakuin University, Japan

Ultra-wide bandgap (UWBG) semiconductors have extended the opportunity for exploring novel application fields in
electronics and optics. Ga$_2$O$_3$, being supported by its bandgap as wide as ~5 eV, is gaining increasing interests as a material for power electronics devices. Progress of monoclinic-structured Ga$_2$O$_3$ (β-Ga$_2$O$_3$) bulks and substrates, which is the thermodynamically most stable phase in a variety of polymorphs of Ga$_2$O$_3$, grown by solution-methods has accelerated the evolutional research on high-performance power devices. On the other hand, our research has directed on semistable corundum-structured Ga$_2$O$_3$ (α-Ga$_2$O$_3$) grown on sapphire (α-Al$_2$O$_3$). One of the reasons for paying attention to α-Ga$_2$O$_3$ is that there are a variety of corundum-structured oxide materials, which can be combined with α-Ga$_2$O$_3$ to establish novel devices. Alloys and heterostructures of Al$_2$O$_3$, Ga$_2$O$_3$, and In$_2$O$_3$ can achieve heterostructure devices by arbitral tuning of the bandgaps. We have succeeded in the bandgap tuning from 3.7 to 8.8 eV, and the n-type conductivity control of α-Ga$_2$O$_3$ with doping Sn and Si, leading to the device-oriented research. A start-up company, FLOSFIA, Inc., has demonstrated Schottky barrier diodes with on-resistance as low as 0.1 mΩcm$^2$, their reasonable heat resistivity, and the low-loss power conversion. Heterojunctions of α-(Al,Ga)$_2$O$_3$ alloys show the type-I band lineup, and this allows fabrication of a variety of heterojuctions and quantum wells for novel devices. α-In$_2$O$_3$ showed the higher electron mobility compared to that of α-Ga$_2$O$_3$, and we demonstrated the operation of an MOSFET with the field-effect mobility of 187 cm$^2$/Vs. The bandgap of α-In$_2$O$_3$ (3.7 eV) is still wider than that of GaN and SiC, suggesting that α-In$_2$O$_3$ can also be a candidate material for power devices.

A various combination of corundum structured oxides allows unique materials properties. One of the examples is above-room temperature ferromagnetic properties of α-(Ga,Fe)$_2$O$_3$ and α-(In,Fe)$_2$O$_3$. α-Rh$_2$O$_3$ and α-Ir$_2$O$_3$ are native p-type materials. Especially, α-Ir$_2$O$_3$ is closely lattice-matched to α-Ga$_2$O$_3$. We demonstrated p-type conductivity of α-Ir$_2$O$_3$, followed by fabrication of α-Ir$_2$O$_3$/Ga$_2$O$_3$ pn junction. Efforts are continueing to control the bandgap and the hole concentration of p-type α-(Ir,Ga)$_2$O$_3$.

For optical applications of UWBG oxide semiconductors, we have focused on UWBG Mg-rich (x>0.7) rocksalt-structured Mg$_{x}$Zn$_{1-x}$O, whose maximum band gap can be ~7.8 eV (at x=1). This attracts its potential as deep UV light emitters in the wavelength region which cannot be reached by III-nitrides, whose maximum band gap is ~6.0 eV of AlN. We used mist CVD method for the growth of MgZnO with the carbon-free source precursors. The x-ray and electron-beam diffraction evidenced rocksalt structure without noticeable incorporation of other phases. In the TEM images, it was revealed that dislocation defects were formed in the MgZnO layer originating from the defects on the MgO substrate surface, that is, the dislocation rocksalt-structured Mg$_{x}$Zn$_{1-x}$O films with x=0.95 and 0.92 showed the CL peaking at 199 and 212 nm at 6 K and at 205 and 217 nm at 300 K, respectively, without noticeable luminescence at the longer wavelengths. However, the luminescence peak energies were lower by 0.5-0.7 eV than the band gap energies. This large Stokes-like shift is attributed to the local band gap fluctuation. Efforts were continued for Mg$_{x}$Zn$_{1-x}$O/MgO quantum wells. For the sample with x=0.92, the CL peak blue-shifted by 1-8 nm (0.08-0.21 eV) at 6 K compared to the single MgZnO layer with decreasing the thickness of the MgZnO layer. The spectrally integrated CL intensity at 300 K over that at 6 K (I$_{6K}$/I$_{300K}$), which is supposed to be the internal quantum efficiency at 300 K, reached ~13%, which was apparently higher than that of the single layer. The overall results suggest that MgZnO can pave the way for deep UV photonics.

8:10 PM *S.EL15.04.05*

**Halide Vapor Phase Epitaxy of Group-III Sesquioxides** Yoshinao Kumagai$^1$, Ken Goto$^1$, Rie Togashi$^2$, Hisashi Murakami$^1$, Akito Kuramata$^3$, Shigenobu Yamakoshi$^4$ and Masataka Higashiwaki$^5$; 1Tokyo University of Agriculture and Technology, Japan; 2Sophia University, Japan; 3Novel Crystal Technology, Inc., Japan; 4Tamura Corporation, Japan; 5National Institute of Information and Communications Technology, Japan

Group-III sesquioxides such as Ga$_2$O$_3$ and In$_2$O$_3$ are ultra-wide bandgap semiconductor materials. It is well known that bulk single crystals of thermally stable phases β-Ga$_2$O$_3$ ($E_g = 4.5$ eV) and c-In$_2$O$_3$ ($E_g = 3.7$ eV) can be grown by melt growth methods [1,2]. At present, high-speed growth of conductivity controlled homoepitaxial layers of β-Ga$_2$O$_3$ and c-In$_2$O$_3$ has attracted much attention to apply both materials for fabrication of vertical high-power electronic devices. In this presentation, the authors introduce high-temperature and high-speed growth of β-Ga$_2$O$_3$ and c-In$_2$O$_3$ by halide vapor phase epitaxy (HVPE) [3-7].

First, source gases and their carrier gases for HVPE growth of Ga$_2$O$_3$ and In$_2$O$_3$ were examined by thermodynamic analyses. The results clarified that by removing hydrogen atoms (H) from the system and using an inert carrier gas such as N$_2$, He and Ar, HVPE growth of high-quality Ga$_2$O$_3$ and In$_2$O$_3$ films becomes possible at high temperatures exceeding 1000 °C using GaCl$_2$ and InCl$_2$ systems, respectively.

Then, based on the results of thermodynamic analyses, HVPE systems for growing Ga$_2$O$_3$ and In$_2$O$_3$ were constructed. GaCl and InCl were generated in the upstream region of the reactor maintained at 800-850 °C by introducing Cl$_2$ gas over Ga and In metal, respectively. It was clarified that homoepitaxial growth at 1000 °C on bulk β-Ga$_2$O$_3$(001) substrates is possible at a
growth rate above 10 μm/h without deterioration of crystalline quality. The unintentionally doped layer showed a low effective donor concentration ($N_d - N_a$) of less than $10^{13}$ cm$^{-3}$, and it was found that n-type carrier density can be controlled in the range of $10^{15}$ to $10^{19}$ cm$^{-3}$ by intentional Si-doping using SiCl$_4$. These results indicate that the HVPE method is a suitable method for producing homoepitaxial wafers for Ga$_2$O$_3$-based vertical power devices. Also in the In$_2$O$_3$ growth, heteroepitaxy at 1000 °C on (0001) sapphire substrates showed c-In$_2$O$_3$ growth at a rate of several μm/h. These results suggest that high-temperature and high-speed growth of (In$_x$Ga$_{1-x}$)$_2$O$_3$ alloy by HVPE is also possible.

This work was partially supported by the Council for Science, Technology, and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), “Next-generation power electronics” (funding agency: NEDO) and Grant-in-Aid for Scientific Research on Innovative Areas (No. 16H06417) from JSPS.


8:40 PM *S.EL15.02.01
Advanced Diamond FET and MEMS Devices Yasuo Koide; National Institute for Materials Science, Japan

Diamond is a candidate material for next-generation power electronics and integrated circuit (IC) and micro-electro mechanical systems (MEMS) devices which operate under extreme environment. In order to use an advantage of high-density hole channel of hydrogenated diamond (H-diamond) surface, we have developed the high-k stack gate dielectrics and AlN heterojunction gate for H-diamond MOSFETs, such as HfO$_2$/HfO$_2$, LaAlO$_3$/Al$_2$O$_3$, Ta$_2$O$_5$/Al$_2$O$_3$, and ZrO$_2$/Al$_2$O$_3$, AlN/Al$_2$O$_3$ prepared by a combination of sputter-deposition (SD) and atomic layer deposition (ALD) techniques. In addition, we developed the routine ion-implantation process for preparing the diamond cantilever with a resonant frequency quality factor as high as one-million. Recently, we demonstrated the artificial diamond Fin-FETs with high-current level and the nanolaminate insulator gate MOSFET with k value as high as 100, and the new transistor concept named by metal-insulator-metal-semiconductor field-effect transistor (MIMS-FET) to achieve normally-off operation by combining the advantages of MOSFET and metal-semiconductor FET. In this presentation, we will show the comprehensive work on the diamond FET and MEMS devices.

Acknowledgements: This work was in collaboration with J-W. Liu, M. Imura, and M-Y. Liao in NIMS and partly supported by JSPS KAKENHI Grant Number JP16H06419.

9:10 PM LIVE Q&A

SESSION S.EL15.01: Gallium Oxide Devices, Processing and Characterization
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL15

5:00 AM *S.EL15.01.01
Toward Fundamental Limits of Ga2O3 Power Devices Huili G. Xing, Wenshen Li and Debdeep Jena; Cornell University, United States

Ga2O3, as a very wide bandgap semiconductor, promises a very high critical breakdown field. The theoretically estimated breakdown field is about 8 MV/cm, and the experimentally observed values are as high as 5.4 to 5.9 MV/cm to date. To take full advantage of the bandgap of Ga2O3, it is necessary to manage the electric field distribution in a Ga2O3 device to be as slow-changing as possible. In this talk, I will review various strategies and their underlying physical principles to manage the field distribution. With these strategies, record high figure-of-merits $BV^2/Ron$ have been demonstrated in Ga2O3 Schottky barrier diodes and fin-transistors [1,2].

Gallium oxide has many compelling material properties that have generated a large and growing interest for applications in opto-electronics, power devices, and RF devices. The wide bandgap of ~4.6-4.8 eV leads to a large breakdown field, which increases the Baliga and Johnson figures of merit, indicating potentially superior performance in high-power and high-frequency devices. Additionally, wide bandgap materials have a propensity for better radiation hardness due to higher required displacement energies. As such, there are many applications for β-Ga2O3 based devices within space technology, where harsh radiation environments may be present. There has been significant work to understand the impact of radiation on the GaN based devices, which degrades device performance due to the introduction of crystal defects. Ga2O3 has been shown to have higher displacement energies compared to GaN, so it may have improved radiation tolerance. The device studied here is a Si δ-doped β-Ga2O3 MESFET, which has already been demonstrated in separate work to be highly scalable and has the potential for RF performance with an experimentally measured cutoff frequency of 27 GHz [1]. The impact of neutron radiation on this device design is explored and monitored by changes in the device characteristics, such as maximum drain current (ID,max), on-resistance (RON), threshold voltage (VT), transconductance (g_m), and effective mobility (μ_eff). The devices are simulated using Silvaco Atlas, informed through bulk radiation studies on Ga2O3, to model how the radiation damage is influencing the device performance.

The MESFETs were grown by plasma-assisted molecular beam epitaxy (PAMBE) on an (010) EFG Fe-doped substrate. The growth was done at a substrate temperature of 630°C (pyrometer calibrated to Si emissivity), with Si being used as the channel dopant. The device has a 550 nm thick buffer to reduce any trapping effects due to the Fe doped substrate, with a 30 nm top layer above the channel. This led to a charge density of 1.19×10^{13} cm^{-2} with a μ_{eff} of 73 cm^{2}/V-s. The process was dropped from 1.19×10^{13} cm^{-2} to 7.78×10^{12} cm^{-2}. The effective mobility vs. ns curve is measured through a gated transfer length method structure, which shows a reduction in mobility over the range of ns. The zero bias condition ns showed a 24% drop in μ_{eff} from 74 cm^{2}/V-s to 56 cm^{2}/V-s. The mobility is currently being modeled to understand the driving scattering mechanism that caused the reduction. The charge is expected to be compensated through the introduction of new defect states in Ga2O3, which trap the free electrons in the channel. These defects cause dispersion in both the VT and RON as shown in prior work [2-3], and the change in the defect spectrum from radiation is being investigated in these devices. Our previous investigations on the radiation-induced trap introduction in bulk Ga2O3 materials studies [4] is currently being used to inform Silvaco simulations to match the pre- and post-radiation device characteristics. The Silvaco modeling will provide an understanding of how the generated defects caused the reduction in charge, as well as how the device design can be modified to be more tolerant to such defects.


5:45 AM S.EL15.01.03
Ultrahigh-Sensitivity Emission Microscopy Study of β-Ga2O3 Schottky Barrier Diodes in Operation Makoto Kasu1, Sdeoeng Sayleap1, Hiroyuki Takaji1, Kohei Sasaki1, Jun Arima3, Katsumi Kawasaki1, Jun Hirabayashi1 and Akito Kuramata2, 1Saga University, Japan; 2Novel Crystal Technology Ltd, Japan; 3TDK Corporation, Japan

β-Ga2O3 with a bandgap of 4.8 eV is expected to be a high-power semiconductor surpassing the capabilities of SiC and GaN. Recently we demonstrated 20 ampere-class β-Ga2O3 Schottky barrier diodes (SBDs). However, the reliability of these SBDs is quite important for their commercialization in power system circuits. In this study, we used an emission microscopy to observe SBDs with various bias conditions in operation.
microscopy comprised a photon-sensitive electron-multiplying CCD camera and a probe station enabling the observation of light emission patterns of an SBD in real time. The sample was HVPE-grown ~10 μm-thick epitaxial layer grown on EFG-grown β-Ga2O3 (001) substrate. The Pt/Ti/Au Schottky electrodes with diameters of 50, 100, 200, 500, 800, and 1000 μm were formed on the surface, and Ti/Au ohmic contacts were formed on the back surface. In the reverse bias conditions, we observed light emission patterns from SBD from the back surface. As reverse bias increased, leakage current increased, and the number of emission spots increased. We confirmed clearly a relation between the number of emission spots and the leakage current. When additional high reverse voltage was applied, new emission spots appeared, and at a certain voltage catastrophic breakdown occurred at the new emission spot. Thus, emission spots could be classified into leakage-current related emission spots and catastrophic-breakdown related emission spots. Finally, we studied the crystal structure of the observed emission spots using the etch pit, AFM, and cross-sectional TEM methods.

A part of this work is supported by New Energy Development Organization Project of Japan.

6:00 AM S.EL15.01.04

Ultrafast Thermal Imaging for Analysis of Transport Characteristics of Ga2O3 Based Field Effect Transistors Nitish Kumar1, Diego Vaca1, Amitav Tikadar1, Chandan Joishi2, Zhanbo Xia3, Siddharth Rajan1 and Satish Kumar1; 1Georgia Institute of Technology, United States; 2Indian Institute of Technology Bombay, India; 3The Ohio State University, United States

β-Ga2O3 has an ultrawide bandgap (~4.8 eV), high critical electric field strength (~8 MV/cm), and significantly higher Baliga’s and Johnson’s figure of merit compared to GaN and SiC, which makes it promising for deep UV solar blind detectors, radio frequency applications, power rectifiers. β-Ga2O3 power MOSFETs emerged as promising candidates for the future high power/high voltage market. However, Ga2O3 has a much lower thermal conductivity (~10 - 30 W/mK) than GaN or Si. The heat dissipation at high voltages can significantly affect the performance and reliability of these devices. It is necessary to understand the thermal characteristics of β-Ga2O3 based electronics for design of packaging and thermal solutions. In this work, we are using Transient Thermoreflectance Imaging (TTI) to perform ultrafast thermal measurements of β-Ga2O3 FETs. TTI is a promising technique to do temporal and spatial measurements with submicron-scale resolution. A thermoreflectance coefficient was first calculated at the top surface of electrode pads of FETs. The selection of LED of appropriate wavelength is important for high signal-to-noise ratio and accurate measurements. Then, this coefficient is used to calculate the temperature over the electrode pads with a spatial and temporal resolutions of nanoscales (approximately up to 50 nm/pixel and 400 ns). We have calculated the Joule heat generation profiles and temperature distribution at different gate voltages using TCAD Sentaurus. The simulations are compared against the experiments and highlighted that peak temperatures are different at different gate voltages even though the power dissipation is same. We have performed thermal measurements at different gate voltages and calculated thermal time constants of a device to better understand the device’s thermal dynamics.

6:15 AM S.EL15.01.06

MacEtch of β-Ga2O3, SiC and GaN—Plasma-Damage-Free and High-Aspect-Ratio Hsein-Chih Huang1, Julian Arthur Michaels1, Charence Yat-Yin Chan1, A F M Anhar Uddin Bhuiyan2, Zixuan Feng2, Hongping Zhao2 and Xiuling Li1; 1University of Illinois at Urbana-Champaign, United States; 2The Ohio State University, United States

Metal-assisted Chemical Etching (MacEtch), discovered in 2000 for porous Si generation originally, is a local (open-circuit) electrochemical etching method capable of producing anisotropic high aspect ratio semiconductor structures with a simple wet etching process catalyzed by a patterned metal film. MacEtch eliminates plasma and high-energy ion induced damage typically occur in conventional reactive ion etching. Nanowires, vias, trenches, and numerous other patterns have been demonstrated using MacEtch for silicon (Si), germanium (Ge), and compound semiconductors (including GaAs, InGaAs, InP, GaP, SiC, GaN, β-Ga2O3), with unprecedented aspect ratio and sidewall quality. In this talk, we present the MacEtch process and characterization of wide bandgap semiconductors including β-Ga2O3, GaN, and SiC. Acknowledgement: NSF ECCS 18-09946.

6:45 AM S.EL15.01.07

MOCVD Epitaxy of β-Ga2O3 Thin Films with Record Mobilities Zixuan Feng, A F M Anhar Uddin Bhuiyan, Md Rezaul Karim, Yuxuan Zhang and Hongping Zhao; The Ohio State University, United States

β-Ga2O3 with an ultra-wide bandgap of 4.5-4.9 eV and capability of n-doping promises its applications for high power electronics. β-Ga2O3 is predicted to have high breakdown field (6-8 MV/cm) with room temperature mobility of ~200 cm²/Vs. The Baliga figure of merit (BFOM) of β-Ga2O3 for power electronics is predicted to be 2 to 3 times higher than that of GaN and SiC. More advantageously, the availability of high-quality native Ga2O3 substrates produced from melt growth
techniques is critical for large scale production. High voltage (>1 kV) devices, as well as RF devices with 27 GHz cut-off frequency, have been demonstrated recently [1, 2]. Nevertheless, development of high-quality β-Ga2O3 thin film growth technology is the cornerstone for high-performance device applications. Epitaxy of β-Ga2O3 has been investigated via different methods, including MBE, MOCVD, LPCVD, PLD, ALD and etc. Recently, MOCVD grown β-Ga2O3 has exhibited record high electron mobilities in both unintentionally doped (UID) [3] and Si-doped films [4].

In this work, we continue optimizing the MOCVD β-Ga2O3 homoepitaxial process on (010) Ga2O3 crystal orientation, and expand our investigation of β-Ga2O3 MOCVD growth along different orientations including (-201), (001) and (100). Key growth parameters, including growth temperature, growth pressure, Ga/O molar ratio, and substrate preparation, were investigated. For films grown on semi-insulating Fe doped (010) Ga2O3, the epi-film exhibit low background doping. From secondary ions mass spectroscopy (SIMS) depth profile, impurities such as hydrogen (H), carbon (C), chlorine (Cl), iron (Fe) were all below the detection limit. With low intentional Si doping, we demonstrated (010) β-Ga2O3 films with controllable doping between 10^{16} to 10^{19} cm^{-3}. From temperature dependent Hall measurements and analysis taking into account various carrier scattering mechanisms, we extracted a very low compensation level of N_i < 1×10^{15} cm^{-3}. Peak electron mobility reaches ~9500 cm^{2}/Vs at T~45 K for an unintentionally doping (010) β-Ga2O3 film. We demonstrated record high room temperature mobility of ~194 cm^{2}/Vs with n = 8×10^{15} cm^{-3}. The superior transport properties of the MOCVD grown (010) β-Ga2O3 films demonstrated high purity MOCVD epitaxy process with low defects densities. For films grown along different crystal orientations, we use scanning electron microscopy (SEM) and atomic force microscopy (AFM) to characterize the surface morphologies, which have shown significant dependence on substrate orientation. Film growth rate, doping incorporation and transport properties are investigated.

In summary, we demonstrated superb electrical transport properties from MOCVD grown (010) β-Ga2O3 thin films with high purity and low defect densities. Growth mechanisms will be investigated for films grown along other orientations. The results from this study will provide fundamental understanding of the material properties of β-Ga2O3, which determines its potential for power device applications.

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References:

7:00 AM S.E.L15.01.08
The Effect of Silicon Ion-Implant on Charge Transport Mechanisms of Ti/Au Ohmic Contacts to β-Ga2O3 Ming-Hsun Lee and Rebecca L. Peterson; University of Michigan, United States

To achieve the full potential of high-power, high-frequency Ga2O3 power devices, a low-resistance ohmic contact with good stability is needed to minimize conduction loss. The location of the β-Ga2O3 charge neutrality level within the ultra-wide bandgap (~4.8 eV) causes upward band bending and a surface depletion layer. This facilitates the formation of rectifying Schottky contacts, but the lack of Schottky-Mott metal-semiconductor band alignment makes ohmic contact formation difficult. One well-known way to improve ohmic contacts is to degenerately dope the semiconductor to enable tunneling across the junction. For the emerging β-Ga2O3 system, this often has been done by performing silicon donor ion implantation, post-implant anneal, and reactive ion etch (RIE) before Ti/Au metallization. Here, we quantitatively analyze the effect of silicon ion implantation, activation, and RIE on the charge transport mechanisms across ohmic Ti/Au - Ga2O3 junctions. Silicon-doped n+ conduction layers (~1.8 × 10^{18} cm^{-3}) were grown by molecular beam epitaxy on bulk semi-insulating Fe-doped (010) Ga2O3. The substrates were solvent cleaned before Ti/Au deposition followed by a 470°C 1-min N2 post metallization anneal. Temperature dependent current-voltage measurements were performed on Circular Transmission Line Model (CTLM) structures, and the results were analyzed to determine the specific contact resistivity versus temperature. We found that Ti/Au metallization on this heavily n-type doped (010) Ga2O3 epi-layer has a specific contact resistivity of 3.29 × 10^{7} Ω cm^{-2} at room temperature. At an elevated temperature of 175°C, the specific contact resistivity decreases significantly to 6.35 × 10^{4} Ω cm^{-2}. The temperature-dependent data fit the thermionic emission (TE) model, in which the barrier height of the pseudo-ohmic junction is ~0.27 eV. Surprisingly, this value agrees with the barrier height predicted from the difference between metal work function and semiconductor electron affinity. To analyze the impact of n++ doping on contact properties, a second sample was made using the same epitaxial substrate, this time with a box-shaped n++ profile of ~3 ×


10^19 cm^-3 by Si ion implantation, a post-implant anneal to remove implant damage, and a RIE process prior to metallization. CTLM measurements show that the ion implant significantly reduces the contact resistance to 1.51 \times 10^{-4} \text{\Omega cm}^2 at room temperature. The contact resistance of the ion-implanted structures is only slightly temperature dependent, with a contact resistance at 175°C of 6.16 \times 10^{-5} \text{\Omega cm}^2. The thermionic-field emission (TFE) model can be used to describe this Ti/Au – implanted-Ga$_2$O$_3$ junction. We will furthermore report our latest results on optimizing the ohmic contacts to gallium oxide and assessing their microstructure and stability.

7:15 AM S.EL15.01.10
Process and Characterization of Ohmic Contacts for Beta-Phase Gallium Oxide

Rebecca L. Peterson and Ming-Hsun Lee; University of Michigan, United States

Power electronic devices require ohmic contacts with low specific contact resistance to ensure low conduction loss and high-frequency operation. Gallium oxide, unlike other oxide semiconductors, has a charge neutrality level that falls within its ultra-wide bandgap of \(-4.8\) eV, causing upward band bending at the semiconductor surface. This upward band bending has enabled easy formation of Schottky rectifiers using a variety of metals and metal oxides. Such Schottky diodes are remarkably stable, with operation recently demonstrated at high temperatures up to 500°C. However the surface electron depletion layer of gallium oxide makes formation of ohmic contacts more challenging. Most of the existing work on ohmic contacts uses titanium as the metal layer directly in contact with gallium oxide. However our thermodynamic calculations predict that titanium will react with gallium oxide even at room temperature, causing formation of various titanium oxides. In this talk, we describe our observation of reactions at the interface between beta-phase (010) surface bulk gallium oxide and titanium/gold contact layers as a function of gallium oxide doping, metallization layer thickness, and post-metallization anneal time. Using transmission electron microscopies such as TEM, HR-TEM, and STEM with EDX and EELS, we observe the formation of a complex multi-layer interfacial structure that includes a defective gallium oxide layer, an approximately 5-nm thick Ti/TiO$_x$ interfacial layer that - under certain processing conditions - is lattice-matched to gallium oxide, and a mixed-metal Ti/Au contact layer containing titanium-rich nanocrystals. The same layers form on both unintentionally doped (UID) and heavily tin-doped gallium oxide. In addition, the same layers form whether the titanium layer is thin (20-nm) or thick (50-nm), however a longer anneal time is required for full reaction of the thick metallization layer. We hypothesize that the thin Ti/TiO$_x$ layer that forms upon annealing acts as an in situ barrier layer preventing further exchange of titanium and gallium across the interface. In addition, Sn-doping appears to play a minor role in reducing the amount of gallium out-diffusion from the gallium oxide bulk into the mixed metal layer. We will also outline some of the future challenges for ohmic contacts to gallium oxide. For the future success of gallium oxide power devices, further work is needed to understand the mechanisms of charge transport across the contact and to assess the stability of the Ti/Au ohmic contact to subsequent anneals and operation at elevated temperatures under bias or current stress. In addition, new methods may be needed to form reliable and stable ohmic contacts to lightly-doped beta-gallium oxide and gallium oxide with different orientations or crystal phases.

7:45 AM S.EL15.01.11
MOCVD Growth and Characterizations of \(\beta-(Al_{1-x}Ga_x)O_3\) Thin Films and n-Type Doping

A F M Anhar Uddin Bhuiyan, Zixuan Feng, Jared Johnson, Zhaoying Chen, Hsien-Lien Huang, Jinwoo Hwang and Hongping Zhao; The Ohio State University, United States

$\beta$-Ga$_2$O$_3$ has attracted significant attention due to its promising advantages such as large energy bandgap (~4.8 eV), controllable n-type doping and high predicted breakdown field strength (6-8 MV/cm). Energy bandgap engineering by alloying Ga$_2$O$_3$ with Al$_2$O$_3$ can expand the accessible bandgap up to 8.8 eV. Lateral device structures based on AlGaO/GaO heterostructures forming two dimensional electron gas (2DEG) has been demonstrated recently [1]. In order to maximize the advantages provided by the AlGaO/GaO heterostructures, the development of high quality AlGaO with controllable Al composition and n-type doping is critical. In this work, $\beta$-(Al$_{1-x}$Ga$_x$)$_2$O$_3$ thin film growth on (010) Ga$_2$O$_3$ substrates via metalorganic chemical vapor deposition (MOCVD) were investigated [2]. Triethylgallium (TEGa), Trimethylaluminum (TMAI) and pure O$_2$ were used as Ga, Al and O precursors, respectively. Argon (Ar) was used as the carrier gas. The growth temperature was varied between 825°C and 920°C [3].

$\beta$-(Al$_{1-x}$Ga$_x$)$_2$O$_3$ thin films with Al composition x \leq 40% were achieved by the systematical tuning of TEGa/TMAI molar flow ratio. For x\textless27%, high quality $\beta$-(Al$_{1-x}$Ga$_x$)$_2$O$_3$ films were achieved, while the XRD spectra showed phase segregation when Al composition x \gt 27%. SEM and AFM characterization show smooth and featureless surface morphology with RMS roughness of 0.51 nm for a $\beta$-(Al$_{0.1}$Ga$_{0.9}$)$_2$O$_3$ film with thickness of \sim 800 nm. As Al composition increases, the films show increased roughness which can be related to the phase separation observed in high-Al AlGaO films. The high resolution scanning transmission electron microscopy (STEM) imaging of $\beta$-(Al$_{0.1}$Ga$_{0.9}$)$_2$O$_3$ thin film demonstrated high crystalline quality without extended defects or dislocations. Atomic resolution STEM images showed coherent growth of 8-periods of...
Device efficiency was reported at an Al content, x>0.25 [2]. It is crucial to understand the structural and chemical evolution of (AlxGa1-x)2O3 as the Al content changes from low (x=0.10) to high (x>0.25) that will provide researchers an insight about the evolution of (AlxGa1-x)2O3 with varying Al compositions.

Atom probe tomography (APT) is a nanoscale characterization tool capable of providing atomic level information of material’s structure and chemistry in sub-nanometer resolution [3]. However, due to massive data points collected in APT, some material’s features are lost as noise along with uncertainty of data arising from multi-hit events. This hinders the exact quantification of chemical heterogeneity within the material. A data mining approach, based on principal component analysis (PCA), can decipher patterns in APT data to understand material’s structural and chemical characterization of the MOCVD grown AlGaO films will provide in-depth understanding of this emerging UWBG material.

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References:

8:00 AM S.E.L.15.01.13
Data Mining for Structural and Chemical Evolution of (AlxGa1−x)2O3 Using Atom Probe Tomography Jith Sarker1, A F M Anhar Uddin Bhuiyan2, Zixuan Feng2, Hongping Zhao2,2 and Baishakhi Mazumder1; 1University at Buffalo, The State University of New York, United States; 2The Ohio State University, United States

(AlxGa1−x)2O3 is an ultra-wide bandgap semiconductor with a bandgap tunability ranging from 4.8 eV (β-Ga2O3) to 8.7 eV (α-Al2O3), highly promising for future high power transistors and deep ultraviolet (DUV) photodetectors [1]. The bandgap of (AlxGa1−x)2O3 increases monotonically with Al content that could be beneficial for device applications. Surprisingly degraded device efficiency was reported at Al content, x>0.25 [2]. It is crucial to understand the structural and chemical evolution of (AlxGa1−x)2O3 as the Al content changes from low (x=0.10) to high (x>0.25) that will provide researchers an insight about the structural transformation of this material. Atom probe tomography (APT) is a nanoscale characterization tool capable of providing atomic level information of material’s structure and chemistry in sub-nanometer resolution [3]. However, due to massive data points collected in APT, some material’s features are lost as noise along with uncertainty of data arising from multi-hit events. This hinders the exact quantification of chemical heterogeneity within the material. A data mining approach, based on principal component analysis (PCA), can decipher patterns in APT data to understand material’s structural chemistry. Here PCA was conducted on time-of-flight (TOF) of atoms collected by APT to study the structural and chemical evolution of (AlxGa1−x)2O3 with varying Al compositions.

β-(Al1-xGa1−x)2O3 samples with Al content of x=0.10-1.0 was grown on (010) β-Ga2O3 substrate by metal organic chemical vapor deposition (MOCVD) [4]. The controlled removal of atoms via field evaporation was achieved using a UV laser with pulse energy of 30 pJ, employing CAMECA LEAP 5000X HR atom probe system. The location of each atom was traced back using its TOF and position on the detector. PCA was performed on the TOF of ions to determine the pattern in structural chemistry of (Al1-xGa1−x)2O3 layers with x=0.1-1.0. Typical APT output is a single TOF spectrum. Our approach converts this spectrum into ten TOF spectra with 4 million ions in each. The count of ions vs. TOF in these spectra were used as input variables for PCA. Principal component 1 (PC1) captures the change in TOF values of the ions while principal component 2 (PC2) provides the randomness of elemental distribution in lateral planes, perpendicular to the growth direction. When PC2<0, the layer is homogeneous due to random Al distribution, while PC2>0, the (Al1-xGa1−x)2O3 layers are inhomogeneous. For Al composition of x=0.10-0.20, PC2<0, indicating the layers are homogeneous. As the Al content increases, the increasing trend of PC2 suggests inhomogeneity starts to appear. For x=0.30, PC2>0, elemental segregation is present in the layer resulting in degraded crystallinity. For x=0.40-0.60, PC2 remains greater than zero, implying chemically inhomogeneous layers. As the Al content continues to increase towards x=0.80, a decreasing trend of PC2 suggests a gradual reduction of chemical heterogeneity. At high Al content (x=0.80-1.0), PC2<0, an indication of (Al1-xGa1−x)2O3 layers regains
Here we investigated the structural and chemical transformation of (AlxGa1-x)2O3 as the Al content varies from low (10%) to high (100%) by employing data mining incorporating PCA in APT data analysis. This approach provides information about structural and compositional alteration of alloy directly by quantifying the degree of layer inhomogeneity correlated to ion’s TOFs. The information thus obtained will be significant for designing of β-(AlxGa1-x)2O3 devices.

Acknowledgement: Bhuiyan, Feng and Zhao acknowledge the funding support from the Air Force Office of Scientific Research No. FA9550-18-1-0479 (AFOSR, Dr. Ali Sayir)

References:

Diamond is a candidate material for next-generation power electronics and integrated circuit (IC) and micro-electro mechanical systems (MEMS) devices which operate under extreme environment. In order to use an advantage of high-density hole channel of hydrogenated diamond (H-diamond) surface, we have developed the high-k stack gate dielectrics and AlN heterojunction gate for H-diamond MOSFETs, such as HfO2/HfO2, LaAlO3/Al2O3, Ta2O5/Al2O3, and ZrO2/Al2O3, AlN/Al2O3 prepared by a combination of sputter-deposition (SD) and atomic layer deposition (ALD) techniques. In addition, we developed the routine ion-implantation process for preparing the diamond cantilever with a resonant frequency quality factor as high as one-million. Recently, we demonstrated the artificial diamond Fin-FETs with high-current level and the nanolaminate insulator gate MOSFET with k value as high as 100, and the new transistor concept named by metal-insulator-metal-semiconductor field-effect transistor (MIMS-FET) to achieve normally-off operation by combining the advantages of MOSFET and metal-semiconductor FET. In this presentation, we will show the comprehensive work on the diamond FET and MEMS devices.

Acknowledgements: This work was in collaboration with J-W. Liu, M. Imura, and M-Y. Liao in NIMS and partly supported by JSPS KAKENHI Grant Number JP16H06419.

Electron sources are widely deployed in communications through travelling wavetubes, industrial applications through magnetrons, and analytical instruments like electron microscopes, x-rays in industrial/medical/security settings and scientific fields, foremost free electron lasers (FELs). These apparatus, in general, utilize electrons from a thermionic cathode where the emission current is determined by the operating temperature as described by the Richardson-Dushman formalism. A figure of merit can be defined by the emission current (A) in terms of the power (W) dissipated in the device, i.e. [A/W]. A novel approach for electron sources exploits the negative electron affinity (NEA) of a diamond p-i-n diode in a mesa etched design. Operating the device under forward bias allows a fraction of the diode current to be released from the NEA sidewall of the diode. We utilized plasma-enhanced CVD to prepare modified diamond p-i-n diodes using boron-doped (111) oriented substrates and a nitrogen-incorporated nano-structured (nanoC) contact layer. Dedicated plasma deposition systems were used for the intrinsic, phosphorus-doped n-layer, and nitrogen-doped nano-structured carbon layer. Photo-lithography was employed to etch mesa structures with varying geometries and Ti/Pt/Au contacts. We present results from diamond p-i-n-nanoC diodes with an intrinsic layer thicknesses of 10μm. To control ohmic losses in the device the reduced thicknesses of
the n-layer and nanoC layer, were 300 nm and 150 nm, respectively. At an applied bias of 2.2 V a diode forward current of 1.15 x 10^-5 A was established and an emission current of 2.14 x 10^-7 A presented an electronic emission efficiency of 1.8% which is significant for electron emitters. With an increase in the bias to 2.7 V the electronic emission efficiency was somewhat reduced to 1.5%. Operating the device at 2.7 V shifted the power efficiency to 0.015 [A/W] which exceeds efficiencies for cathodes used in commercially available travelling wavetubes (TWTs) and magnetrons. We will discuss the p-i-n-nanoC diode operation and emission efficiency in terms of doping concentrations and layer structure and elaborate on the contribution of excitons to the electron emission.

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5:45 AM S.EL15.02.04
Space Charge Limited Current in Diamond Diodes Harshad Surdi, Mohammad Faizan Ahmad, Franz A. Koeck, Trevor J. Thornton, Stephen M. Goodnick and Robert J. Nemanich; Arizona State University, United States

Diamond based Schottky barrier and PIN diodes are currently of great interest for high power high temperature applications. To improve performance in terms of device metrics such as the on resistance and breakdown voltage, it is critically important to understand the current conduction mechanisms in the different voltage regions of operation of such diodes. Current in diamond diodes has been shown to exhibit space charge limited Mott-Gurney behavior some research groups. However, there has never been a systematic study of the various voltage and current regimes in forward biased diamond diodes. We perform Silvaco Atlas drift-diffusion simulations of Schottky PIN (SPIN) and PIN diamond diodes in comparison to experimentally measured J-V characteristics on the same structures.Incomplete ionization of dopants and nearest-neighbor/variable range hopping mobility models are included in the Silvaco simulations. Space charge limited current (SCLC) with single carrier injection is dominant in Schottky PIN (SPIN) diamond diodes with a relatively low doped and thin n-layer whereas SCLC with double carrier high injection limits current in PIN diamond diodes with a high doped and thicker n-layers. Measurements of SPIN and PIN diamond diode with i-layer ~1.5 μm show evidence of a Mott-Gurney region where J ∝ V^2 within a wide operating voltage range. For SPIN and PIN diamond diodes with thinner i-layers (~1 μm) the Mott-Gurney region is short lived only for a small voltage range and the current transitions back into a linear region limited by the resistivity of the quasi-neutral region. Furthermore, temperature dependent simulations and measurements were also performed to observe a "cross-over voltage" beyond which the increasing trend of diode forward current as a function of temperature is reversed, which is additional evidence of space charge limited current as corroborated by temperature dependent analytical curves of the Mott-Gurney law.

This research is supported by the NASA HOTTech program.


6:00 AM S.EL15.02.06
Low On-Resistance Diamond PIN Diodes Franz A. Koeck, Harshad Surdi and Robert J. Nemanich; Arizona State University, United States

Diamond is a wide band gap semiconductor with outstanding semiconductor properties and the highest known thermal conductivity. The high electron and hole mobilities of diamond are unusual compared to all other wide band gap semiconductors, and support both high power and high frequency applications. PIN diodes have been used for microwave switching where the high power capability of diamond diodes may have a distinct advantage over other semiconductors. In this project, PIN diamond diodes were fabricated on (111) diamond substrates. High performance diodes show light emission during forward bias operation confirming bipolar operation. These diodes show a reduction in on-resistance as the forward voltage is increased beyond 10 V. The reduction of the on-resistance is achieved with a phosphorus doped n-type layer and a
nanocarbon interfacial layer between the metal contact and n-type diamond. This presentation discusses the role of the n-type contact resistance in achieving bipolar device characteristics and an exceedingly low differential on-resistance for high power microwave switching applications.

6:15 AM S.EL15.02.08
Nanostructured Boron Doped Nanocrystalline Diamond for Superconducting Devices Georgina M. Klemencic, Majdi Salman, Scott Manifold, Evan Thomas, Soumen Mandal, Sean R. Giblin and Oliver A. Williams; Cardiff University, United Kingdom

Diamond, when boron doped above the metal-insulator transition, is known to enter the superconducting state below a transition temperature of approximately 4 K for nanocrystalline films. The high normal state resistance of boron doped nanocrystalline diamond is particularly attractive for application to Josephson junction-based devices, while the high Young’s modulus is well suited to nanoelectromechanical devices. A severely limiting factor – with some similarity to many high temperature superconductors – is the short coherence length $\xi \sim 10$ nm, coupled with the naturally top-down nature of the device fabrication.

Here we describe the fabrication and measurement of nanoscale superconducting diamond devices, highlighting the technical challenges involved. We discuss the impact of the morphology on the results, and present some surprising results given the length scales involved.

6:30 AM S.EL15.02.09
High Current (0.7 A/mm) for Diamond MOSFETs with 1.4-µm Gate and NO2 P-Type Doping on High Quality Heteroepitaxial Diamond Substrates Niloy Chandra1, Toshiyuki Oishi1, SeongWoo Kim2, Yuki Kawamata2, Koji Koyama3 and Makoto Kasu1; 1Saga University, Japan; 2Adamant Namiki Precision Jewel Co., Ltd., Japan

Diamond semiconductor with a bandgap of 5.47 eV can be used in high-power devices beyond SiC and GaN. Kubovic and Kasu [1] demonstrated that NO2 p-type doping on H-diamond produced a high hole sheet concentration of $1.4 \times 10^{14}$ cm$^{-2}$. Moreover, Hirama and Kasu et al. [2] fabricated a diamond p-type MOSFET with NO2 p-type doping and obtained a high drain current of 1.3 A/mm for a gate length of 0.4-µm length by using EB lithography. In this paper, we demonstrate a drain current of 0.7 A/mm with a gate length of 1.4-µm length using all photolithography, except EB lithography. Diamond MOSFETs were fabricated on a 1-inch heteroepitaxial diamond. In heteroepitaxy, epitaxial overgrowth (ELO) technology is used to drastically decrease the dislocation density. Furthermore, microneedle technology has been proposed and used to delaminate heteroepitaxial diamond from the substrate without cracking[Editor4] it. In the final process of heteroepitaxy, chemical mechanical planarization process is important to obtain a damage-free and smooth heteroepitaxial diamond surface. The FWHM of (004) was as low as 0.03°, indicating the world’s highest quality level of heteroepitaxial diamond. NO2 p-type doping was performed on H-diamond. Al2O3 as gate insulator and passivation layers were deposited by ALD. All pattern processes including gate formation were made by photolithography, not EB lithography. The gate electrode was deposited overhang to reduce the source resistance. In the DC drain-voltage characteristics, the drain current of 0.7 A/mm was obtained for FET with a gate length of 1.4-µm.


6:45 AM S.EL15.02.10
Machine Learning (ML) Based Study of Chemical and Electronic Properties of Doped Molybednum Trioxide (MoO3) Surface Mahesh R. Neupane1, Michael Groves2, Anthony G. Birdwell1, Dmitry Ruzmetov1, Kevin Crawford1, Pankaj Shah1, James Weil1 and Tony Ivanov1; 1U.S. Army Research Laboratory, United States; 2California State University, Fullerton, United States

Molybednum trioxide (MoO3) is a widely used transition metal oxide with high electron affinity (EA) and work function (WF) and frequently employed as electron acceptor layers in surface-doped diamond field effect transistors (SDFET). The process of electron transfer from the hydrogen-terminated diamond surface to the acceptor layer i.e. MoO3, while creating a hole channel in the surface, is a central mechanism that governs the operating principle of these devices. In addition, the electron extraction strength of the MoO3 layer is defined by its molecular chemical properties such as acidic strength and band gap. In order to understand the role of chemical composition and local structural configuration in modulating the acidic properties of the MoO3 layer, we have performed a density functional theory study and probed the acidic properties of the MoO3 (010) surface doped with other transition metals (Zr, Nb, V, Re, and W). A suitable doping site for each of the dopant
is accelerated using a machine learning (ML) approach. Most of the dopants tend to prefer the first few layers of the surface as their preferred sites. Using the optimized doped configuration, the acidic properties of the surface was evaluated by calculating the adsorption potential energy (APE) of ammonia on the surface because the Lewis acidity of a surface is related to its ability to act as an electron acceptor. A correlation between the electronegativity of the dopant and the Lewis acidity of the surface was observed. Specifically, metals with an electronegativity lower than Mo increased the acidity of the surface while metal dopants with an electronegativity higher than Mo tended to decrease the acidity of the surface. In addition, the size and the electronegativity of the dopants significantly influences the overall electronic properties of the host oxide. This result will help guide the development of SDFETs with properties tuned to desired specifications for high-power RF applications.

SESSION S.EL15.03: Nitride Materials and Devices
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

5:00 AM *S.EL15.03.01
Development of High-Voltage Vertical GaN PiN Diodes Robert J. Kaplan¹, Andrew A. Allerman¹, Brendan P. Gunning¹, Mary H. Crawford¹, Gregory Pickrell¹, Andrew Armstrong¹, Jeramy Dickerson¹, Andrew Binder¹, Jack Flicker¹, Jason Neely¹, Ozgur Aktas², James Cooper³, Karl Hobart³, Travis Anderson³, Andrew Koehler⁴, Marko Tadjer⁴, James Gallagher⁴, Mona Ebrish⁵, Matthew Porter⁵, Srabanti Chowdhury⁵, Ke Zeng⁵ and Rafael Martinez⁵; ¹Sandia National Laboratories, United States; ²EDYNX, United States; ³Sonrisa Research, United States; ⁴U.S. Naval Research Laboratory, United States; ⁵U.S. Naval Postgraduate School, United States; ⁶Stanford University, United States

With its high avalanche breakdown electric field and resulting high figure-of-merit, Gallium Nitride (GaN) represents today’s state-of-the-art semiconductor for high-performance power electronics. However, the most prevalent GaN-based power device, the High Electron Mobility Transistor (HEMT), has not realized the full potential of GaN. This is partly due to the epitaxial growth of GaN on Silicon substrates for such devices, which results in a high density of defects in the material. Further, the HEMT typically shows breakdown at a voltage lower than ideal, due to a complex electric field distribution resulting from its lateral structure, as well as the related problem of the proximity of the high electric field to the surface of the device. Thus, HEMTs not only need to be over-designed for their rated voltage, but typically show catastrophic destructive breakdown (often dominated by surface effects) and do not have avalanche ruggedness. While this is acceptable for many lower-voltage applications (typically 650 V or less), it is not suitable for higher-voltage applications. In contrast, vertical GaN power devices grown on native GaN substrates do not possess these limitations. Breakdown voltages of nearly 5 kV have been reported, and several groups have shown evidence for avalanche breakdown in such structures. However, vertical GaN power devices are immature relative to GaN HEMTs as well as other wide-bandgap power semiconductor devices such as those based on Silicon Carbide. Fundamental materials challenges for vertical GaN in areas such as substrate quality and the epitaxial growth of thick (of order 100 um), low-doped (less than 10¹⁶ cm⁻³ n-type) drift layers are topics of current research. Additionally, challenges exist in the processing of epitaxial layers into vertical device structures. One notable challenge is the realization of selective-area doping, which is needed not only for the functionality of many devices, but also for the edge-termination structures needed to prevent premature breakdown. Finally, minimal manufacturing infrastructure currently exists that can produce devices in quantity with good yield and good long-term reliability. In this talk, we will describe our team’s progress on the design, fabrication, and characterization of vertical GaN PiN diodes ultimately targeted at voltage ratings as high as 20 kV. We will discuss the growth of thick, low-doped drift layers by Metal-Organic Chemical Vapor Deposition as well as the design and processing of these layers into high-voltage devices. The processing effort includes the establishment of a foundry capability to demonstrate pilot production of these vertical GaN diodes, which encompasses evaluation of yield as well as extensive reliability testing and failure analysis. We will also describe methods to test the avalanche ruggedness of the devices, including the time response of the avalanche breakdown process. Finally, we will discuss some potential applications of the devices, including protection of the electric grid. This work was supported by the ARPA-E OPEN+ kilovolt devices cohort managed by Dr. Isik Kizilyalli. Sandia National Laboratories is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

5:30 AM *S.EL15.03.04
GaN-on-Si Power Devices Takeya Okuno, Kenichiro Tanaka, Yasuhiro Uemoto, Tsuguyasu Hatsuuda and Tetsuzo Ueda; Panasonic Corporation, Japan
GaN transistors are very promising for power switching applications taking advantages of the material’s superior properties. Successful demonstration of the epitaxial growth of GaN on large diameter Si substrates has made the GaN devices emerged as a viable alternative with expectation of the low cost fabrication. Use of AlGaN/GaN hetero-junction as the current channel is one of the most notable features of the GaN transistor. Two dimensional electron gas (2DEG) with extremely high carrier concentration originated from the polarization-induced electric fields and the high electron mobility greatly help to reduce the on-state resistances. Lateral GaN transistors with the hetero-junction formed on the insulating buffer layers exhibit extremely low parasitic capacitances as well. These features of the GaN transistor enable high frequency switching with low operating losses. Thus, the GaN transistors can make power switching systems highly efficient and very compact by increasing the switching frequencies. Although achieving normally-off operation overcoming the high carrier concentration of the 2DEG had been the most critical issue for the practical use of GaN transistors, a newly proposed Gate Injection Transistor (GIT) with p-type gate has successfully demonstrated the normally-off operation with low on-state resistance.

In this presentation, current status of the GaN power devices on Si is reviewed. Here, the updated structure of the GIT called as Hybrid Drain-embedded GIT (HD-GIT) is described. Holes are injected from the p-type region formed as a part of the drain. The holes fill the trapping states in the GaN, which suppresses the current collapse even at higher drain voltages. Switching lifetime tests using an inductive load that can be called as dynamic high-temperature operating life (D-HTOL) test are proposed as the severe reliability test considering the practical application of GaN transistors. The HD-GITs ensure sufficient long lifetime under the D-HTOL test. Based on acceleration factors extracted from the Weibull plots of the D-HTOL test results, the D-HTOL lifetime of the 3kW totem-pole PFC (Power Factor Correction) is estimated to be 23.8 years. At present, the above-mentioned GITs are commercially available and the wide-spread use is expected as a game-changing HTOL test results.
High crystal quality AlGaN epitaxial films are highly desirable for near to deep UV optoelectronics applications due to a tunable wide bandgap ranging from 3.4 to 6.0 eV. For many years, the use of foreign substrates for AlGaN epitaxy resulted in highly-mismatched heterostructures with high dislocation densities. The use of recently available AIN single crystals allowed for close matching to AlGaN lattice parameters and thermal expansion coefficients. This lead to high crystalline quality AlGaN epitaxial films exhibiting a significantly reduced dislocation density resultant in improved device performance. However, the lattice mismatch between AlGaN and AIN results in compressively strained alloy films, varying in strain magnitude with composition. This compressive misfit strain can consequentially affect the properties of AlGaN-based devices leading to undesirable compositional non-uniformities to wavelength shifts or unreliable performance. This would require novel strain management schemes to minimize the influence of this strain. Nevertheless, there are no current models to describe AlGaN relaxation mechanisms on c-plane AIN as it is expected that these films are pseudomorphic on these substrates. This is expected as there is no resolved shear stress to activate the primary slip systems in hexagonal wurtzite structure under biaxial strain. As such, in this work, the strain relaxation of AlGaN on AIN single crystal substrate with relatively large lattice mismatch is investigated.

Mismatch strain relaxation could happened by dislocation nucleation, dislocation bending, crystallographic tilting or surface roughening. In the case of preexisting dislocations in the substrate, their propagation through the film would play an important role in strain relaxation through dislocation bending. Al,Ga, N layers were grown by MOCVD either on a c-plane AIN single crystal substrate or an AIN template on sapphire substrate to elucidate the role of these preexisting dislocations. The dislocation density in an AIN substrate is below 10⁶ cm⁻², whereas it’s around 2×10¹⁰ cm⁻² in an AIN layer grown on sapphire. Al mole fraction was varied from 30% to 90% by varying metalorganic precursor flow rates. High resolution X-ray diffraction (HRXRD) was employed to determine the composition and strain relaxation. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) were carried out to characterize the surface morphology and defect structures. HRXRD symmetric (002) and asymmetric (105) reciprocal space mappings (RSMs) revealed that Al,Ga, N layers grown on AIN substrate were pseudomorphic, regardless of alloy composition (0.5<x<0.9). Instead of plastic relaxation, the AlGaN films exhibited so-called “epilayer tilt”. The crystallographic tilt increased linearly with substrate miscut, as expected from the Nagai tilt model. In contrast, full relaxation of the in-plane lattice parameter was observed in Ga-rich 1 μm thick Al,Ga, N layers grown on AIN substrates. The relaxed Al,Ga, N layer did not show a strain gradient. This is in contrast to the strain gradient that was observed in AlGaN on AIN/sapphire, which is believed to result from dislocation inclination. The comparison between Al,Ga, N/AIN and Al,Ga, N/AlN/sapphire indicates that Al,Ga, N layer was abruptly relaxed due to a lack of the preexisting dislocations in AIN substrate. In addition, AFM revealed high density of growth spirals on the relaxed Al,Ga, N layer. X-ray rocking curve measurement also showed much broader AlGaN peaks compared the AIN bulk crystal. Therefore, Ga-rich AlGaN is plastically relaxed on AIN by generating dislocations seemingly contradicting the hypothesis that there is no resolved shear stress activating the primary slip system due to the expected biaxial strain. The dislocation structure in the relaxed AlGaN layer will be presented as well as possible relaxation mechanism including the resulting critical layer thickness.

Significant challenges in point defect control in AlGaN epitaxy has precluded commercialization of AlGaN based devices. Si and recently Ge are typically employed as n-type dopant in AlGaN and exhibit a low activation energy (<50 meV) in Al,Ga, N with x<0.8 and x<0.5 respectively. However, Si doped AlGaN exhibits a “knee behavior” resulting in a conductivity and carrier concentration maxima at a specific Si concentration. Hence a high doping limit exists for Si in AlGaN that lowers the maximum achievable carrier concentrations that are necessary for AlGaN based optoelectronics. Similarly, a low doping limit (a minimum achievable carrier concentration with a corresponding maximum mobility) exists in AlGaN similar to that in
GaAs which precludes implementation of AlGaAs power electronics that require low doped drift regions. Hence a major “point defect problem” exists in AlGaAs that needs to be solved for implementation of AlGaAs technology.

In this work, we demonstrate a systematic chemical potential control (CPC) based point defect control (PDC) where we relate the growth environment parameters to the defect formation energy by determining and controlling the impurity chemical potentials and optimize the growth environment accordingly for minimal point defect incorporation or generation. Here, we employed this framework to provides a quantitative relationship between point defect formation energies and growth process parameters for the case of Si and Ge doping over the whole Al composition range of AlGaAs. This allowed for classifying the difference between these two dopants in terms of incorporation and major compensating defect formation.

Accordingly, the $\text{V}_{\text{III}}\text{nSi}_{\text{III}}$ and $\text{V}_{\text{III}}\text{nGe}_{\text{III}}$ complexes and $\text{C}_{\text{V}}$ were identified as the primary defects responsible for the doping limits in AlGaAs with different compositions grown by metalorganic chemical vapor deposition (MOCVD) on c-plane sapphire substrate and AlN single crystal substrates. We demonstrate control over the knee behavior (improving the peak carrier concentration by impeding the formation of complexes) and low doping limit (achieving lower carrier concentrations by reducing the compensating impurity ($\text{C}_{\text{V}}$) density) by controlling the chemical potentials of III/N and growth temperature for both types of dopants. Si was more effective for doping Al-rich (>40%) AlGaAs while Ge was more effective for Al-poor (<40%) AlGaAs. For the case of Ge doped AlGaAs with Al composition of 40%, a plateau with constant carrier concentration (1-2×10^19 cm^-3) followed by a sharp drop (one order of magnitude to 10^18 cm^-3) in carrier concentration is observed which differs from the Si “sharp knee” doping behavior. This behavior is explained by formation of different types of complexes in Ge doping than Si. Moreover, two orders of magnitude increase in conductivity is observed by decreasing NH$_3$ flow rate from 3 slm to 0.3 slm, which results in III-richer growth environment and the resulting high formation energy of cation vacancy-related point defects. We also demonstrate the strong increase in vacancy formation with increase in growth temperature and consequently higher peak conductivity at lower growth temperatures.

6:45 AM S.EL15.03.12
Identification of Point Defects for the Full Compositional Range of Al$_x$Ga$_{1-x}$N (0≤x≤1) via Photoluminescence Jihyun Kim¹, Isaac Bryan¹, Ronny Kirste², Zach Bryan¹, Pramod Reddy¹, Doug Irving¹, Ramón Collazo¹ and Zlatko Sitar¹; ¹North Carolina State University, United States; ²Adroit Materials Inc, United States

GaN, AlN, and its ternary alloy have had significant development and implementation in commercial devices due to its wide range of applications in UV optoelectronics and power devices. However, it is subject to various point defects that limit their electrical and optical properties. Correct identification of point defects can aid in developing methods to reduce or eliminate undesirable defects that will lead to the properties needed for the devices exploiting the intrinsic material properties. The defects discussed here include self-compensating native defects, unintentional impurities, and various defect complexes. These are mainly point defects that are commonly present in undoped and doped Al$_x$Ga$_{1-x}$N of different compositions with various doping levels of n-type and p-type dopants such as Si, Ge, and Mg.

Photoluminescence (PL) is a widely used characterization technique for the identification of point defects in GaN, AlN, and its ternary alloy. While PL is a commonly used technique that provides significant insight into various materials, analyses of the spectra are a major topic of debate in the community. Point defect identification has been a contentious issue especially due to previous DFT analyses underestimating the bandgap. Therefore, with the development of photoluminescence techniques along with updated hybrid functional studies, there have been many corrections and updates to previous statements regarding identification of point defects. However, hybrid functional studies still have a limitation when it comes to ternary alloys. This study utilizes defect energy values of GaN and AlN identified via hybrid functional studies and confirmed with PL as end points to identify the energy values of the defects in AlGaAs experimentally via PL. The samples were grown via metal organic chemical vapor deposition at different growth conditions to ensure the presence of the point defect of interest. The measured PL spectra of the samples grown with precise growth parameters elucidate the energy of the defect over the entire Al composition of AlGaAs. As expected, the defect energies increase with the increase of Al content. The energy values of the point defects follow a similar trend seen by the bandgap of AlGaAs as a function of Al content as described by Vegard’s law with a bowing parameter. With this defined relationship, this work aims to provide up-to-date identifications of common point defects and their energies for the entire Al composition range of Al$_x$Ga$_{1-x}$N for future development of AlGaAs based technologies.
Our studies have focused on epitaxial growth of hBN and other 2D nitride layers by metalorganic chemical vapor deposition (MOCVD). High temperature epitaxial growth of hBN on c-plane sapphire was investigated using B2H6 and NH3 precursors to achieve high purity films. Gas phase pre-reactions between B2H6 and NH3 result in a significantly reduced growth rate for hBN at 1350°C and 50 Torr in a H2 carrier gas. Sequential precursor pulsing was used to minimize gas phase mixing and enable the growth of films with controlled thicknesses ranging from 5-100 nm. The hBN films on sapphire were subsequently used as templates for epitaxial growth of 2D transitional metal dichalcogenides such as MoS2 and WSe2. We have also investigated novel methods to stabilize 2D forms of conventional III-nitride materials such as GaN. This process uses controlled intercalation and reaction of group III and V precursors within the interfacial region of quasi-free standing epitaxial graphene formed on SiC to form stable ultrathin GaNx films. The graphene capping layer provides thermodynamic stabilization of a unique R3m structure as identified by aberration-corrected scanning transmission electron microscopy. Density functional theory predicts a bandgap energy in the range of 4.79-4.89 eV for this structure which correlates well with experimental results from UV-visible reflectance and absorption measurements. The realization of few layer films of group III-nitride heterostructure devices. In the case of hBN, flakes and films have been formed by exfoliation of bulk crystals and CVD growth on metal substrates, respectively, but further advances are needed to realize wafer-scale single crystal films and expand the available range of wide bandgap 2D materials.

There is growing interest in wide and ultra-wide bandgap 2D materials such as hexagonal boron nitride (hBN) to serve as dielectric encapsulation layers for 2D heterostructures, as a host matrix for single photon emitters and as an integral part of III-nitride heterostructure devices. In the case of hBN, flakes and films have been formed by exfoliation of bulk crystals and CVD growth on metal substrates, respectively, but further advances are needed to realize wafer-scale single crystal films and expand the available range of wide bandgap 2D materials.

While high-performance n-type transparent conductive materials (TCMs) have existed for decades, heavy p-type doping of wide band-gap materials has proven much more challenging. The simple cubic compound CuI (band gap 3.1 eV) was recently rediscovered for this application and is currently the p-type TCM with the highest figure of merit. However, the native defects responsible for p-type conductivity in CuI, as well as compensating defects limiting the maximum achievable doping levels, have not yet been identified experimentally. Furthermore, there is disagreement in the literature on the work function and absolute band positions of CuI relative to vacuum. In this experimental study, we employ temperature- and intensity-dependent photoluminescence to draw new conclusions on the defect landscape of CuI. We then employ a combined photoemission spectroscopy-Kelvin probe system to show that the measured band positions depend critically on surface phenomena related to air exposure, with variations in work function up to 900 meV. Finally, we demonstrate that terahertz spectroscopy is an ideal tool for characterizing the electrical properties of CuI reliably and non-destructively.

Ultra-wide gap (UWG) semiconductors with band gap, $E_G$, in the range of 4-6 eV can offer significant device performance improvements over their narrow-gap counterparts in high-power RF electronics, and provide unique research opportunities including deep-UV optoelectronics, extreme-environment electronics, and exploration of ultra-high-field transport [1]. SrSnO3 (SSO), a perovskite oxide, is an emerging UWG semiconductor with $E_G$ in the range of 4-5 eV [2] that offers particular advantages over other UWG materials including potential p-type doping, and a greater range of device engineering achievable via integration with other functional perovskites including ferroelectrics. High-quality epitaxial SSO films have been grown using hybrid molecular beam epitaxy (MBE) [2], and long-channel field effect transistors (FETs) with promising performance have recently been demonstrated [3]. However, RF-compatible FETs that validate the potential of this material system have not yet been reported. This is due in part to the high contact resistance, $R_c$, of ~38 Ω-mm for Sc contacts used in previous studies [3]. Therefore, identifying Ohmic contacts with low $R_c$ to doped SSO is essential before high-performance SSO FETs can be realized. In this study, we report the results of contact work-function engineering on Nd-doped n-type SSO thin films. Specific contact resistance, $R_{c,sp}$, in the range of 0.1-0.5 mΩ-cm² were achieved.

Ultra-Wide Bandgap 2D Materials—Challenges and New Approaches

Ohmic Contacts to MBE-Grown n-Type SrSnO3 Thin Films

Defects and Band Positions in the P-Type Transparent Conductor CuI

5:00 AM S.EL15.04.01
5:30 AM S.EL15.04.02
5:45 AM S.EL15.04.03
A controlled experiment was performed on heavily Nd-doped $n$-type SSO thin films and contact passivation was explored. The details of the MBE growth technique can be found elsewhere [4]. A 10-nm-thick unintentionally-doped SSO buffer layer was first grown on a 5 mm × 5 mm GdScO$_3$ insulating substrate followed by a 25-nm-thick $n$-SSO active layer. The concentration of Nd was controlled in the active layer by setting the Nd effusion cell temperature to 940 °C during growth. A sheet resistance, $R_s$, of 1874 Ω/□, carrier concentration of $3.5 \times 10^{19}$ cm$^{-3}$, and a mobility of 37 cm$^2$/Vs was obtained using Van der Pauw Hall measurements. A combination of electron-beam lithography, Ar plasma etch, evaporation and lift-off were used to pattern transfer length measurement (TLM) structures. A pre-treatment using O$_2$ plasma clean and a 45 s Ar plasma etch was performed prior to the contact formation. Sc, Mn, Ti, Al, and Cr metals whose work functions are in the range of 3.5 to 4.6 eV were explored, and all contact metals were capped with additional Ti/Au to form the metal lines in the TLM structures. Al and Cr contacts were found to be highly resistive when measured immediately after lift-off and were not considered for further studies. Sc, Mn, and Ti were less resistive, with Mn having the lowest $R_s$ of 11 ± 3 Ω-mm, immediately after lift-off. To test the effect of annealing, contact passivation was performed by depositing 55 nm of Al$_2$O$_3$ via atomic layer deposition at 200 °C. After this process, all three metals showed strong Ohmic behavior. The Ti contacts had the lowest $R_s$ of 2.3 ± 0.3 Ω-mm after passivation, with a resultant $R_s$ of 1687 ± 71 Ω/□ obtained from the TLM measurements. Annealing at 300 °C did not result in any significant change in the $R_s$. $R_{sp}$ values of 0.1, 0.26 and 0.5 mΩ-cm$^2$ were determined for Ti, Sc, and Mn respectively. In conclusion, we have performed a thorough study of metal contacts to $n$-doped SSO and the results show that Ti provides the lowest $R_s$ among the metals analyzed. This work is an important step for evaluating SSO in electronic applications and can pave the way for demonstration of high-performance RF FETs using this emerging high-mobility UWG perovskite oxide.

The work was supported by the AFOSR through award number FA9550-19-1-0245.


6:00 AM S.EL15.04.04

Metallic Line Defect in Perovskite BaSnO$_3$ Thin Films Hwanhui Yun and K. Andre Mkhoyan; University of Minnesota, United States

In perovskite oxides, defects are present in various dimensions and structures, where each defect forms unique and localized atomic bondings different from the host material. Crystalline defects not only modify physical and chemical properties of the host materials locally, but also create specific local electronic and magnetic structures. Defects often exhibit distinct properties such as enhanced chemical activity [1], different bandgaps [2], etc, which provides an opportunity to exploit defects as functional nanostructures. In recent years, new types of line defects have been discovered in oxides thanks to atomic-resolution imaging with scanning transmission electron microscopy (STEM) [2,3]. These defects are reported to alter the local electronic structures showing potential for defect-based nano-devices. Here, we present a new metallic-like line defect in La-doped BaSnO$_3$ thin films. The line defect is aligned along the film growth direction and exhibits a unique atomic arrangement. Structural and compositional analyses are performed using STEM-energy dispersive X-ray (EDX) spectroscopy. Ab-initio calculations including structure optimization and ground-state electronic structure calculations are also carried out. STEM-electron energy-loss spectroscopy (EELS) is employed to test the calculated electronic structures of the line defect.

La-doped BaSnO$_3$ films studied here were grown on various substrates by DC sputter deposition [4] and hybrid molecular beam epitaxy [5]. Plan-view STEM samples were prepared by mechanical polishing. STEM experiments were carried out using an FEI Titan G2 60-300 (S)TEM equipped with EDX and EELS. Ab-initio calculations were performed using the Quantum Espresso package [6] for structural relaxation and WIEN2K code [7] for ground-state calculations and EELS cord-edge simulations.


6:15 AM S.EL15.04.05

Halide Vapor Phase Epitaxy of Group-III Sesquioxides Yoshinao Kumagai$^1$, Ken Goto$^1$, Rie Togashi$^2$, Hisashi Murakami$^1$, Akito Kuramata$^3$, Shigenobu Yamakoshi$^4$ and Masataka Higashiwaki$^5$; $^1$Tokyo University of Agriculture and
Rutile GeO2—An Ultra-Wide-Band-Gap Semiconductor with Ambipolar Doping

S. Chae1, Kelsey Mengle1, Hanjong Paik2, John T. Heron1 and Emmanouil Kioupakis1; 1University of Michigan, United States; 2Cornell University, United States

Ultra-wide-band-gap (UWBG) semiconductors have tremendous potential to advance electronic devices as device performance improves superlinearly with increasing gap. Ambipolar doping, however, has been a major challenge for UWBG materials as dopant ionization energy and charge compensation generally increase with increasing band gap. Using hybrid density functional theory, we demonstrate rutile germanium oxide (r-GeO2) to be an alternative UWBG (4.68 eV) material that can be ambipolarly doped. We identify SbGe, AsGe, and F0 as possible donors with low ionization energies and propose growth conditions to avoid charge compensation by native acceptor-type defects. Acceptors such as AlGe have relatively large ionization energies (0.45 eV) due to the formation of localized hole polarons. Yet, we find that the co-incorporation of AlGe with interstitial H can increase the solubility limit of Al and enable hole conduction in the impurity band. We also calculate electron (153.6 cm2V-1s-1) and hole mobilities (4.7 cm2V-1s-1) of r-GeO2 at 300 K, suggesting r-GeO2 has outstanding electronic properties that can compete with the state-of-the-art UWBG semiconductors such as β-Ga2O3. We will also discuss on our recent experimental progress on thin-film growth and electrical characterization of r-GeO2.

This work was partially supported by the Council for Science, Technology, and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), “Next-generation power electronics” (funding agency: NEDO) and Grant-in-Aid for Scientific Research on Innovative Areas (No. 16H06417) from JSPS.


6:45 AM SEL15.04.06

Rutile GeO2—An Ultra-Wide-Band-Gap Semiconductor with Ambipolar Doping

Sieun Chae1, Kelsey Mengle1, Hanjong Paik2, John T. Heron1 and Emmanouil Kioupakis1; 1University of Michigan, United States; 2Cornell University, United States

Ultra-wide-band-gap (UWBG) semiconductors have tremendous potential to advance electronic devices as device performance improves superlinearly with increasing gap. Ambipolar doping, however, has been a major challenge for UWBG materials as dopant ionization energy and charge compensation generally increase with increasing band gap. Using hybrid density functional theory, we demonstrate rutile germanium oxide (r-GeO2) to be an alternative UWBG (4.68 eV) material that can be ambipolarly doped. We identify SbGe, AsGe, and F0 as possible donors with low ionization energies and propose growth conditions to avoid charge compensation by native acceptor-type defects. Acceptors such as AlGe have relatively large ionization energies (0.45 eV) due to the formation of localized hole polarons. Yet, we find that the co-incorporation of AlGe with interstitial H can increase the solubility limit of Al and enable hole conduction in the impurity band. We also calculate electron (153.6 cm²V⁻¹s⁻¹) and hole mobilities (4.7 cm²V⁻¹s⁻¹) of r-GeO2 at 300 K, suggesting r-GeO2 has outstanding electronic properties that can compete with the state-of-the-art UWBG semiconductors such as β-Ga2O3. We will also discuss on our recent experimental progress on thin-film growth and electrical characterization of r-GeO2. This work was supported by the Designing Materials to Revolutionize and Engineer our Future (DMREF) Program under Award No. 1534221, funded by the National Science Foundation. It used resources of the National Energy Research Scientific Computing Center, a DOE office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

S. Chae, J. Lee, K. A. Mengle, J. T. Heron, and E. Kioupakis, Rutile GeO2: An Ultrawide-Band-Gap Semiconductor with
MBE Growth and Doping of Ultra-Wide Gap Perovskite SrSnO$_3$

Tristan Truttmann$^1$, Jin Yue$^1$, Laxman R. Thoutam$^1$, Abhinav Prakash$^1$, Tianqi Wang$^1$, Fengdeng Liu$^1$, Ashley Bucsek$^1$, Yongqi Dong$^2$, Tom Mates$^3$, Dillon D. Fong$^2$, Jong-Woo Kim$^3$, Philip J. Ryan$^2$, Hua Zhou$^2$, Turan Birol$^1$, Richard D. James$^1$ and Bharat Jalan$^1$; $^1$University of Minnesota, United States; $^2$Argonne National Laboratory, United States; $^3$University of California, Santa Barbara, United States

The perovskite alkaline-earth stannates are gaining research attention due to their unparalleled room-temperature mobility among perovskite oxides and as wide-bandgap semiconductors. Most research attention is invested in the cubic aristotype member BaSnO$_3$ despite its unsolved challenges of large substrate-film misfit and consequent mobility disparity between thin films and bulk single crystals. The less-studied non-cubic member SrSnO$_3$ (SSO) has a smaller lattice parameter—closer to commercially available substrates—and thus has the potential to overcome the challenges associated with thin-film BaSnO$_3$. First, by using a novel radical-based hybrid molecular beam epitaxy (MBE) approach, we show that SSO can be grown coherently—free of any misfit or threading dislocations—on commercially available substrates, hence solving a long-standing challenge in the stannate community [1]. Secondly, we show—in the first strain engineering study of stannates—that epitaxial compressive strain can control the octahedral rotations in SSO, hence stabilizing a high-temperature tetragonal polymorph at room temperature by more than 700 K below its stability range in bulk. Thirdly, by combining controlled doping, Hall measurements and secondary ion mass spectroscopy (SIMS), we show that SSO can be successfully doped n-type with rare-earth elements showing 100% dopant activation [2]. A record-high room-temperature mobility of 70 cm$^2$V$^{-1}$s$^{-1}$ at 1 $\times$ 10$^{20}$ cm$^{-3}$ was obtained in a 12 nm La-doped SSO film, making this the thinnest perovskite oxide semiconductor with electron mobility exceeding 25 cm$^2$V$^{-1}$s$^{-1}$ at room temperature. By suppressing electron scattering using heterostructure design, we further boosted the room-temperature mobility to 80 cm$^2$V$^{-1}$s$^{-1}$ in doped SSO—the highest reported value to-date among any distorted perovskite oxide.

Finally, we discuss that the electron-electron interaction effect plays an important role in determining low-temperature transport. The quantitative analysis of the magnetoresistance data yielded a large phase coherence length of electrons exceeding 450 nm at 1.8 K and revealed the electron-electron interaction to be accountable for the breaking of electron phase coherence in La-doped SSO films. These results, while providing critical insights into the fundamental transport behavior in doped stannates, also suggest the potential application of stannates in quantum coherent electronic devices owing to their large phase coherence length [3].


Engineering Quaternary Monoclinic AlInGaO for III-Oxide Power Electronics

Xiaoli Liu and Chee-Keong Tan; Clarkson University, United States

In recent years, β-Ga$_2$O$_3$ has drawn much attention in power electronic technology, attributed to the advantages of ultrawide bandgap (~4.9 eV), stability, and affordable large-diameter wafer. The ultrawide bandgap enables β-Ga$_2$O$_3$-based devices to exhibit high breakdown field, while there is limitation including the p-type doping difficulty and low thermal conductivity issue. In addition, heterostructure design in III-Oxide based materials is still limited, even though it is important for carrier confinement as demonstrated in the Si and III-V based technology. Extensive research works on III-Oxide binary and ternary alloys (In$_2$O$_3$, Ga$_2$O$_3$ and InGaO, AlGaO) have been reported, but there has been no literature on the β-Ga$_2$O$_3$-based quaternary material. Thus, investigating the optoelectronic properties of the β-Ga$_2$O$_3$-based quaternary materials is critical to gauge their potential use in device applications. In this work, β-(Al$_{0.5}$In$_{0.5}$Ga$_{1-x-y}$)$_2$O$_3$ alloys with Al- and In-content each up to 18.75% are investigated using Density function theory (DFT) calculations. The effect of Al and In atoms on the electronic band structures of β-Ga$_2$O$_3$ quaternary alloys is studied combining with density of states analysis. Additionally, the lattice constants of β-(Al$_{0.5}$In$_{0.5}$Ga$_{1-x-y}$)$_2$O$_3$ alloys are analyzed and presented. The band alignment between β-Ga$_2$O$_3$ and (Al$_{0.5}$In$_{0.5}$Ga$_{1-x-y}$)$_2$O$_3$ is also investigated to explore the potential use of β-Ga$_2$O$_3$ / (Al$_{0.5}$In$_{0.5}$Ga$_{1-x-y}$)$_2$O$_3$ materials system in electronic devices. Preliminary experimental work is also discussed.
x-y)2O3 alloys with high Al and In-content are not considered in this study to avoid the known phase separation issue happened to the β-Ga2O3-based ternary alloys. The band structure calculations for β(AlxIn1-x-y)2O3 alloys were performed using the projector augmented wave (PAW) method. The semilocal generalized gradient approximation (GGA-PBE) is applied to treat the exchange-correlation potential in the calculations. Other computational details have also been carefully chosen to optimize the DFT calculations.

Analysis from the DFT-calculated band structures of β(AlxIn1-x-y)2O3 alloys with different Al/In-content indicate that the alloys exhibit indirect band gaps, which is similar to β-Ga2O3. The direct bandgap of β-(AlxGa1-x)2O3 increases from 4.835eV to 5.171eV when the Al-content increases from 0% to 18.75%, while the direct bandgap of β-(InxGa1-x)2O3 alloys decreases from 4.835eV to 4.432eV when the In-content goes up to 18.75%. In addition, the lattice parameters of the AlInGaO alloys have been investigated and analyzed. Our analysis shows that adding Al and In will reduce and increase the lattice of Ga2O3 alloys respectively. As a result, the quaternary β-(AlxInyGa1-x-y)2O3 alloys can be designed to be lattice-matching with β-Ga2O3 alloy, implying the possibility of adjusting the band properties of β-Ga2O3-based material without creating compressive or tensile strain within the material systems. In addition, electron effective mass is calculated using the energy dispersions of β-(AlxInyGa1-x-y)2O3 alloys. The average effective mass of electrons of β-(AlxInyGa1-x-y)2O3 alloys are obtained by taking the geometric mean of effective masses in different directions since the alloys exhibit anisotropy property. The electron effective mass values are generally within 0.22~0.28m0, while the addition of Al and In has an obvious effect on the effective mass changing. Our findings could be valuable for carrier transport related applications such as power electronic and deep UV photodetector devices. Experimental details on AlInGaO alloys will be further discussed.

SESSION S.EL15.05: Wide Bandgap and Ultrawide Bandgap Technology and Challenges
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL15

5:00 AM *S.EL15.05.01
Dependence of Critical Electric Field on Semiconductor Bandgap—An Analytical Study Mark A. Hollis1, Oleksiy Slobodyan2, Jack Flicker2, Jeremy Dickerson2, Andrew Binder2, Trevor Smith2 and Robert J. Kaplar2; 1MIT Lincoln Laboratory, United States; 2Sandia National Laboratories, United States

An accurate understanding of the critical electric breakdown field (Ecrit) characterizing semiconductor materials is necessary for the design of power switches, power diodes, and RF power transistors. It is particularly important to understand the dependence of Ecrit on bandgap (Eg) as new ultrawide-bandgap materials are developed. Unfortunately, the reported dependencies of Ecrit on Eg cover a surprisingly wide range in the literature. Moreover, while Ecrit is often assumed to be constant for a given material, it is more accurately a function of the device depletion-region width and doping. Further, there are wide discrepancies in the literature where Ecrit values for punch-through and non-punchthrough structures are compared without regard for these differences. We report a new normalization procedure that enables an equivalent comparison of Ecrit values across materials, doping, and punch-through/non-punch-through device types. An extensive examination of many experimental avalanche-breakdown and ionization references reveals that the dependence Ecrit ~ Eg1.86 best fits the most reliable and newest data for both direct and indirect semiconductors over the range from Eg = 0.66 to 5.5 eV (comprising Ge, Si, InP, GaAs, 4H-SiC, GaN, and diamond). It may therefore be reasonable to use this Ecrit ~ Eg1.86 dependence as an approximate rule of thumb for predicting the critical electric fields of novel ultrawide-bandgap materials until precise measurements are made. Based on the Ecrit ~ Eg1.86 dependence, the relationship between specific on-resistance (RON,sp), breakdown voltage (VBD), and Egd for power switches over this bandgap range is best described by RON,sp ~ VBD2 Eg0.58 for both direct- and indirect-gap semiconductors.

5:30 AM S.EL15.05.02
DFT Study of Structural and Electronic Properties of hBN/Diamond (100) Heterostructure Pegah S. Mirabedini1, Mahesh R. Neupane2, Alex Greaney1, Anthony G. Birdwell2, Dmitry Ruzmetov2, Kevin Crawford2, Pankaj Shah2, James Weil2 and Tony Ivanov2; 1University of California, Riverside, United States; 2CCDC US Army Research Laboratory, United States

Diamond has the highest breakdown field and carrier mobility among all wide band-gap semiconductors making it attractive for use in next generation high-speed and high-power electronic devices [1]. Unfortunately, unlike other semiconductors such
as Silicon, diamond cannot be doped with shallow dopants [2], and so other techniques such as surface doping and delta doping are required for doping diamond. Particularly, for the surface-doping technique, a thin-layer of acceptor layer is interfaced with the hydrogenated diamond surface which creates high-mobility hole channel at the interface. Motivated by this, we explore the possibility of using 2D materials such as graphene or hexagonal boron nitride (hBN) as acceptor layers. Though the surface lattice constants of (111) surface is nearly lattice matched and easy to create epitaxial heterostructure with h-BN, surface doped diamond field effect transistors (SDFETs) with diamond (100) surfaces are widely proposed as a next generated in p-type RF-power electronic devices [3]. Herein, we perform a first-principle study to investigate the structural alignment and electronic properties of h-BN/H-diamond (100) heterostructures. As a comparison, we also study the graphene/H-diamond (100) heterostructures. We perform a full analysis of the structural alignments of the 2D layers on Diamond (100) surface and identify optimal strain-compensated h-BN (graphene)/H-diamond (100) heterostructure. Using the optimized heterostructure, we perform electronic structure calculations and compare charge transfer through the van-der-Waal (vdW) gaps between the constituent layers in the heterostructures. Our results show that in spite of a relatively larger vdW-gap, the degree of charge transfer in h-BN and Diamond (100) is higher than that of graphene and H-diamond (100). We believe that our theoretical observations will help the fabrication of novel high-frequency and high-power electronic devices.


5:45 AM S.E.L15.05.03
Material and Electrical Characterization of Ohmic Contacts to 4H-SiC for Stable Operation at 800 °C Robert Okojie1 and Dorothy Lukco2; 1NASA Glenn Research Ctr, United States; 2Vantage Partners, LLC, United States

High power and high temperature electronics and sensing devices that would perform reliably on a long term basis are mostly implemented in wide bandgap (WBG) and ultra-WBG (>3 eV) semiconductors. However, critical factors that are central to their successful implementation and reliable field operations remain technologically challenging. These include the availability of relevant substrates and doped epitaxies, packaging, contact metallization (Ohmic and Schottky) and diffusion barrier systems (DBS). The DBS essentially protects the ohmic contacts to the WBG semiconductors from the inward migration of oxygen (O) from the atmosphere and gold (Au) that is typically the top bond pad layer. Reaction and diffusion kinetics are generally accelerated with increasing temperatures, resulting in corresponding short lifetime to failure of these devices. It is, therefore, imperative to develop the appropriate metallization schemes that would provide effective ohmic contact and DBS to the semiconductor.

In this work, we report the results of the material analysis and electrical characterization of Ti (100 nm)/TaSi2 (300 nm)/Ti (100 nm)/Pt (300 nm) ohmic contacts and Ti (100 nm)/Pt (300 nm) DBS on n-type 4H-SiC epilayer up to 800 °C. Device level evaluation was demonstrated on 4H-SiC micro pressure sensors to operate reliably for over 100 hours at 800 °C. Key sensor performance parameters [zero offset voltage (ZPO) and bridge resistance] that are critical to sensor measurement reliability were extracted. The results showed a strong dependency of the electrical parameters on the microstructures of the ohmic contact and DBS.

The ohmic contact sputter deposition and patterning was followed by rapid thermal anneal (RTA) at 800 °C for 10 seconds in near vacuum condition. The subsequent diffusion barrier metallization was similarly annealed. Finally, a TaSi2 (20 nm)/Pt (100 nm)/Au (1 μm) bond pad metallization was deposited and furnace annealed at 800 °C in Ar for 30 minutes. This final layer also underlying the DBS. The in-situ measured sensor resistance and output voltage during atmospheric heating up to 800 °C was matched with corresponding periodic Focused Ion Beam-Field Emission Scanning Electron Microscopy (FIB-FESEM), Energy Dispersive Spectroscopy (EDS), and Auger Electron Spectroscopy (AES) depth profiling. The depth-resolved AES and EDS revealed three prominent intermixing and reaction zones within the diffusion barrier and metal/SiC ohmic interface. The reaction products were primarily silicides and carbides of Ti, which had combined to form the ohmic contact on the n-type SiC surface. The diffusion barrier zones consisted of intermixed Ti/Pt and silicide complexes of Pt while the top zone comprised of intermix of Pt-rich/Ti that effectively prevented O and the bond pad Au from diffusing toward the ohmic contact. The overall stability of the bridge resistance and output voltage were predicated upon the effectiveness of the diffusion barrier scheme in preventing the migration of O and Au.

During the first 100 hours of atmospheric heating at 800 °C, the changes in the resistance correlated well with the diffusion of Au and O into the Ti/Pt layer. Both the bridge resistance and the ZPO simultaneously leveled off thereafter and remained relatively stable for the remaining duration of thermal treatment. The before and after comparisons of the results of thermal activities within the metallization showed direct correlation between the ZPO characteristic trend and the microstructural changes as a result of O and Au migration and new reaction products.

This work is very significant in that future WBG based sensors and electronics can be inserted further into the hotter section...
of engines, thereby eliminating the need for costly cooling and packaging schemes. It would help capture wider thermoacoustic frequency bandwidth, thereby improving the measurement needed for accurate validation of computational fluid dynamics codes.

6:00 AM S.EL15.05.04
Initial-Growth Mechanism of High-Quality Diamond Heteroepitaxial Layer on Sapphire Substrate Makoto Kasu1, Ryota Takaya1, Yuki Kawamata2, Koji Koyama2 and SeongWoo Kim2; 1Saga University, Japan; 2Adamant Namiki Precision Jewel Co., Ltd., Japan

Diamond semiconductor with a bandgap of 5.47 eV is expected to be used in high-power devices surpassing the capabilities of SiC and GaN. Diamond heteroepitaxial growth has been successfully demonstrated on cubic (001) MgO substrate [1] and yttria-stabilized zirconia / (001) Si substrate [2]. However, recently, S.-W Kim et al. demonstrated the highest quality heteroepitaxial diamond growth on a sapphire substrate. The FWHMs of (004) and (311) rocking curves were as low as 120 arcsec (0.03°) and 269 arcsec (0.07°) respectively, which are the world’s best values in heteroepitaxial diamond. Heteroepitaxial diamond growth on sapphire [3.4] has previously been reported, but the crystal growth mechanism remains unclear. Therefore, the present research focuses on revealing the growth mechanism. We investigated initial diamond growth initiated by bias-enhanced nucleation on an Ir buffer layer deposited on (11–20) sapphire substrate. First, we revealed the crystal orientations of diamond, Ir buffer, and sapphire substrates using X-ray diffraction. Next, we observed diamond nucleation, nucleus coalescence, and layer growth processes sequentially by using atomic force microscopy and scanning electron microscopy. In particular, using cross-sectional transmission electron microscopy, we studied the interface of diamond nuclei with the Ir buffer layer. The mechanism would be different from Ref. 2. We documented the Ir buffer layer epitaxial growth on sapphire substrate and diamond nuclei growth on the Ir buffer layer.

References

SESSION S.EL15.06: Growth and Characterization of Gallium Oxide Materials
On Demand Abstracts Available for Viewing Starting Saturday, November 21, 2020

5:00 AM S.EL15.06.01
Deep Level Defects in LPCVD-Grown β-Ga2O3 (010) Hemant Jagannath Ghadi, Joseph McGlone, Zixuan Feng, Yuxuan Zhang, Hongping Zhao, Aaron Arehart and Steven Ringel; The Ohio State University, United States

Interest in β-phase gallium oxide (β-Ga2O3) has been growing tremendously in recent years due to its great potential for power devices and RF electronics. The major factors causing this surge are its ultra wide direct bandgap (~4.6-4.8 eV), large breakdown fields, ease of n-type doping, availability of large area, melt-grown substrates and high predicted device figures of merit compared with GaN and SiC. Most epitaxial growth efforts are focused on molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD) but low pressure chemical vapor deposition (LPCVD) allows for high growth rates in a high temperature growth regime and with additional features like large area scalability. LPCVD can achieve growth rates as high as 10 µm/hr and growth temperatures up to 1100°C using economical and eco-friendly high purity precursors or sources. LPCVD is recently gaining significant attention due to its ability to grow β-Ga2O3 films with thicknesses as high as 40 µm, with uniform and controllable Si-doping on β-Ga2O3 substrates or sapphire. LPCVD grown β-Ga2O3 films exhibit room temperature mobilities as high as 150 cm²/Vs. However, recent studies indicate the LPCVD grown β-Ga2O3 films are still unable to achieve high mobility at low temperatures with higher background acceptor compensation compared to MOCVD or MBE grown material. This study provides the first known full-bandgap evaluation of defect states of LPCVD-grown β-Ga2O3. Here we use deep level optical spectroscopy (DLOS), deep level transient (thermal) spectroscopy (DLTS), and admittance spectroscopy (AS) to identify bandgap states in LPCVD material. By comparing with our earlier work on β-Ga2O3 grown by other methods, the goal of this work is to identify the critical defects in LPCVD material and develop correlations with possible sources in order to guide strategies to suppress them. A 1.2 µm thick layer of Si-doped β-Ga2O3 was homoepitaxially grown at 1050°C on a Sn-doped (010) Tamura
Ga₂O₃ substrate using an in-house built LPCVD system using metallic gallium and O₂ sources [1]. Thin Ni Schottky diodes were fabricated to facilitate defect spectroscopy. The net doping from C-V was measured to be 2.3×10¹⁷ cm⁻³ and Hall measurements on separate samples revealed electron mobilities of ~120 cm²/Vs at 300 K. Admittance spectroscopy (AS) detected a donor state at E_c-0.04 eV with a concentration of 2.3×10¹⁷ cm⁻³, which matches the doping from C-V and is the likely Si donor state. AS also revealed another state at E_c-0.12 eV with a lower concentration of 9.1×10¹⁵ cm⁻³ that was also seen by DLTS. Three other states were observed by DLTS, at E_c-0.18 eV, E_c-0.21 eV, and E_c-0.78 eV with trap concentrations of 2.1×10¹⁴ cm⁻³, 5.7×10¹⁴ cm⁻³, and 2×10¹⁶ cm⁻³, respectively. The state at E_c-0.78 eV matches prior reports attributing this to Fe impurities [2] and dominates the DTLS spectrum. States deeper in the bandgap, which cannot be detected by AS or DLTS, were seen from DLOS measurements at E_c-2.0 eV, E_c-3.7 eV and E_c-4.4 eV with concentrations of 1.6×10¹⁵ cm⁻³, 9×10¹⁵ cm⁻³, and 1.5×10¹⁶ cm⁻³, respectively. Of all six observed traps, only the deep level at E_c-3.7 eV appears to be unique in the LPCVD material compared to prior work on MBE, EFG and MOCVD-grown b-Ga₂O₃ [3,4] material, and is under specific investigation. Lighted C-V measurements are ongoing to correlate specific traps with the high degree of carrier compensation observed in this material, which will be compared with similar studies made on b-Ga₂O₃ grown by other methods, along with a detailed comparison of trap properties and concentration distributions from our prior work [3,4].


5:15 AM S.EL15.06.03
Polarized Transmittance and Photoluminescence Spectra of Fe-Doped Ga₂O₃ Crystals Rujun Sun, Yukee Ooi and Michael Scarpulla; The University of Utah, United States

Fe-doped Ga₂O₃ is the only commercially available but also highly desirable semi-insulating substrates/crystal. In this work, optical properties of Fe-doped Ga₂O₃ were studied by polarized transmittance and photo-luminescence spectroscopy. The optical bandgaps of electrical field vector parallel to a*, and c were 4.46 ev and 4.40 eV of (010) sample while 4.74 eV and 4.50 eV for b and c axes of (100) sample. An absorption band around 4.0 eV was observed when electrical field vector was parallel to b and a* axes. Two sharp peaks at 689nm and 697nm superimposing a broad peak at 710nm were emitted from Fe-doped Ga₂O₃ under UV laser excitation (233nm-270nm) at room temperature, while the almost zero PL intensity between 300 nm and 600nm. Temperature dependent PL showed that the broad peak diminished while two sharp peaks intensified with temperature decreasing, which matches the emission feature from transition metal Cr. ICP-MS was employing to check the existence of Cr impurity. PLE showed the 689 nm peak intensity reached its maximum when excitation wavelength was near the band gap, indicating energy transfer from electron at Ga site to this impurity site. This work demonstrates that Fe-doped Ga₂O₃ substrate is promising to provide zero PL background for ultra-thin epi-layer as well as to probe trace impurities.

5:30 AM S.EL15.06.04
The Influence of Polymorphism on the Electronic Structure of Ga₂O₃ Jack Swallow¹, Tim Veal¹ and Anna Regoutz²; ¹University of Liverpool, United Kingdom; ²University College London, United Kingdom

Ga₂O₃ is an ultra-wide band gap oxide material, which promises great improvements in a range of applications, including power electronics, solar blind UV photodetectors, and gas sensing devices. Its high conductivity, high breakdown field, and large band gap have led to a flurry of research in the past few years. Most of the work has focused on its most stable form, monoclinic β-Ga₂O₃. However, Ga₂O₃ presents pronounced polymorphism and a number of other polymorphs beyond β exist, including hexagonal α-Ga₂O₃, cubic γ-Ga₂O₃, and orthorhombic ε-Ga₂O₃. Although this wealth of possible structures opens up opportunities to control and tune structure, electronic structure and ultimately physical characteristics, the polymorphs beyond β-Ga₂O₃ are comparatively unexplored. In particular experimental results are scarce due to the general difficulty in producing high quality materials and the lack of theoretical results for the more structurally complex polymorphs.

Here, we present an in-depth study of the electronic structure of the α, β, γ, and ε polymorphs of Ga₂O₃. The samples investigated are either bulk single crystals or epitaxial films grown using molecular beam epitaxy (MBE) or atomic layer deposition (ALD), selecting the highest quality samples available for each of the polymorphs. We report high-resolution valence bands from hard and soft X-ray photoelectron spectroscopy (SXPS and HAXPES) which are directly compared to theoretical partial and total electronic densities of states as calculated within the framework of density functional theory (DFT). Both deep and shallow core level spectra are compared to DFT results to explore the influence of structure, rather than solely the oxidation state, on the core level behaviour. X-ray absorption spectroscopy (XAS) is used to probe the
unoccupied states and in combination with SXPS is used to gain an estimate of the changes in the band gaps of the polymorphs. Ultimately, this work presents a systematic and comprehensive study of the electronic structure of Ga2O3 polymorphs, providing an insight into electronic trends and their relationship to crystal structure. This comparative study helps to discern trends between the different structures and advances our understanding of this polymorphic material. It lays the foundation for further exploration of Ga2O3 in applications beyond its β phase.

SESSION S.EL15.07: Oxide Materials and Applications
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EL15

5:00 AM *S.EL15.07.01
Ultra-Wide Bandgap Oxide Semiconductors for Power Electronics and Deep-UV Optics Shizuo Fujita1, Kentaro Kaneko1 and Takayoshi Onuma2; 1Kyoto University, Japan; 2Kogakuin University, Japan

Ultra-wide bandgap (UWBG) semiconductors have extended the opportunity for exploring novel application fields in electronics and optics. Ga2O3, being supported by its bandgap as wide as ~5 eV, is gaining increasing interests as a material for power electronics devices. Progress of monoclinic-structured Ga2O3 (β-Ga2O3) bulks and substrates, which is the thermodynamically most stable phase in a variety of polymorphous of Ga2O3, grown by solution-methods has accelerated the evolutionary research on high-performance power devices. On the other hand, our research has directed on semistable corundum-structured Ga2O3 (α-Ga2O3) grown on sapphire (α-Al2O3). One of the reasons for paying attention to α-Ga2O3 is that there are a variety of corundum-structured oxide materials, which can be combined with α-Ga2O3 to establish novel devices. Alloys and heterostructures of Al2O3, Ga2O3, and In2O3 can achieve heterostructure devices by arbitral tuning of the bandgaps. We have succeeded in the bandgap tuning from 3.7 to 8.8 eV, and the n-type conductivity control of α-Ga2O3 with doping Sn and Si, leading to the device-oriented research. A start-up company, FLOSFIA, Inc., has demonstrated Schottky barrier diodes with on-resistance as low as 0.1 mΩcm², their reasonable heat resistivity, and the low-loss power conversion. Heterojunctions of α-(Al,Ga)2O3 alloys show the type-I band lineup, and this allows fabrication of a variety of heterojunctions and quantum wells for novel devices. α-In2O3 showed the higher electron mobility compared to that of α-Ga2O3, and we demonstrated the operation of an MOSFET with the field-effect mobility of 187 cm²/Vs. The bandgap of α-In2O3 (3.7 eV) is still wider than that of GaN and SiC, suggesting that α-In2O3 can also be a candidate material for power devices.

A various combination of corundum structured oxides allows unique materials properties. One of the examples is above-room temperature ferromagnetic properties of α-(Ga,Fe)2O3 and α-(In,Fe)2O3. α-Rh2O3 and α-Ir2O3 are native p-type materials. Especially, α-Ir2O3 is closely lattice-matched to α-Ga2O3. We demonstrated p-type conductivity of α-Ir2O3, followed by fabrication of α-Ir2O3/Ga2O3 pn junction. Efforts are continuing to control the bandgap and the hole concentration of p-type α-(Ir,Ga)2O3.

For optical applications of UWBG oxide semiconductors, we have focused on UWBG Mg-rich (x>0.7) rocksalt-structured Mg,Zn1-x,O, whose maximum band gap can be ~7.8 eV (at x=1). This attracts its potential as deep UV light emitters in the wavelength region which cannot be reached by III-nitriles, whose maximum band gap is ~6.0 eV of AlN. We used mist CVD method for the growth of MgZnO with the carbon-free source precursors. The x-ray and electron-beam diffraction evidenced rocksalt structure without noticeable incorporation of other phases. In the TEM images, it was revealed that dislocation defects were formed in the MgZnO layer originating from the defects on the MgO substrate surface, that is, the dislocation defects density in the MgZnO layer at present is dominated by the quality of the MgO substrate. Mg,Zn1-x,O films with x=0.95 and 0.92 showed the CL peaking at 199 and 212 nm at 6 K and at 205 and 217 nm at 300 K, respectively, without noticeable luminescence at the longer wavelengths. However, the luminescence peak energies were lower by 0.5-0.7 eV than the band gap energies. This large Stokes-like shift is attributed to the local band gap fluctuation. Efforts were continued for Mg,Zn1-x,O/MgO quantum wells. For the sample with x=0.92, the CL peak blue-shifted by 1-8 nm (0.08-0.21 eV) at 6 K compared to the single MgZnO layer with decreasing the thickness of the MgZnO layer. The spectrally integrated CL intensity at 300 K over that at 6 K (I6K/I300), which is supposed to be the internal quantum efficiency at 300 K, reached ~13%, which was apparently higher than that of the single layer. The overall results suggest that MgZnO can pave the way for deep UV photonics.
Hafnium oxide (HfO$_2$) is an insulator that has a wide range of applications due to its high dielectric constant and wide band gap. Recent discoveries from 2011 on emergent ferroelectricity in doped HfO$_2$ thin films, have enabled it as a candidate for ferroelectric random-access memory, ferroelectric field-effect transistors, and ferroelectric tunnel junctions. However, the origin of the ferroelectricity of HfO$_2$ and doped versions has not been systematically studied yet. Furthermore, a significant amount of work has been done only on polycrystalline thin films. We are exploring the synthesis of epitaxial Hf-Zr-O$_2$ as a function of thickness with epitaxial oxide top and bottom electrodes by pulsed laser deposition to explore these ferroelectric transitions. We utilize high-resolution transmission electron microscopy to explore the atomic structure of epitaxial HfO$_2$ thin films and identify the ferroelectric phase transition with multislice simulation. The robust ferroelectric phase of HfO$_2$ can be found at a thickness below 10nm, even below 5nm, which is identified as the non-centrosymmetric orthorhombic phase with space group Pca2$_1$. The oxygen atom plays an important role in allowing a phase transition from the monoclinic to the orthorhombic phase.

Titania polymorphs have been shown to crystallize when thin-film amorphous precursors deposited by pulsed laser deposition are annealed [1]. This non-equilibrium deposition method, coupled with particular oxygen partial pressure ranges [2] and film thicknesses defined a region of phase space where particular polymorphs formed.

We have extended this study to investigate amorphous TiO$_2$ precursors deposited by RF-sputtering from a Ti target with an Ar/O$_2$ sputter mix of different ratios and find broadly similar trends. We can produce uniform thickness high-fraction brookite, anatase and rutile films by changing the oxygen deficiency in the precursor films and controlling the thickness in the range 30 – 200 nm. Synchrotron XRD analysis of a series of precursor and annealed films shows that the precursor films are fully amorphous and the crystallized films confirm the phases identified by the Raman analysis.

We observe the growth morphology and growth rates of the three major TiO$_2$ polymorphs. We anneal amorphous precursor films in-situ in flowing nitrogen at 300 – 450°C in a heating stage mounted on a microscope attached to a Raman spectrometer. We record the crystallization on video and distinguish the phases optically due to their different refractive indices and different morphologies, confirming phase identification with Raman spectroscopy. We find a particular precursor film yields the same polymorph when annealed at different temperatures, only the rate of formation changes. With in-situ analysis we found that brookite crystallizes faster than rutile and anatase. We also observed that RF-sputtered films have more crystallization centers than pulsed laser deposited films and crystallize slower. Brookite tends to grow anisotropically, while the rutile and anatase growth habits are more symmetric. The growth morphologies are complex in mixed-phase films. Photocatalysis measurements indicate that photo-degradation of methylene blue by the polymorphs differ from each other. Some photoactive films also revealed unusual XRD spectra.

Metal-fluoride thin films have previously been investigated as gate insulators in MISFETs (CaF$_2$/Au/Diamond) and this work expands upon that investigation. AlF$_3$ is an ultra-wide-bandgap (10.8 eV) material with a low dielectric constant (2.2). These properties indicate that AlF$_3$ may be a suitable insulator for high power high frequency devices. AlF$_3$ films have been deposited on hydrogen terminated boron-doped polycrystalline diamond in a plasma enhanced atomic layer deposition (PEALD) process. PEALD is an emerging energy enhanced ALD technique that utilizes plasma radicals to drive surface reactions rather than thermal energy. PEALD allows for lower impurities, increased growth rates, improved stoichiometry, and lower deposition temperatures. The reactants used were trimethylaluminum, pyridine-hydrogen fluoride, and a hydrogen plasma. 

In-situ X-ray photoelectron spectroscopy was used to determine the band alignment of AlF$_3$ films on polycrystalline diamond. The valence band maxima are measured at 9.15 eV and 0.05 eV for AlF$_3$ and diamond, respectively. A type II staggered gap is formed with a conduction band offset of 3.77 eV and a valence band offset of 9.1 eV. The results indicate that AlF$_3$ should be appropriate as a dielectric on p-type diamond.

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S.EL15.08.03
Investigations of Ultrawide Bandgap (AlIn)$_2$O$_3$ Alloy for AlInN / GaN Devices

Xiaoli Liu and Chee-Keong Tan;
Clarkson University, United States

Recent progress in wide band gap semiconductor based power electronics technology sparked humongous interest in the development of the semiconductor materials. With the aim of further reducing the cost, size, compactness while improving energy efficiency and performance of electrical systems, semiconductor materials of larger energy bandgap have been highly sought after. Recent studies show that ternary AlInN material grown lattice-matched with GaN provides access of energy bandgap of ~4.5 eV, allowing theoretically higher Baliga figure of merit than GaN-based devices and similar to that of β-Ga$_2$O$_3$ based devices. However, it also poses some difficulty in controlling the field effect since insulating material with larger energy bandgap is required to create conducting channel and block electron leakage from devices. Finding an insulator material with energy bandgap larger than 4.5eV that can be grown on AlInN material is thus important towards realizing the AlInN / GaN field effect transistor based devices. Most recently, AlInO material has been proposed as a viable material that can serve as the insulator through thermal oxidation of the AlInN material. While the AlInO material is expected to exhibit chemical formula of (Al$_{1-x}$In$_x$)$_2$O$_3$, it is unclear if the AlInO material is thermodynamically stable and the information of AlInO material is extremely limited to date. Understanding the material properties of AlInO material from the viewpoint of structural and electronic properties is therefore critical for AlInN / GaN devices.

In this work, (Al$_{1-x}$In$_x$)$_2$O$_3$ alloys covering complete In compositions are investigated using Density Functional Theory (DFT) calculations. Two different phases of AlInO alloys will be investigated: corundum and hexagonal. The effect of In atoms on the electronic properties of AlInO alloys is investigated. For structural properties, lattice constants and equilibrium volume of AlInO alloys are analyzed. Moreover, band alignment between AlInO and AlInN is studied, exploring possible heterojunction lineups in various orientations.

For DFT calculation, supercell approach is implemented in which a 60-atom AlInO crystal is constructed. The In composition is varied through the number of Al atoms being replaced in the crystal structure. DFT calculations were carried out using commercial package MedeA-VASP software. Band structure calculations were performed by using projector augmented wave (PAW) method, with the use of semilocal generalized gradient approximation (GGA-PBE) functional to treat the exchange correlation potential in the system. Other computational details such as the k-spacing and cutoff energy have been optimized to ensure reasonable DFT results. Surface supercells for both AlInO and AlInN alloys were also created in order to calculate the band alignment, and the parameters are set to be similar to bulk DFT calculations.

Our DFT-calculated band structures of AlInO alloys indicate the possibility of direct bandgap property crossing over to indirect bandgap property when In-content is larger than 20%. Preliminary analysis of the DFT-calculated band structures show that the energy bandgap of Al$_2$O$_3$ reduces significantly when In content is added into the alloy. The energy bandgap of AlInN with 20%In is less than 5eV. The results are expected since In atoms are much larger than the Al atoms, and significant bowing occurs in atomic size mismatch condition. Further studies on density of states are required to understand the contribution of each orbital in the bandgap reduction. Note that Al$_2$O$_3$ and In$_2$O$_3$ have bandgap of ~8.8eV and ~3eV, respectively. Adding In in Al$_2$O$_3$ also results in significant reduction of lattice constants, but lattice matching condition with AlInN is possible with proper tuning of In-content. From the formation energy analysis, it is also expected that more than 20% In will result in phase separation issue in the AlInN alloys. Details on AlInN alloys will be further discussed.

S.EL15.08.09
Morphological and Electrical Study of Ga2O3-Ti Nanofilms Processed by Co-Sputtering

Lucia Ivonne Juárez Amador;
2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
In this work an experimental study to characterize titanium (Ti) doped amorphous-Gallium Oxide (Ga$_2$O$_3$) nano-films (a-Ga$_2$O$_3$:Ti) produced by magnetron sputtering at 300K is reported. The nano-films were deposited by the co-sputtering process using Ti and Gallium oxide (Ga$_2$O$_3$) targets with a two magnetron system; the films were deposited over glass substrates covered with a 20 nm of non-doped buffer Ga$_2$O$_3$ layer grown by the same process. The Ga$_2$O$_3$ concentration was changed by varying the RF-power of the Ga$_2$O$_3$ magnetron at 75 or 150 W, while the DC-power for the Ti target was set at 80W. Due to the non-equilibrium character of the sputtering technique the grown films can be considered as a distribution of Ti clusters embedded into an a-Ga$_2$O$_3$ matrix when the growth process is done at low temperatures, therefore post-grown annealing processes can be used to adjust the film properties fixing appropriately the annealing conditions, temperature or atmosphere composition. The annealing temperatures were 400, 450, 500 and 550 °C by periods of 10 min, in a high purity N$_2$.atmosphere. When the samples were annealed at low temperatures the resistivity of the films were varied from 5.74x10$^4$ to 134.63 Ω-cm, electron concentration from 10$^{22}$ to 10$^{16}$ cm$^{-3}$ and mobility of 0.475 to 6.689 cm$^2$/V-s. by annealing the samples at 550°C electrical insulating nano-films were produced by the complete oxidation of the Ti clusters. The relatively low mobility of the doped nano-films suggests the Ti dopant produces carrier dispersion suggesting the presence of Ti deep levels in the material. According to the X-ray diffraction analysis the Ti clusters in a-Ga$_2$O$_3$ matrix helps in reducing the required temperature to transform amorphous films to β-Ga$_2$O$_3$ at ~400 °C. The required temperature to produce the phase change was confirmed by SEM studies producing octahedral shape nanocrystallites with sizes from ~5 to 50 nm.

S.EL.15.08.10

Diamond P-I-N Diodes for Receiver Protectors Mohammad Faizan Ahmad$^1$, Harshad Surdi$^1$, Franz A. Koeck$^1$, Robert J. Nemanich$^1$, Stephen M. Goodnick$^1$, Trevor J. Thornton$^1$ and Josephine Chang$^2$; $^1$Arizona State University, United States; $^2$Northrop Grumman Mission Systems, United States

The intrinsic properties of diamond are attractive for use in high power receiver protector (RP) systems such as those required at the input of radar systems. At low input power, the RP device presents a low capacitance and high resistance so that it adds negligible insertion loss to the desired signals. However, at high input power levels the RP turns on with a resistance much smaller than the 50 Ω characteristic impedance and the majority of the input power is reflected away from the receiver input. P-I-N diodes made of Si and GaAs used in today’s conventional RP systems have limitations at high-power. The wide bandgap of diamond coupled with its higher thermal conductivity give it a superior RF power handling capability that can protect sensitive RF front-end components from high power incident signals. Vertical diamond P-I-N diodes were fabricated with an n$^+$-i-p$^+$ structure consisting of: a heavily phosphorus-doped n-type diamond layer with a doping concentration >1x10$^{19}$ cm$^{-3}$ and a thickness of approximately 300 nm; an intrinsic diamond layer of thickness approximately 0.5 μm; and a heavily boron-doped diamond <111> substrate with doping concentration of 5x10$^{20}$ cm$^{-3}$ and a thickness of 300 μm. The sample was patterned by photolithography and Ti/Pt/Au contacts were deposited on both top and bottom surfaces of the diode. The PIN test structures consist of a total of 144 diodes with diameters of 50 μm, 100 μm, 200 μm, and 400 μm. A SiO$_2$ hard mask of thickness 2 μm was deposited on the diamond surface prior to the isolation etch step. Reactive ion etching was used to define electrically isolated mesa regions etched to a depth of ~600 nm. The SiO$_2$ etching was carried out using fluorine RIE with 25 sccm of CHF$_3$ and Ar at a chamber pressure of 30 mTorr at 200 W. Diamond etching was done in the chamber with 38 sccm of O$_2$ and 2 sccm of SF$_6$ at a chamber pressure of 15 mTorr at 300 W. The electrical characteristics of the P-I-N diodes were measured using DC and RF probe stations. The diodes show significant forward current starting at around 10 V. The lowest specific on-resistivity at high forward bias was measured using the DC probe station and found to be 4.5x10$^4$ Ω cm$^2$. The capacitance of the diodes at zero bias was extracted from small-signal S-parameter measurements in the frequency range 0.1 – 10 GHz and found to be 7.6 nF/cm$^2$. Taken together these values suggest a figure of merit, FOM = $R_{on}.C_{eff}$ = 6.81 ps corresponding to a frequency of 23.37 GHz.

A 200 μm diameter PIN diode was attached to a coplanar waveguide (CPW) for RF small-signal measurements as follows. The p-type substrate of the diode was soldered onto the ground plane of the signal-ground-ground strip-line of the CPW while the n-type top contact was wire bonded to the signal line. The diode was DC biased with a bias-T connected to the input of the CPW. S-parameters were measured at no bias and 12 V of forward bias, over a frequency range of 0.5 to 5 GHz at 10 dBm power. $S_{11}$ and $S_{21}$ were found to be -15 dB and -0.4 dB respectively with no bias at 500 MHz, confirming negligible insertion loss with no forward bias applied. At 12 V of forward bias, $S_{11}$ and $S_{21}$ were found to be -2.5 dB and -13 dB respectively at the same frequency, confirming that up to 95% of the input power is reflected by the forward biased PIN diode. With further optimization of the diode growth and fabrication it will be possible to reduce the on-resistance and the associated $R_{on}.C_{eff}$ figure of merit with the goal of achieving PIN diodes that provide > 30 dB isolation for high power.
receiver protection applications.
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S.EL15.08.11
Defect Structure and Distribution of Electrons in Ga2O3 and IGZO Stack Yong-Seok Lee, Min-Ju Choi, Yonghee Lee, Ho Won Jang and Young-Woon Kim; Seoul National University, Korea (the Republic of)

Epitaxial Ga2O3 film was grown on the Al2O3 substrate using magnetron sputtering. Because of the lattice mismatch between Ga2O3 and substrate, epitaxial films reveal mosaic domain structure with high number density of interfacial dislocations. Interfacial Domain size has an average diameter of ~ 40 nm. On the top of the Ga2O3, without additional treatment, semiconducting indium gallium zinc oxide (IGZO) was stacked to obtain the oxide/semiconductor structure. An external electron beam control system for SEM and TEM was designed and built in house to acquire position specific physical properties – direct measurement for the electron density and luminescence characteristics from the optical energy states. External control system was successfully adopted to Electron Beam-Induced Current Imaging (EBIC) to visualize 2-dimensional distribution of electrons at the interface, which can be indirect indication of preferred electron conduction paths. Cathodoluminescence in TEM was also adopted to identify the 2-dimensional distribution of optical bandgap. Defects, originated from the interface, works as dead centers of luminescence, not wavelengths shifters as can be typically seen from the partial dislocation in GaN/InGaN lighting emitting diode structure.

S.EL15.08.13
Exploring the Role of Defects Produced by Ion Irradiation on Near and Sub-Surface GaN Thomas W. Pfeifer1, Ethan A. Scott2,1, David Olson1, Patrick E. Hopkins1, Khalid Hattar2 and Stuart Van Deusen2; 1University of Virginia, United States; 2Sandia National Laboratories, United States

The wide band gap and high thermal conductivity of gallium nitride semiconductors makes them ideal for high power and high frequency applications. These properties however are dependent upon the order and impurity concentration of the crystalline structure. In this study, we use Time Domain Thermoreflectance (TDTR) to investigate the role of defects on the thermal performance of GaN semiconductors. He atoms were implanted into GaN, with dosing concentrations varying between 1x10^13 and 1x10^19 cm^-2 and implantation energies at both 400eV and 400keV. TDTR is a pump-probe technique that measures the change in thermoreflectance on the surface of a sample as a function of pump-probe delay time from picoseconds to nanoseconds; this change in thermoreflectance is related to both the temporal temperature decay from impulse heating driven by the sub-picosecond pump pulse and the frequency-dependent temperature rise induced from the modulated pump pulse train. Thus, TDTR is well suited to measure both the thermal conductance across near surface interfaces along with thermal property changes of buried damaged regions from the ion irradiation. Our TDTR apparatus includes an 800nm 80MHz femtosecond pulsed laser, the pump is modulated at 8.4MHz, and all samples included an aluminum transducer deposited on the surface. Ions implanted at low powers localize near the surface of the GaN, and their effect can be observed when measuring the Aluminum-GaN thermal boundary conductance. Ions implanted at higher powers penetrate to a depth greatly exceeded the thermal penetration depth of the TDTR measurement technique. Here, the role of defects due to the passage of the ions is observed and measured. We believe the results and trends observed in this study are not limited to GaN, and a deeper understanding of the effects of doping on thermal properties could assist in cooling of doped semiconductor devices.

S.EL15.08.14
Crystal Defects in GaN and Diamond Transistor Structures Aris Christou; University of Maryland, United States

The state-of-the-art power switching devices made from SiC and GaN semiconductors contain a high density of crystal defects. Most of these defects are present in starting wafers and some are generated during device processing. There is little conclusive evidence so far on the exact role that the crystal defects paly on device performance, manufacturing yield, and more importantly, long-term field-reliability especially when devices are operating under extreme stressful environments. This paper provides a review of the current state-of-the-art of Diamond and GaN power semiconductor material technology, and the potential impact crystal defects may have on power switching electronics. UWBG Nitride materials suffer from both extended and point defects, each of which will challenge the material’s application in both vertical and lateral power devices. The extended defects include vertical threading dislocations of both edge and screw type. The latter defects have been shown to be correlated to leakage in vertical two terminal device structures while the influence of the former is still undetermined and remains a critical research issue. Channel surfaces in vertical three terminal devices will also degrade due to vertical threading dislocations. These extended defects occur in all epitaxial layers grown on c-plane substrates (the predominant and
largest area substrate type) and are the result of the lack of a high quality substrate bulk material as well as substrate surface. Diamond faces the challenge of achieving n type doping. We report our results on delta doped channels in diamond CVD epitaxial layers and the achievement of delta doped field effect transistors. Finally, our recent experiments of proton and gamma radiation effects show that diamond transistors transfer characteristics do degrade as a result of radiation induced defects.

S.EL15.08.17
Investigating F-Doped MZO as the Emitter in CdTe Solar Cells Manoj K. Jamarkattel, Adam Phillips, Jacob Gibbs, Kamala Khanal Subedi, Fadhil K. Alfadhili, Randy J. Ellingson and Michael Heben; University of Toledo, United States

Recently, incorporation of MgZn1-xO (MZO) as the emitter in CdSeTe solar cells has resulted in improved open circuit voltage and efficiency. However, the MZO layer appears to be sensitive to subsequent device processing, possibly due to unoptimized conduction band alignment or insufficient doping in the MZO layer. Unfortunately, the carrier concentration in the MZO is dominated by oxygen vacancies, which is difficult to control. Here we investigate how doping MZO films with F affect the CdSeTe properties. We deposit the MZO:F in two ways. The first method is by depositing an MZO/MgF stack followed by high temperature anneal, while the second method will be cosputtering ZnO, MgO, and MgF. Our preliminary results on the bilayer stack show that, peak PL intensity and bulk carrier lifetime of MZO:F/CdTe device increased after annealing. There is evidence of intermixing of the MZO and MgF after annealing, suggesting that the Fermi level of the MZO is closer to the conduction band at the film interface. If this is the case, band bending in the CdSeTe layer will be enhanced, leading to reduced interface recombination. Further investigation into the cause of these results will be presented, as will the results obtained when a cosputtered MZO:F emitter is used. The findings of this study may lead to higher efficient CdTe devices.

SYMPOSIUM S.EN01

Next Steps for Perovskite Photovoltaics and Beyond
November 21 - November 21, 2020

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5:00 AM *S.EN01.01.02
Efficient, Stable and Scalable Perovskite Solar Cells Jangwon Seo; Korea Research Institute of Chemical Technology, Korea (the Republic of)

Power conversion efficiencies (PCE) of perovskite solar cells (PSCs) has rising from the initial 3.8% to the state-of-the-art
25.2% within the past few years. Current PSCs intended for commercialization in the near future require both high efficiency and good long-term stability. Most highly efficient PSCs utilize an n-type layer of mesoporous titanium dioxide or tin oxide in an n-i-p device configuration, in which organic conductors are widely used to transport holes into an adjoined metal. Thus far, a variety of efforts have been devoted to achieve a defect-less perovskite film with high-quality morphologies to realize reduced loss-in-potential outcomes and enhanced efficiency levels. In this talk, we will discuss several challenges that need to be addressed in improving the photovoltaic performance and the stability of the perovskite solar cells, i.e. (1) preparation of high crystalline film of (FAPbI3)1-x(MAPbBr3)x with a large grain size and a preferred orientation, (2) incorporation of wide band gap halide into narrow band gap halide perovskites, (3) development of selective charge-transporting layers (CTL) with a superior stability, (4) interfacial control between the perovskite and the CTLS, and (5) the ion migration at the interface boosted by oxygen and light. Finally, our recent works on scale-up of PSCs will be discussed. Our strategy as presented in this work will offer new directions for those involved in the fabrication of highly efficient, stable and scalable PSCs.

5:00 AM S.EN01.01.04
Elucidating the Role of a Tetrafluoroborate-Based Ionic Liquid at the n-Type Oxide/Perovskite Interface Nakita K. Noel; Princeton University, United States

Halide perovskites are currently one of the most heavily researched emerging photovoltaic materials. Despite achieving remarkable power conversion efficiencies, perovskite solar cells have not yet achieved their full potential, with the interfaces between the perovskite and the charge-selective layers being where most recombination losses occur. In this study we employ a fluorinated ionic liquid (IL) to modify the perovskite/SnO2 interface. Using Kelvin probe and photoelectron spectroscopy measurements, we show that depositing the perovskite onto the IL results in the crystallisation of a perovskite film which has a more n-type character, evidenced by a decrease of the work function and a shift of the Fermi level towards the conduction band. We use photoluminescence spectroscopy and time-resolved microwave conductivity to investigate the optoelectronic properties of the perovskite grown on neat and IL-modified surfaces and find that the more n-type perovskite exhibits an order of magnitude lower trap density than the control film. When incorporated into solar cells, this interface modification results in a reduction in the current-voltage hysteresis and an improvement in device performance, with the best performing devices achieving steady-state PCEs exceeding 20%. Combining this modification with passivation treatments at the perovskite/HTM interfaces, allow us to achieve further enhanced PCEs (>22%) and improved long-term stability.

5:00 AM S.EN01.01.05
Interfacial Engineering in Vacuum Deposited Perovskite Solar Cells—From Metal Oxide Extraction Layers to Large Area Devices Daniel Pérez-del-Rey, Pablo P. Boix, Michele Sessolo and Henk J. Bolink; University of Valencia, Spain

Vacuum deposition is a key technique in the field of perovskite photovoltaics because it presents significant advantages with respect to the classical solution deposition methods. In particular, avoiding the use of solvents and perovskite annealing steps makes it a good candidate for industrialization and upscaling, as it has already been demonstrated in the OLED field. Despite these advantages, tuning the interfaces is essential to reach power conversion efficiencies as high as those achieved by solution processed perovskite solar cells. Metal oxides are an interesting choice for extraction layers due to their improved properties of the perovskite grown on neat and IL-modified surfaces and find that the more n-type perovskite exhibits an order of magnitude lower trap density than the control film. In this work we present our recent advances in using metal oxides as extraction layers optimising the interfaces in order to reach record open circuit voltages in CH3NH3PbI3 perovskite and being able to use MoO3 as extraction layer in both PiN and NiP structures through molecular passivation improving the stability and opening new possibilities for tandem applications. The developed pinhole-free interfaces show a perfect compatibility with the intrinsically large scalable vacuum deposition, making possible the implementation of those into large area devices and mini modules with minimal losses, opening an interesting door for industrial purposes.

5:00 AM *S.EN01.01.06
Photovoltaic Performance of Metal-Halide Perovskites—What is General and What is Special? Uwe Rau; Forschungszentrum Juelich GmbH, Germany

After many decades of photovoltaic research we would expect that there should be a common scientific understanding on the necessary ingredients to make almost perfect solar cells. However, the unprecedented success of metal-halide perovskites (MHPs) stimulated discussions on whether there could be a certain, yet non-established secret that distinguishes this material from others. The present contribution compares the performance of MHPs to other photovoltaic materials in terms of a general top-down approach. This direct comparison allows one to judge the strengths and weaknesses of different technologies but also gives some insight on the specific achievements, e.g. that, on the one hand, the radiative yield of MHPs is second only to the best GaAs solar cells, which implies open circuit voltages that come close to the thermodynamic limits. On the other hand the relative contribution of fill factor losses to the overall efficiency losses in MHPs is relatively large.
Metal halide perovskites (MHP) are the best solution-processed solar cell device technology to date. While record device have been achieved using spin-coating, larger area prototype realization requires the translation of processing strategies to scalable deposition methods. An in-depth understanding of how solvent molecules dictate the molecular structure of solution complexes as well as define thin film morphology by being incorporated into crystalline intermediate phases enables rational process optimization. This talk will portray our team research on solution-processing of larger area MHP prototypes by inkjet printing and slot-die coating. We employ combinatorial inkjet printing for the systematic optimization of MHP composition for multi-junction solar cells as well as light-emitting devices. We discuss our approach to rapidly identify MHP compositions of suitable stability for large-scale deployment of MHP-based devices.

By investigating fundamental solution chemistry explaining spectral features of solution species through a combination of experiment and DFT calculations we rationally design inks for slot-die coating and inkjet printing. Spectral features of fundamental building blocks of MHP semiconductors identified in solution are then tracked to investigate the association of molecular species into extended poly-complexes, colloids and small perovskite seed crystals. Through in-situ photoluminescence and absorption measurements during spin-coating we were able to identify the formation mechanism of several mixed cation/anion MHP semiconductors that enables us to translate film deposition strategies to scalable process techniques such as inkjet printing and slot-die coating. In-line process monitoring is used to optimize processing parameters to manufacture high-quality MHP semiconductor layers.

We will be presenting results on the fabrication of prototypes of MHP-based devices demonstrating inkjet-printed and slot-die coated small area solar cell devices with power conversion efficiencies > 15% and laser-scribed series interconnected mini-modules of > 12% on active areas > 10 cm². These results will be compared with the collected data of all MHP solar cells devices published that we are currently collecting in an open database through a crowd-sourced effort and that will be launched in spring 2020.

Study of the Anomalous Ambipolar Charge Transport at Hybrid Perovskite- Liquid Electrolyte Interface

Maniﬁested by high absorption coeﬃcient, large carrier diﬀusion length, ambipolar charge transport and moderate mobility of charge carriers, organo-lead halide perovskites recently emerging as promising candidate for high efficiency and low cost solution processed solar cells, needs no introduction. Perovskite Solar Cells (PSCs) have already gathered considerable attention, showing a tremendous hike in eﬃciency from 3.8%1 by Kojima et al. (2009) to 22.1%2 by Yang et al. (2017). A lot of research has been done on the eﬃciency improvement of PSCs by optimization of the film morphology at the interfaces by various characterization techniques including electrochemical impedance spectroscopy (EIS) in a solid state active device geometry.3 Recently, the optimization of the film morphology at liquid electrolyte interface by EIS is trending as a more simpliﬁed approach. Li et. al. have measured the ﬂat band potential, density and type of charge carrier at the perovskite-liquid interface from Mott-Schottky plot for spin coated and spray coated ﬁlms of methylammonium lead tri-iodide (MAPbI3) perovskite.4 Srivastava et.al have optimized the morphology of MAPbI3 perovskite thin ﬁlms at liquid interface by controlling nucleation and growth during ﬁlm fabrication by spin coating the ﬁlms on preheated substrates.5 However, there is a need of understanding the charge transfer at these interfaces in more detail.

Here, we have studied the kinetics of charge transfer and diffusion at the hybrid organic-inorganic perovskiteliquid electrolyte interface under the eﬀect of applied bias. By applying the diﬀerent dc bias from 0 to +1V and 0 to -1V, it was found that the ion diﬀusion at low frequency regime gets modulated due to charge accumulation. The charge transport resistance is initially increased to a maximum at around 0.4 V applied bias along with the decrease in the space charge capacitance. A transition state is observed at around 0.4 V to 0.6 V due to strong electronic-ion interaction where charge transport resistance decreases and capacitance increases. However at higher applied bias voltage charge transport resistance increases again and capacitance start to decrease due to excess ion accumulation. The perovskite ﬁlms show similar trend of...
change in impedance under both positive and negative bias. The Mott-Schottky Plot for forward and reverse voltage scan shows n-type and p-type behavior which indicates the ambipolar nature of perovskite semiconductor. The significant difference in the impedance spectra can be seen in dark and light which is attributed to the high absorption coefficient of the perovskite material. We have proposed a model to explain the charge kinetics across the perovskite-liquid electrolyte interface.

References

5:00 AM S.EN01.01.09
Interface Engineering and Defect Passivation in Perovskite Photovoltaics by Implementing Organic Components Ali Buyruk, Thomas Bein and Tayebeh Ameri; University of Munich (LMU), Germany

so far, an enormous progress has been made for perovskite photovoltaics reaching over 23% power conversion efficiencies. The compositional engineering as well as controlling the crystallization process were key factors in achieving such highly efficient devices. However, fundamental problems, such as the toxicity of hybrid lead halide perovskites, hysteresis and structural instability remain to be solved for perovskite solar cells. Indeed, the low-temperature solution-processing of perovskite films inevitably causes formation of a certain amount of defects on the surface and at the grain boundaries, which lead to serious trapping, charge accumulation, and recombination problems as well as stability issue. In this work, we will pursue the interface engineering and defects passivation by introducing organic ammonium salts on the perovskite active layer. We will discuss the origin of crystallization changes and performance improvement of treated devices based on the results achieved from optoelectrical and structural investigations.

5:00 AM *S.EN01.01.12
High Efficiency Perovskite Solar Cells Shengzhong (Frank) Liu1,2; 1Shaanxi Normal University, China; 2Chinese Academy of Sciences, China

A new type organic-inorganic hybrid perovskite has appeared to be a wonder material for its excellent optical absorption, long range charge-carrier diffusion and apparent tolerance to defects. In the last few years, it has been emerged as a primary candidate material for various photovoltaic, optoelectronic and photoelectronic applications. In just a few years, its solar cell efficiency has been improved from 3.8% to >25%. Moreover, the solar cell fabrication processes based on the planar architecture have been particularly enthusiastic thanks to their low temperature fabrication and compatibility with a range of substrates. Comparing solution deposition with vacuum deposition, the vacuum processes for thermal co-deposition and sequential deposition of PbCl2 and CH3NH3I materials are recognized as efficient means to prepare perovskite film with good uniformity and high surface coverage. A vacuum deposition process has been developed to fabricate high efficiency perovskite solar cells with high stability using alternating layer-by-layer vacuum deposition. The new deposition process allows us to relax the strict deposition monitoring and control measures, while realizing superior uniformity in film morphology, surface coverage and smoothness, together with crystalline phase purity.

For the high efficiency perovskite solar cells, the power conversion efficiencies for the planar device is as high as 23.4%. More importantly, we have developed a superior low temperature modified SnO2 material for ETL and transferred the cell fabrication process onto lightweight flexible polymeric substrate. The highest cell efficiency achieved was over 20%, it is also the highest efficiency among the flexible perovskite cells reported. Meanwhile, the devices show very good stability over long term exposure in ambient with very low degradation. After a representative cell was exposed in ambient lab condition for a year, its final cell efficiency is as high as 95% of its initial efficiency with its degradation accounts for only smaller than 5%. Further analysis on the stability of the perovskite solar cells will be discussed. We have also developed a series of single-crystalline perovskites with superior stability and optoelectronic performance.

Reference

5:00 AM *S.EN01.01.13
Understanding and Tailoring Interface Microstructures of Halide Perovskites Yuanyuan Zhou; Hong Kong Baptist University, Hong Kong

Microstructures of various interfaces (grain boundaries, heterophase interfaces, etc.) in halide perovskite materials/devices play very significant roles on the physical properties and optoelectronic functions. While enormous effort has been devoted to modifying the HP interfaces for better device performance, the insights into the interface microstructures and their exact role in devices have been obscured. In this talk, I will first present a fundamental discussion on HP interface microstructures from a materials-science perspective. Then, I will demonstrate several unique chemical approaches to tailor the HP interface microstructures in a precisely-controlled manner, which will not only lead to electronic passivation of defects, but also endow these interfaces with new functions. Finally, I will share my perspectives about future research in this promising direction.

5:00 AM *S.EN01.01.14
At the Interface—Probing the Energetic Alignment and Composition between Perovskites and Charge Extraction Layers Selina Olthof; University of Cologne, Germany

In recent years, the interest in halide perovskites rose at a rapid pace due to their tremendous success in the area of photovoltaics; but other fields, like light emitting diodes, show great potential as well. In optoelectronic devices, the function and performance depend crucially on the proper alignment of the energy level landscape throughout the device, i.e. allowing for efficient charge transport across the various interfaces.

In perovskites it turned out that these interfaces can be rather complex. On the one hand, interface dipoles and band bending occur. But more importantly, the perovskite composition and formation can be significantly influenced by chemical reactions taking place at these interfaces.

In this talk I will show how UV as well as X-ray photoelectron spectroscopy measurements can help to probe and understand the processes going on at the various bottom contact materials. Intriguingly, clear differences are found between the formation of interfaces to organic materials and to metal oxide; furthermore, the perovskite processing (i.e. solution vs. evaporation) as well as the perovskite composition play significant roles as well.

5:00 AM S.EN01.01.15
Characterization of Electrical Properties of Perovskite Solar Cells—The Impact of Charge-Transport Layers Rasha A. Awni1, Zhaoning Song1, Cong Chen1, Chongwen Li1, Changlei Wang1, Mohammed Razooqi1, Lei Chen1, Xiaoming Wang1, Randy J. Ellingson1, Jian V. Li2 and Yanfa Yan1; 1University of Toledo, United States; 2National Cheng Kung University, Taiwan

The electrical properties of metal halide perovskite solar cells (PSCs) have been intensively studied by many researchers using capacitance-based techniques such as thermal admittance spectroscopy (TAS) and capacitance–voltage (C–V) measurements. The capacitance–frequency–temperature (C–f–T) spectra of PSCs reported in the literature [1-4] typically show two capacitance signatures, one at high frequency (> 10^5 Hz) and the another at low frequency (> 10^3 Hz). These capacitance signatures have been used to evaluate the properties of defects in PSCs [1-5]. Here, we show that the charge-transport layers (CTLs) in PSCs can have significantly influence on the capacitance signatures. We find that the capacitance signature at high-frequencies and low temperatures is due to the trap and detraps of charged carriers in the hole-transport layer (HTL). We further show that high-frequency capacitance measured from HTL-free PSCs represents the geometric capacitance, allowing a reliable calculation of the dielectric constant of perovskite layers. The presence of HTL in PSCs leads to apparent temperature dependent dielectric constant [3], due to the capacitance contribution of HTL. The low-frequency capacitance signature can be used to characterize the ionic transport properties of the perovskite layer. However, to ensure meaningful results, the capacitance coupling between perovskite layer and CTLs must be carefully avoid, by choosing the appropriate CTLs and device configuration. Our results explain well the large discrepancies of electrical properties of perovskites reported in the literature.

5:00 AM S.EN01.01.18

Modeling Recombination Mechanism in Perovskite Solar Cells by Simulating Temperature-Dependent Transient Light Ideality Factor Spandankumar H. Ranpariya and Dhirendra K. Sinha; Indian Institute of Information Technology Vadodara, India

This decade witnessed rapid progress in the development of organic-inorganic hybrid lead-halide perovskite-based solar cells. In particular, this class of solar cells showed high power conversion efficiency and significant potentiality to realize a low-cost terawatt-scale power generation. This is mainly due to its high optical absorption coefficient with sharp absorption onset, long charge-carrier lifetime, tunable band-gap and low-cost fabrication. However, despite advancement in the device performance, the underlying physics of charge-carrier dynamics needs important attention to develop insight into the performance bottlenecks and thereby better control and optimization over the device performances. Among the performance bottlenecks, the charge-carrier recombination is considered to be one of the dominant mechanisms that limit solar cell behavior. Therefore, in this work, the underlying interest is to propose a phenomenological model of recombination by simulating the temperature-dependent transient light ideality factor. We consider a standard sandwich device structure with CH3NH3PbI3 as an active layer. The Spiro and TiO2 are taken as hole- and electron-transporting layers, respectively. We utilized one-dimensional drift-diffusion equation to simulate transient open-circuit voltage Voc (t) with varying light-intensity, Φ between 0.2 to 2.0 Sun-equivalent and device temperature, T between 100 to 300 K. The transient light ideality factor, nid (t) is determined by evaluating the slope of the plots between Voc (t) vs ln(Φ). The plot of temperature-dependent transient light ideality factor shows a fast rise in its value between the temperatures 100 to 150 K and tends slowly towards 2.0 at room temperature and above. The observations clearly indicate that the recombination of charge-carriers are predominantly due to trap-states, interfacial or bulk, activated at higher temperatures. The work shed light on the recombination mechanisms in such class of solar cells and their alternative variants.

5:00 AM S.EN01.01.21

Exploring Halide Perovskite Structural Tunability to Design Materials for Dynamic Photovoltaic Windows Jeffrey A. Christians and Elizabeth V. Cutlip; Hope College, United States

Halide perovskites offer exciting potential as photovoltaic materials and simply as semiconductors. Specifically, their structural tunability has become of greater interest as researchers begin to search for novel ways to tune the materials to achieve improved solar cell stability or to target new applications. One potential technology which halide perovskites could enable is dynamically switchable photovoltaic windows, windows which a user can transition between photovoltaically active (dark) and non-photovoltaic (transparent). We build toward this goal in this work by investigating the intercalation and deintercalation of methylamine gas into 2-dimensional Ruddelson-Popper phase halide perovskites. As has been shown with methylammonium lead iodide films, the intercalation of methylamine into the halide perovskite lattice results in a color change to a clear crystal phase. We find that in some 2-D perovskite systems, deintercalation of the methylamine gas is incomplete, resulting in the formation of some CH3NH3PbI3; however, other 2-D perovskite phases show reversible intercalation/deintercalation with methylamine, indicating stronger binding between the long-chain ligand and the lead halide octahedra of the 2-D perovskite sheet. When integrated into a hybrid 2-D/3-D structure of the type A’2(CH3NH3)nPbnI3n+1, where A’ is a strongly binding R-NH3+ moiety such as phenethylammonium (PEA), these materials show promising reversibility for methylamine intercalation/deintercalation with little change in absorption or morphology. This work reveals the relative affinity of various R-NH3+ molecules for the halide perovskite lattice, showing that many of these are not replaced by methylamine, and indicates that templating the 3-D CH3NH3PbI3 structure with long-chain ammonium cations could lead to better reversibility in dynamic photovoltaic windows.
Tackling Perovskites’ Instabilities through Environmentally-Controlled Optical Measurements and Machine Learning  
Marina S. Leite; University of California, Davis, United States

We tackle the individual and combined effects of extrinsic (humidity and oxygen) and intrinsic (light, bias, and temperature) stressors on halide perovskite materials by implementing photoluminescence (PL) under environmentally controlled conditions. These experiments are critical to assess the stability of the large variety of perovskite materials available for light-absorbing and -emitting applications. We clarify the influence of distinct humidity levels on the charge carrier recombination in $\text{Cs}_x\text{FA}_{1-x}\text{Pb(I}_y\text{Br}_{1-y})_3$ perovskites through \textit{in situ} PL, where we temporally and spectrally measure light emission within loops of critical relative humidity (rH) levels. Our results demonstrate that the Cs/Br ratio strongly affects the spectral stability of light emission hysteresis, as well as its extent. The photo-emission dynamics in metal halide perovskites with both I and Br is also interrogated by environmental PL, where we find that the presence of Br suppresses hysteresis. The isolated effects of both temperature and photon excitation energy are also investigated. To pursue optimal ‘rest’ and ‘recovery’ conditions for device stable operation, we propose the implementation of a machine learning approach based on supervised learning combined with PL measurements upon exposing the samples to distinct values of humidity, oxygen, illumination, bias, and temperature, which will be discussed in details.

Non-Arrhenius Thermal Degradation Rates in Perovskite Films  
Eli Wolf$^1$ and Michael D. McGehee$^2$; $^1$Stanford University, United States; $^2$University of Colorado Boulder, United States

Commercialization of perovskite solar cells is dependent upon improving the stability of these devices. It has been shown that global average stress of a perovskite film is one significant contributing factor to its degradation rate. The global average stress of a perovskite film is mainly determined by two components: 1) the thermal expansion coefficient mismatch between the perovskite film and the substrate and 2) the temperature at which the perovskite is formed (1). Most perovskite films are made on a glass substrate, whose thermal expansion coefficient is about an order of magnitude smaller than the perovskite film. They are commonly formed at temperatures around or above 100°C, resulting in residual tensile stresses of over 50 MPa in the film.

We show that due to the convolution of the effects of stress on degradation with classic thermal degradation, the resulting degradation rate in a perovskite film (Glass/FA$_{0.83}$Cs$_{0.17}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$) is not Arrhenius. Stress is relieved at higher temperatures, reducing the degradation rate due to stress, which directly competes with the increasing degradation rate due to increased thermal energy for exceeding an energetic barrier associated with the degradation reaction. We use in-situ temperature dependent X-Ray Diffraction Spectroscopy to measure the degradation rate of perovskite films at multiple temperatures. The degradation rate of the perovskite film is measured by monitoring the growth of a PbI$_2$ peak and the regression of a perovskite peak.

Additionally, we directly measure the global average stress of a perovskite film as a function of temperature using in-situ temperature dependent profilometry to measure the changes in substrate curvature. The stress in a perovskite film changes with the temperature of the substrate even after the film is initially formed.

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Metal Halide Perovskite Dynamics and Methods for Their Prediction  
John M. Howard$^{1,2}$ and Marina S. Leite

While the efficiency of metal halide perovskite (MHP) solar cells and light-emitting diodes continues to increase, their stability remains a critical challenge. Optical and electrical dynamics with varying degrees of reversibility arise in the presence of isolated or combined intrinsic (light, temperature, bias) and extrinsic (oxygen, water) operating factors [1]. My talk will discuss our investigations into the transient behavior of common MHP compositions, along with the ongoing implementation of statistical and machine learning techniques to predict these effects. First, we highlight our investigation into dynamics induced by environmental factors, such as light and moisture. For the archetypal MAPbI$_3$ and MAPbBr$_3$ (MA = CH$_3$NH$_3$) perovskites we investigated the impact of illumination wavelength on surface photovoltage with Kelvin probe measurements [2]. For each composition, we record the transient voltage throughout an OFF-ON-OFF light cycle. Interestingly, after turning the light OFF, MAPbBr$_3$ displays a wavelength-dependent voltage decay 10x slower than the I-containing film, which exhibits no effects due to photon energy. Concerning moisture, we evaluated the in situ light-emission response of MAPbI$_3$ and MAPbBr$_3$ across multiple humidity cycles using micro-photoluminescence (micro-PL) [3, 4]. Our results establish that the intercalation of water molecules into the perovskite lattice depends on the lattice constants, with the I-based composition showing a 6× increase at 40% relative humidity (rH) while the Br-containing samples register a 15× enhancement at 65% rH. Subsequent dehydration of the MHP thin films returns the PL intensity to their original values. Our results, along with those from many other research groups, clearly establish that the issue of stability, or lack thereof, in perovskites calls for the ability to model and predict performance as a function of time. This includes times series forecasting of fundamental properties, such as photoluminescence and photoconductivity, as well as the overall macroscopic power output. With examples of their dynamics already introduced, I focus the second half of my talk on the implementation and evaluation of statistical and machine learning methods for predicting perovskite behavior. We explore and optimize standard methods, such as multiple linear regression, autoregressive integrated moving average (ARIMA), and echo state networks (ESN) on our rH-PL measurements, as well as J-V datasets from the literature. We provide a powerful analytical framework for evaluating any time-dependent MHP phenomena and, thus, tackling the open problem of stability. Our in situ measurements are a critical platform for informing the fabrication of devices with improved stability and the associated data analytics may serve as an essential tool for effectively predicting perovskite PV performance. We foresee further integration between combinatorial studies, in situ characterization, and predictive analytics, where all data streams can be collated as input for algorithms that optimize compositional tuning for sustained efficiency.


5:35 AM S.EN01.02.05
Active-Rest-Recovery Cycle in Metal-Oxide Based Semi-Transparent Perovskite Solar Cells Enabling Long-Term Stability
Yuanhang Cheng1, Chenchao Xie1,2, Ho-Wa Li1 and Fen Lin1; 1Solar Energy Research Institute of Singapore(SERIS), National University of Singapore, Singapore; 2National University of Singapore, Singapore

Despite the rapid development in power conversion efficiency (PCE) from 3.8% to 25.2% within ten years, the long-term stability of perovskite solar cell (PVSC) severely hinders its commercial deployment. Herein, we have systematically studied the long-term stability of NiO$_x$ based p-i-n structured PVSCs. After aging at maximum power point (MPP) under AM 1.5 G illumination, the PVSCs with organic interlayer (bathocuproine, BCP) and Ag electrode exhibit permanent degradation due to BCP failure and Ag diffusion. To address the above stability issue, an aluminum-doped zinc oxide (AZO) layer was employed as buffer layer to replace BCP and an indium tin oxide (ITO) layer was sputtered as top electrode to replace Ag. With this metal-oxide based structure, the long-term stability of the PVSCs has been significantly enhanced retaining 95% of its initial PCE after 30 days aging in glovebox. Furthermore, the PCE of metal-oxide based PVSCs exhibit active-rest-recovery (ARR) cycles under MPP tracking testing. During the active phase, the PVSCs produce output power under AM 1.5 G illumination at MPP and the device performance degrades gradually. Interestingly, the PVSC recovers to its initial PCE repeatedly after a rest phase under dark condition. Optoelectronic investigations such as electroabsorption (EA) and capacitance-frequency (CF) have illustrated that the ion migration within perovskite bulk is the origin of the ARR cycle. Finally, combining with an efficient Si bottom cell, a perovskite/Si 4T tandem solar cell with over 23% efficiency has been.
In the last decade, hybrid perovskite photovoltaics have emerged as a promising new thin-film technology, capable of solution processing, with champion power conversion efficiencies (PCEs) exceeding 25% on a laboratory scale. The ability to solution process, coupled with an abundance of precursor materials, enables the fabrication of low-cost, large-area modules, either in a single junction configuration, or as a tandem solar cell utilizing established commercial photovoltaics, such as silicon and CIGS. However, PCEs of perovskite solar cells fabricated by scalable deposition techniques such as blade coating, spray coating or inkjet printing are consistently inferior to the record PCEs obtained from lab-scale spin coated devices. To overcome losses when transitioning to scalable deposition technologies, efficient optimization strategies are required.

As a novel strategy, we demonstrate simultaneous in situ thickness monitoring at multiple probing positions and exact drying control for a blade coated perovskite film. Control of the drying is established by a laminar air flow around a wing-shaped substrate holder in a flow channel, while in situ characterization is performed by five diode lasers, each with a respective photodiode probing the reflectivity of the film over time. This unique combination, simultaneously controlling and monitoring the drying process, ensures that the environment parameters of the fabrication process are exactly defined.

Therefore, it becomes possible to derive an analytical drying model for perovskite solution films, using fundamental kinetic and thermodynamics equations. This model can accurately describe the measured, dynamic shrinkage of the film thickness during solvent evaporation in line with the inherent chemical properties of the perovskite solution. Because the mass transfer coefficients are precisely controlled, the model can be applied to arbitrary industrial-scale drying machines, for which these coefficients are mostly known.

In order to illustrate the relevance of the strategy presented here, we determine the optimal drying conditions for blade coated methylammonium lead iodide films incorporated into solar cells with the planar architecture ITO/SnO2/perovskite/Spriomo- MeOTAD/Au. Obtained PCEs and measured polycrystalline perovskite morphologies demonstrate a clear correlation with the drying parameters of substrate temperature and air flow velocity. Although both temperature and air flow velocity can control the drying speed, their effects on the crystal growth are fundamentally different. Obtaining a pinhole-free perovskite film and a high PCE requires restricting these variables to a distinct processing window. At optimal drying conditions, champion PCEs of 19.5% (as measured by the backward IV) and champion stabilized PCEs of about 17.3% are reached. These device PCEs do not differ significantly from those obtained from entirely spin coated devices fabricated with the same cell architecture from the same precursor solution. This equivalent device performance is evidently an example of an optimal process transfer from lab-scale spin coating to scalable blade coating fabrication method.

In summation, we provide a sophisticated upscaling strategy based on a fundamental understanding of the drying process in perovskite solution films. The derived drying model enables the prediction of the polycrystalline perovskite thin-film morphology for an arbitrary drying machine prior to experimental testing of the system. In future works, additional characterization methods will be explored to extend the model to apply beyond the onset of the crystallization process. More detail on the described work can be found in the original, open access paper "Drying Dynamics of Solution-Processed Perovskite Thin-Film Photovoltaics: In Situ Characterization, Modeling, and Process Control" published in Advanced Energy Materials / Volume 9, Issue 39, October 17, 2019.

5:55 AM *S.EN01.02.07
Carbon Materials for Perovskite Solar Cell Applications Wei Zhang; University of Surrey, United Kingdom

Perovskite solar cells are emerging candidates for next-generation thin-film photovoltaic technologies with the potential of extremely low fabrication cost and highest power conversion efficiency. Over the last decade, perovskite solar cells have gone through a rapid development in device efficiency from an initial 3.8% to a most recently certified 25.2%, though the challenges of long-term stability and lead toxicity still remain. Beyond the concerns in stability and lead toxicity, the cost of widely used materials such as ITO and Spiro-OMeTAD for high efficiency devices becomes another obstacle for the commercialization of perovskite solar cells in the near future. Carbon materials, ranging from zero-dimensional carbon quantum dots to three-dimensional carbon black materials, are promising candidates for reducing the material cost meanwhile boosting both efficiency and stability of perovskite solar cells, offering unique advantages for incorporation into various device architectures. In this talk, we will present a concise overview of important and exciting advancements of perovskite...
solar cells that incorporate different dimensions of carbon materials in their device architectures, followed by the research progress in our group utilising carbon materials (nanotubes and graphene) for a range of perovskite solar cell applications in an effort to simultaneously reduce the material cost and improve the long-term stability. We will discuss the major advantages and potential challenges of each technique that has been developed in our most recent work. Finally, we outline the future opportunities towards low-cost, efficient and stable perovskite solar cells utilising carbon materials.

6:10 AM S.EN01.02.08
Correlating Microstructure with Optoelectronic Properties to Enable Open-Air Fabrication of Stable Perovskite Solar Modules Nicholas Rolston, Austin Flick, Hannah Elmaraghi, Justin Chen, William J. Scheideler, Oliver Zhao, Jinbao Zhang and Reinhold H. Dauskardt; Stanford University, United States

Hybrid organolead-halide perovskite materials, with their remarkable optoelectronic properties, hold real promise for use as the active layer in low-cost next-generation solar cells. High-throughput open-air fabrication methods offer low capital-expenditure routes to continuous manufacturing of perovskites, but achieving reproducibility with ambient conditions and varying relative humidity (RH) has been a persistent challenge for achieving high performance and device stability. Our group has recently developed a Rapid Spray Plasma Processing (RSPP) method, where perovskite films are spray coated and immediately exposed to an open-air plasma at an ultrafast linear processing rate > 10 cm/s. The combination of reactive species (ions, radicals, metastables, and photons) and convective thermal energy produced by the plasma enables rapid (~100 ms) crystallization with high tolerance to RH.

In this work, we first control the plasma dose to vary curing kinetics and grain size in open-air spray coated Cs\(_{0.17}\)FA\(_{0.83}\)Pb(Br\(_{0.17}\)I\(_{0.83}\)) perovskite films. We then correlate microstructure with carrier lifetime and photoluminescence measurements to show the relationship between curing source (room-temperature gas vs plasma), grain size, and film roughness on carrier dynamics and recombination. Improved steady-state photoluminescence is observed for plasma curing, an effect that is independent of microstructure and is attributed to the quenching of trap states during film deposition from the plasma. However, a strong correlation is observed between microstructure and carrier lifetimes: increased grain size in the plasma-cured perovskite films results in lifetimes > 1000 ns—exceeding spin-coated films fabricated in a glovebox by 5X—and suggesting that RSPP perovskite films have a lower defect density.

By optimizing plasma dose to produce perovskite films in 12.5 cm\(^2\) series-connected perovskite modules, we demonstrate >14% stable power output fabricated entirely with scalable deposition processes of spray coating and evaporation. We identify smooth morphologies (R\(_q\) < 30 nm) as a key parameter to enable module stability under both maximum power point tracking and accelerated humidity (25°C, 70% RH) and heating (85°C, 25% RH) conditions for >100 hours without encapsulation. The control of microstructure using RSPP therefore improves optoelectronic properties, module performance, and stability compared to traditional spin coating.

SESSION S.EN01.03: Upscaling and Industrial Considerations
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN01

5:00 AM *S.EN01.03.02
Scalable Fabrication of High-Quality Crystalline and Stable FAPbI\(_3\) Thin Films Maria Antonietta Loi; University of Groningen, Netherlands

Formamidinium lead iodide (FAPbI\(_3\)) is one of the most extensively studied perovskite materials due to its narrow band gap and high absorption coefficient, which makes it highly suitable solar cells applications. Deposition from a solution containing lead iodide (PbI\(_2\)) and formamidinium iodide (FAI) or by sequential deposition of PbI\(_2\) and FAI usually leads to the formation of films with poor morphology and unstable crystal structure that readily crystallizes into two different polymorphs: the yellow phase and the black phase. I will show that, 2D 2-phenylethylammonium lead iodide (PEA\(_2\)PbI\(_3\)) thin films deposited by a scalable doctor-blade coating technique can be used as a growth template for the high-quality 3D FAPbI\(_3\) perovskite thin films, by organic cation exchange. I will discuss the structural, morphological and optical properties of these converted 3D FAPbI\(_3\) perovskite films, comparing them to the properties of directly deposited 3D FAPbI\(_3\) films. The converted FAPbI\(_3\) thin
films are compact, smooth, highly oriented and exhibit better structural stability in comparison to the directly deposited 3D films. These results not only underscore the importance of the employed deposition techniques in the formation of highly crystalline and stable perovskite thin films but also reveal a strategy to easily obtain very compact perovskite layers using doctor-blade coating.

5:15 AM *S.EN01.03.03
Progress in Materials and Process of Perovskite Solar Cells toward Commercialization

Hyun Suk Jung and Hyunjung Shin; Sungkyunkwan University (SKKU), Korea (the Republic of)

All solid-state solar cells based on organometal trihalide perovskite absorbers have already achieved distinguished power conversion efficiency (PCE) to over 25% and further improvements are expected up to 27%. Now, the research on perovskite solar cells has been moving toward commercialization. To facilitate commercialization of these great solar cells, some technical issues such as long-term stability, large scale fabrication process, and Pb-related hazardous materials need to be solved. Also, flexible perovskite solar cell using plastic substrate can be used in niche applications such as portable electrical chargers, electronic textiles, and large-scale industrial roofing.

This talk is dealing with our recent efforts to facilitate commercialization of perovskite solar cells. For examples, we introduce a recycling technology of perovskite solar cells, which covers the regeneration process of Pb contained perovskite layer as well as recycling process of Au electrodes and transparent conducting oxide glass. Also, recent interesting results regarding ultra-flexible perovskite cells will be discussed in terms of stress analysis. Finally, simple fabrication technologies for realizing large scale perovskite module is going to be introduced.

5:30 AM S.EN01.03.04
Combinatorial Sputtering and Characterization of Computationally Predicted Ternary Nitrides in the Magnesium-Antimony-Nitrogen Phase Space

Karen Heinselman1, Stephan Lany1, John D. Perkins1, Kevin Talley2 and Andriy Zakutayev1; 1National Renewable Energy Laboratory, United States; 2Colorado School of Mines, United States

Nitrides provide a rich, and generally underexplored, field of chemistries for solar energy conversion, with many of them displaying excellent optoelectronic, electronic, and mechanical properties, as well as chemical stability. Prediction of ternary nitrides via computational modeling can significantly streamline the materials discovery process. First principles calculations were used to facilitate materials discovery within the Mg-Sb-N phase space, providing crystal structures to compare to and a predicted chemical potential phase diagram to help tune parameters. Guided by these predictions of favorable phases and the required conditions to achieve them, radio-frequency (RF) magnetron co-sputtering was used to deposit the films. The computationally predicted Mg2SbN3 phase, which has a wurtzite-derived structure, and a lattice constant similar to that of GaN, has been experimentally synthesized for the first time [1]. In addition, the antiperovskite Mg3SbN phase, which has previously been seen only in bulk form, has been grown as a thin film. This Mg-rich phase has a variety of predicted properties ideal for photovoltaics, such as a large dielectric constant, low effective masses, and a measured near-gap PL at room temperature, at around 1.3 eV. Both of these phases show up within the same combinatorial sample across the spread of Mg to Sb.

[1] Heinselman et. al., Chemistry of Materials (2019), DOI: 10.1021/acs.chemmater.9b02380

5:40 AM S.EN01.03.05
Directed Mesoscale Self-Assembly of 3.0 nm Diameter, Fully-Inorganic Perovskite Nanocrystals into Hierarchical Superstructures

Jacob Lee and Rajesh Sardar; Indiana University Purdue University Indianapolis, United States

Due to quantum confinement effects, nanoscale materials offer vastly different optoelectronic properties from their bulk counterpart. In the last decade, one promising nanomaterial that has emerged is the perovskite which has a crystal structure of ABX3 where A and B are metallic cations and X is a halide anion. Perovskites have shown extremely large molar absorptivity, high quantum yield photoluminescence, wide visible spectral coverage, and large defect tolerance that together make them ideal for many optoelectronic applications including photovoltaics, light emitting diodes, and lasing. To maximize device applicability, monodispersed nanocrystals (NCs) must be synthesized and then assembled into superstructures over multiple length scales. Currently, most syntheses control the size of NCs by using long aliphatic surface passivating ligands which are inherently insulating molecules and create a barrier for interparticle electronic interactions. To overcome these challenges, we have synthesized nearly monodispersed (~3 nm) CsPbX3 NCs (X = Cl, Br, and I) with poly(ethylene glycol)6 (PEG–NH2/COOH) surface passivating ligands. We selected PEG6 ligands because they offer several unique advantages including increased conductivity through electron dense oxygen atoms and their effectiveness to lead to hierarchical superstructure formation. Importantly, by varying the PEG concentrations in the reaction mixture, we control the mesoscale
assembly of our NCs from lamellar to nanorice structures. Interestingly, these mesoscale assemblies result in a band gap variation of 240 meV with the same ~3 nm NCs due to the delocalization of the exciton wavefunction. We believe that the dipole-dipole interactions between NCs, along with van der Waals attractions between PEGs, induce the mesoscale assemblies. Furthermore, these mesoscale assemblies form micron length twisted ribbon superstructures. Thus, by using polymer assisted forces at the nano- and meso- scales, we synthesize various CsPbX₃ NCs assemblies, which interact collectively through exciton wavefunction delocalization providing a pathway to enhance future device applications.

5:50 AM S.EN01.03.06
The Development of a Tamper Indicating Toolbox: Monitoring Degradation of Silica Sol-Gel Materials through the Use of Piezoelectrics Angela Suriyakumaran¹,1, Anthony J. Croxford¹, Sean A. Davis¹ and Ian Hayes₂; ¹University of Bristol, United Kingdom; ²AWE Plc, United Kingdom

The integration of ultrasonic monitoring techniques with silica sol-gel materials, for the purpose of tamper indication, presents a novel set of challenges and with it, various solutions through integration of both fields. Tamper indication plays a vital role in the dismantlement of nuclear equipment by ensuring that the intergrity of the stored equipment can be maintained. Due to the responsive nature of sol-gel silica, it has the potential to be used as a visual indicator of tamper as sealants. In this research, the sol-gel precursor samples are synthesised using tetramethyl orthosilicate (TMOS) as a precursor and a base catalyst to amplify the effects of tamper. However, this technique can be subject to human error, therefore to alleviate such problems, ultrasonics will be explored in conjunction with the sol-gel chemistry. Ultrasonics has been used within the field of structural health monitoring (SHM) due to its high sensitivity and non-destructive nature. Piezoelectric materials are used to transmit the acoustic waves through a sample, as well as, receive any waves reflected back from the samples or any present defects. The combination of these techniques has not previously been fully explored, so the aim of this research is to develop a highly effective and accurate interdisciplinary method of tamper indication. Metastable sol-gel formulations show shrinking and fracturing upon solvent evaporation but varying the catalyst concentration can tailor the material stability, so an appropriate concentration was decided upon. Initial experiments were then done to check compatibility of the piezoelectric transducer with the sol-gel formulations. After which, bulk wave transducers were used to test out the responsiveness of the system to sol-gel degradation. Results indicate that it is possible to use these piezoelectric transducers to monitor these sol-gel degradation points, as well as, determine the point of exposure.

The presentation will explore the capabilities of the ultrasonic components to monitor the degradation of sol-gel formulations during simulation of a tamper, as well as, the challenges overcome to ensure integration of both materials.

References:

6:00 AM S.EN01.03.07
High-Performance Ternary Alkali Nitrides for Renewable Energy Applications Jiban Kangsabanik and Aftab Alam; Indian Institute of Technology Bombay, India

Rapid decline in fossil fuel energy necessitates the immediate need for renewable energy resources. Here, we report a previously unexplored class of nitrides AMN₂ (A=Na, K, Rb, Cs, M=V, Nb, Ta) keeping renewable energy applications in mind. Using a detailed structure and stability analysis using first principles simulation, we discovered twelve such compounds (few of which were already synthesized before), which are chemically, mechanically, and dynamically stable. These twelve compounds were then evaluated for their suitability for three renewable energy applications: (i) photovoltaics, (ii) water splitting, and (iii) thermoelectrics. Careful analysis of electronic structure reveals high optical transition strength resulting in a sharp rise in absorption. This in turn yields high short circuit current and hence excellent solar efficiency for a few compounds namely CsVN₂ and RbVN₂. Along with excellent absorption quality, some compounds show favorable band edge positions compared to water redox levels and hence are promising as photoelectrodes in photo(electro)chemical water...
splitting devices. Mixture of flat and dispersive bands in the band structure yields both high Seebeck and electrical conductivity, thus an excellent power factor for six compounds. Simulated lattice thermal conductivity shows moderate to ultralow values and thus the possibility of achieving a high thermoelectric figure of merit (ZT), even at lower temperatures. From the experimental perspective, we discuss the possible challenges that may arise while utilizing these compounds for the desired applications and suggest possible pathways to overcome them. We believe such theoretical prediction of promising materials is extremely useful for new materials discovery and anticipate rapid response from the experimental community.


SESSION S.EN01.04: Tandems
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN01

5:00 AM S.EN01.04.01
The Role of Dimethylammonium in Bandgap Modulation for Efficient All-Perovskite Tandem Solar Cells Giles Eperon1, Tomas Leijtens2, Axel F. Palmstrom1, Taylor Moot1, Michael D. McGehee3, Joseph Luther1, David Moore1 and Joseph J. Berry1; 1NREL, United States; 2Swift Solar, United States; 3University of Colorado Boulder, United States

Multijunction all-perovskite solar cells offer a route towards efficiencies of III-V materials at low cost by combining the advantages of low thermalization loss in multijunction architectures with the beneficial properties of perovskites - namely low processing cost, high throughput fabrication, and compatibility with flexible substrates. One of the main limitations of all-perovskite tandems is the difficulty in achieving stable, high voltages with the wide bandgap subcell. Voltage losses in wide gap perovskites are generally high due to iodide-bromide segregation; mixing iodide and bromide on the X-site is the most common way to achieve the bandgaps of 1.7-1.85 eV suitable for tandems.

Here, we demonstrate a bandgap tuning strategy based on incorporating A-site cations of mismatched size, namely dimethylammonium (DMA) and cesium cations. This increases the bandgap and therefore reduces the amount of bromine needed to attain a certain bandgap. We achieve a band gap of 1.7 eV with a bromine concentration of only 20%, minimizing photoinduced halide segregation. We find that this strategy results in higher voltages and efficiencies that are stable under operation.

Surprisingly, we find that adding either DMA or cesium alone produce increases in bandgap. While cesium shrinks the lattice (as would be expected for an increase in bandgap), adding DMA causes the lattice to expand but still produces a bandgap increase. We will discuss the nature of this unusual mechanism and its use for further advances in high voltage wide bandgap devices. We will discuss the latest results demonstrating excellent stability of the DMA-containing materials under operation, thermal stress, and the combination of the two.

The robust and efficient nature of the DMA-containing wide bandgap materials makes them perfect for use in all-perovskite tandems. By combining these cells with advances in atomic layer deposition for robust and stable interlayers, we have fabricated two-terminal all-perovskite tandem solar cells with over 23% PCE; we will also discuss the latest developments in all-perovskite tandems.

5:10 AM S.EN01.04.02
Effects of Interfacial Reaction at Metal Oxide Interface on Perovskite Stability and Degradation Pathway Sampreetha Thampy, Boya Zhang, Weijie Xu and Julia W. Hsu; The University of Texas at Dallas, United States

Addressing the stability of organic-inorganic perovskite solar cells (PSCs) is needed to propel PSCs towards commercialization. Due to the inherent chemical reactivity of halide perovskites, most efforts have focused on improving their stability due to environmental agents. In contrast, intrinsic instability, including possible reaction between perovskite layer and contact materials in a device, has not been examined closely. Previously we showed that the stability is lowered and decomposition reaction is altered in methylammonium iodide (MAI) and methylammonium lead iodide (MAPbI3) when they are in contact with NiO, but no change was observed when contacting TiO2. In this talk, we will present a comprehensive study on thermal stability and degradation pathway in neat formamidine hydroiodide (FAI) versus when it is in contact with NiO or TiO2. Using a combined temperature programmed desorption-mass spectrometry-Fourier transform infrared spectroscopy apparatus, we observe that the bulk decomposition of FAI powders proceeds with the formation of triazine (C3H3N3) and hydrogen cyanide (HCN) as the major gas products at 265 °C, while ammonia (NH3) gas evolve above 300 °C. However, when FAI is mixed with NiO nanoparticles, the decomposition temperature lowers to 172 °C with NH3 and water.
vapor releasing first, whereas C$_3$H$_3$N$_3$ and HCN are released at 243 °C. The releasing of NH$_3$ and water vapor at low temperature, which is absent when FAI is by itself, indicate interfacial reactions. Moreover, studies on FAI and FAI/NiO$_x$ films show that the interfacial stability of films is further lowered to ≤ 150 °C, much lower than powder samples. These findings emphasize that interfacial reactions can be significant at typical processing conditions of FAI based perovskite devices and can induce intrinsic degradation in perovskite devices. We will explain the experimental results based on thermodynamic free energy calculations and propose mitigation strategies.

5:20 AM S.EN01.04.03
Triple Halide Perovskite Absorbers for >27% Perovskite/Silicon Tandem Solar Cells with Excellent Stability Caleb C. Boyd$^{1,2}$, Jixian Xu$^{3,4,2}$, Zhengshan J. Yu$^{2}$, Axel F. Palmstrom$^{2}$, Daniel J. Witter$^{1,2}$, Bryon Larson$^{2}$, Ryan M. France$^{2}$, Jérémie Werner$^{1,2}$, Steven P. Harvey$^{2}$, Eli Wolf$^{1,2}$, William Weigand$^{2}$, Salman Manzoor$^{2}$, Maikel F. van Hest$^{1}$, Joseph J. Berry$^{2}$, Joseph Luther$^{2}$, Zachary C. Holman$^{5}$ and Michael D. McGehee$^{2,4}$; $^{1}$Stanford University, United States; $^{2}$National Renewable Energy Laboratory, United States; $^{3}$University of Science and Technology of China, China; $^{4}$University of Colorado Boulder, United States; $^{5}$Arizona State University, United States

Wide bandgap metal halide perovskites are promising candidates to pair with low bandgap silicon, copper indium gallium diselenide, or perovskite photovoltaics for highly efficient next-generation tandems due to their excellent optoelectronic properties, low-cost manufacturability, and bandgap tunability.(1) However, wide bandgap perovskite solar cells have larger open circuit voltage deficits than their low or medium bandgap counterparts due to both their inferior charge carrier diffusion lengths and photoinduced halide phase segregation into high bandgap (bromine-rich) and low bandgap (iodine-rich) domains.(2) Here, we overcome these material challenges by alloying chlorine into the perovskite lattice to create a triple halide perovskite absorber, a phase space that has thus far been overlooked. Using x-ray diffraction and external quantum efficiency onsets, we show that chlorine is incorporated into the lattice in molar amounts up to 15% and increases the bandgap of the alloy to a greater extent than addition of bromine or cesium, which are commonly used in perovskite bandgap tuning. Importantly, the addition of chlorine drastically improves the optoelectronic properties of the material, resulting in doubled charge carrier mobilities and lifetimes. We show that a 1.67 eV wide bandgap triple halide perovskite does not experience photoinduced halide phase segregation as determined by photoluminescence at laser intensities up to 100 suns. Finally, we incorporate the triple halide perovskite absorber into solar cells, obtaining >20% efficient single junction devices with open-circuit voltages >1.2 V and 1 cm$^2$ monolithic perovskite/silicon tandem solar cells with voltages approaching 1.9 V and efficiencies >27%, exceeding the silicon single-junction record.(3) Solar cells with the triple halide perovskite absorber retain 95% of their initial efficiency under maximum power point tracking at 60°C under white light illumination for 1000 hours.


5:30 AM *S.EN01.04.04
Band Gap Tuning of Perovskite Semiconductors and Insights from a Device Simulator that Includes Affects Associated with Mobile Ions Michael D. McGehee; University of Colorado, United States

Our progress at developing both low and high band gap perovskites for tandem solar cells will be presented. We have made highly stable low band gap cells with greater than 19% power conversion efficiency and triple halide high band gap cells with > 20% stability that do not suffer from light-induced phase separation.

We will also show drift-diffusion modeling results that take into account how mobile halogen vacancies modify the electric field within perovskites. We have input reasonable ranges of charge carrier mobilities, bulk recombination rate constants, surface recombination velocities, mobile ion density and energy levels into the simulator. We will explain mysterious trends reported in the literature and make predictions of what needs to be done to improve efficiency.

5:45 AM *S.EN01.04.05
Composition and Interface Engineering of All-Inorganic Perovskite Absorbers with Dopant-Free Carrier Transporters Tsutomu Miyasaka; Toin University of Yokohama, Japan
Enormous efforts have been made in the last 8 years to upgrade the performance of lead halide hybrid perovskite solar cells (PSCs). Although efficiency level has reached 25%, PSCs face serious challenges of practical stability and durability required for industrialization. Compositional engineering of lead halide perovskites by mixing different cations and anions, using modulator molecules and mixing 2D and 3D structures have improved the stability of perovskites against heat and moisture. However, organic cations in halide perovskites (methylammonium, etc.) and use of diffusible ionic dopants in hole transport materials (HTMs) are responsible for low stability of perovskites at high temperatures (>120°C). In this respect, use of all-inorganic perovskite materials and dopant-free HTMs is highly desired. We have conducted some work in this direction which includes stabilization of CsPbI₂ black phase and use of dopant-free HTMs. We could show that PSCs with all-inorganic perovskites and dopant-free HTMs are capable of efficiency up to 15%. Further, Open-circuit voltage was found to be enhanced over 1.4V, amply high level as a visible light absorber. In preparation of all-inorganic perovskites, a big challenge should be directed to development of lead-free perovskite materials for environmental safety in practical applications. Among extensive applications of PSCs for outdoor and indoor power generation, use of PSCs in space environments is also promising because thin perovskite photovoltaic films demonstrate high stability and tolerance against exposure to severe space environment having high energy particle irradiations (proton and electron beams). Thin absorbers (<500 nm) avoid accumulation of particles and due to intrinsic defect tolerant nature of perovskites, radiation-induced collision damage is highly suppressed. Our current efforts in making PSCs based on both lead and lead-free perovskites, and future perspectives of perovskite photovoltaics will be introduced.

REFERENCES
in general much more stable with respect to oxidation or decomposition into the binary halides. Furthermore the doubling of the formal charge on the B site compare with the perovskites allows a range of different compositions to be explored. In addition, the vacancies at half of the B site positions have consequences for the electronic structure, charge transport and optical properties and the tolerance of the structure to non ideal ion sizes. Understanding these issues, especially how they differ compared to the ABX₃ perovskites, will be necessary for identifying opportunites for A₂BX₆ materials in optoelectronic applications.

In this talk I will summarise our findings on the basic crystal chemistry of A₂BX₆ materials. We have studied a range of compounds, with A = Rb⁺, Cs⁺, CH₃NH₃⁺, B = Sn⁴⁺, Te⁴⁺ and X = Cl⁻, Br⁻, I⁻, and mixtures of ions on the A, B and X sites. We have identified distortion mechanisms analagous to the octahedral tilting well known in the perovskites, and also new distortions that cannot ouur in ABX₃ compounds. Local structure can be determined using Raman spectroscopy, which can identify the distribution of anions in the mixed halide materials: control of the anion distribution can lead to different optical properties in samples with the same overall chemical composition. We have studied the defect properties of these materials through divalent doping on the B site, as well as introduction of rare earth and post transition metal elements.

5:30 AM S.EN01.05.03
Sr and Ba Substitution in Cu₂XSnS₄—Towards Tail-Free Earth-Abundant Absorbers with New Solar Cell Structures
Andrea Crovetto, Moritz Fischer, Kristine Borsting, Rasmus Nielsen, Alireza Hajijafarassar, Nicolas Stenger, Ole Hansen, Brian Seger, Ib Chorkendorff and Peter Vesborg; Technical University of Denmark, Denmark

We present fundamental characterization, single-junction solar cells, and tandem solar cells based on the kesterite-inspired Cu₂BaSnS₄ (CBTS) and Cu₂SrSnS₄ (CSTS) absorbers. While CBTS has been investigated for a couple of years, CSTS material properties and solar cells are characterized here for the first time. Both absorbers are grown by thermal conversion of sputtered oxide films (Cu₂BaSnO₄ and Cu₂SrSnO₄) in an H₂S atmosphere at the same temperature normally used for sulfurization of kesterite [1]. Unlike the tetrahedrally-coordinated Cu₂ZnSnS₄, the CBTS and CSTS absorbers crystallize in a trigonal structure where Cu, Ba(Sr), and Sn have distinct coordination environments, making substitutional defect formation generally less favorable than in kesterite. In fact, both CBTS and CSTS are found to have sharper absorption and emission edges than kesterite, and their room-temperature photoluminescence peaks are well aligned to the band gap. These findings indicate that changing the cation in CXTS has dramatic consequences on band tailing in the material, as also confirmed by recent experiments on the Cu₂CdSnS₄ system [2]. Aided by temperature- and intensity-dependent photoluminescence experiments, will try to identify chemical trends in the deep and shallow defects of the CXTS material system and the X cation is changed.

In CBTS and CSTS solar cells, we modify the commonly used device architecture by using the high work-function metallic back compound TaS₂ as a back contact. The goal is to mitigate the losses associated with carrier transport across the semiconducting MoS₂ layer that invariably forms on a Mo back contact. Encouragingly, the TaS₂ back contact yields a 10% relative efficiency improvement over the Mo back contact. As CBTS and CSTS have optimal band gaps for a top absorber in tandem cells, a proof-of-concept monolithic CBTS/Si tandem cell is fabricated to evaluate possible process incompatibilities between the two subcells. Using a thin Ti(O,N) interlayer as a diffusion barrier and as a recombination layer between the two subcells, a working tandem cell is realized. Finally, we discuss the main hurdles in the development of more efficient single-junction and tandem cells based on CBTS and CSTS.


SESSION S.EN01.06: Materials Discovery Beyond Perovskites—Theory, Experiment, Data
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN01

5:00 AM *S.EN01.06.02
Vapor Phase Deposited Perovskites
Jorge Avila, Daniel Pérez-del-Rey, Chris Dreessen, Paz Sebastia-Luna, Pablo P. Boix, Michele Sessolo and Henk J. Bolink; University of Valencia, Spain

2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
We will report on the progress on vapor phase deposited perovskites, including low bandgap Pb-Sn and wider bandgap multiple cation versions. The performance of these materials in both single and double junction solar cells will be reported. The influence of the use of thin organic charge extraction layers, using strong dopants, ionic compounds and conjugated polymers will be described.

5:15 AM S.EN01.06.03
Accurate Photocurrent Assessment for the Rational Design of Monolithic All-Perovskite Tandem Solar Cells Zhaoning Song, Chongwen Li, Cong Chen, Biwas Subedi, Nikolas J. Podraza and Yanfa Yan; University of Toledo, United States

All-perovskite tandem solar cells, in which two perovskite solar cells with complementary bandgaps are monolithically integrated and electrically connected in series, offer a viable approach to suppress the Shockley-Queisser (SQ) radiative efficiency limits for single-junction solar cells. To date, all-perovskite solar cells have demonstrated power conversion efficiencies (PCEs) of up to ~25%.\textsuperscript{1-4} To further improve the PCE of all-perovskite tandem solar cells, it is important to accurately assess photocurrent generation in individual subcells and rational design the tandem device architecture to maximize current output. However, accurate photocurrent assessment of individual perovskite subcells via external quantum efficiency (EQE) measurements presents some unique challenges due to the possible presence of shunting paths and unclear electric field distribution in both perovskite subcells. The accurate EQE experiments of tandem cells need to be carried out under representative illumination and electrical bias conditions to maintain accurate short-circuit condition for each subcell. Still, the detailed and accurate descriptions of EQE measurements of all-perovskite tandem solar cells have not been reported in the literature. Here, we report on a method to determine the required bias illumination and bias voltage for the EQE measurements, based on the behavior of individual subcells and optical modeling of tandem configuration. We show that the short-circuit current densities of the subcells in our all-perovskite tandem cells with PCEs of ~23%\textsuperscript{1} obtained from the EQE integration are consistent with those from optical modeling and current-voltage measurements under AM1.5G illumination.


SESSION S.EN01.07: Hot Carriers and Characterization
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN01

5:00 AM S.EN01.07.01
Long-Range Hot Carrier Transport in Hybrid Perovskites Visualized by Ultrafast Microscopy Libai Huang; Purdue University, United States

The Shockley-Queisser limit for solar cell efficiency of ~ 33% can be overcome if hot carriers can be harvested before they thermalize. Recently, carrier cooling time up to 100 picoseconds was observed in hybrid organic-inorganic lead halide perovskites, but it is unclear whether these long-lived hot carriers can migrate long distance for efficient collection. We report direct visualization of hot carrier migration in CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} thin films by ultrafast transient absorption microscopy, demonstrating three distinct transport regimes. Quasi-ballistic transport was observed to correlate with excess kinetic energy; resulting in up to 230 nanometers transport distance in 300 fs that could overcome grain boundaries. The nonequilibrium transport persisted over tens of picoseconds and ~ 600 nanometers before reaching the diffusive transport limit. These results suggest potential applications of hot carrier devices based on hybrid perovskites.

5:15 AM S.EN01.07.03
Heterogeneous Photon Recycling and Charge Diffusion Enhance Charge Transport in Quasi-2D Lead-Halide Perovskite Films Silvia G. Motti\textsuperscript{1}, Timothy Crothers\textsuperscript{1}, Rong Yang\textsuperscript{2}, Michael B. Johnston\textsuperscript{1}, Jianpu Wang\textsuperscript{2} and Laura Herz\textsuperscript{1}; \textsuperscript{1}University of Oxford, United Kingdom; \textsuperscript{2}Nanjing Tech University, China

The addition of large hydrophobic cations to lead halide perovskites has significantly enhanced the environmental stability of
photovoltaic cells based on these materials. However, the associated formation of two-dimensional structures inside the material can lead to dielectric confinement, higher exciton binding energies, wider bandgaps and limited charge-carrier mobilities. In this work we investigate the impact of such effects to the charge transport properties of perovskite films comprising a 3D MAPbI3 perovskite layer and a self-assembled quasi-2D perovskite region on the substrate side. We apply a combination of time-resolved photoluminescence and terahertz (THz) photoconductivity spectroscopy to reveal the charge-carrier recombinations and transport through the film profile, when either the quasi-2D or the 3D layers are selectively excited.

Through modelling of the photoconductivity dynamics, we demonstrate that while the charge-carrier mobility is lower within the quasi-2D region, charge-carrier diffusion to the 3D phase leads to a rapid recovery in photoconductivity even when the quasi-2D region is initially photoexcited. In addition, the blue-shifted emission originating from quasi-2D regions overlaps significantly with the absorption spectrum of the 3D perovskite, allowing for highly effective heterogeneous photon recycling. We show that this combination compensates for the adverse effects of electronic confinement, yielding quasi-2D perovskite films with highly efficient charge transport properties.

SESSION S.EN01.08: Structure-Property Relations
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN01

5:00 AM S.EN01.08.01
Understanding Defects in Perovskite Solar Cells by Advanced Characterization Techniques Juan Pablo Correa Baena; Georgia Institute of Technology, United States

Perovskite solar cells promise to yield efficiencies beyond 30% by further improving the quality of the materials and devices. Electronic defect passivation, and suppression of detrimental charge-carrier recombination at the different device interfaces has been used as a strategy to achieve high performance perovskite solar cells.

In this presentation, I will discuss the role of electronic defects and how these can be passivated to improve charge-carrier lifetimes and to achieve high open-circuit voltages. I will discuss the characterization of 2D and 3D defects, such as grain boundaries, crystal surface defects, and precipitate formation within the films, by synchrotron-based techniques. The importance of interfaces and their contribution to detrimental recombination will also be discussed. As a result of these contributions to better understanding 2D and 3D defects, the perovskite solar cell field has been able to improve device performance. Albeit the rapid improvements in performance, there is still a need to improve these defects to push the solar cells beyond the current state-of-the-art.

5:15 AM S.EN01.08.02
Crystal Phase Control toward the Perovskite Superlattice Solar Cells Satoshi Uchida1, Naoyuki Shibayama1, Koichi Tamaki1, Keishi Tada1, Miwako Furue1, Ludmila Cojocaru2 and Hiroshi Segawa1; 1The University of Tokyo, Japan; 2Institute des sciences Moleculaires Universite de Bordeaux, France

Recently organic–inorganic halide perovskite solar cell have great attention for its high performance together with easy production and wide variety of the process & flexibility of substrate materials. The power conversion efficiency has already reached over 25% in 2019 much beyond another solar cells such as CIGS or amorphous Si. The further performance still looks promising toward the Shockley–Queisser limit at around 30%. For that purpose, physical chemistry understanding based on the crystallography must be essential to design the good light harvesting, good charge separation and good charge transfer. Recently we reported the scientific revelation that the crystal phase of thin film CH3NH3PbI3 consists of the mixture of tetragonal phase and cubic phase. They are about 15-20 nm well crystallized domain and randomly oriented in high resolution TEM analysis. Furthermore, multi stack sequence such as tetra-cubic-tetra resulted to form the superlattice with d-spacing 10.989Å (2θ=8.03°for CuKα). Such a superlattice may act beneficial for good charge separation & charge transfer that are well known property as a Type II superlattice. To make more efficient performance, the crystal phase control with some different approaches were examined as below.

(1) High pressure post treatment by cold isostatic pressing (CIP)
(2) Photo-flash rapid curing
(3) Crystal growth under the high voltage electrostatic field
Here in this research the results of advantage-disadvantage will be discussed.

References

5:25 AM S.EN01.08.04
Efficient Monolithic Perovskite/Silicon Tandem Solar Cells Based on Blade-Coated Perovskites on Textured Silicon
Bo Chen1, Zhengshan J. Yu2, Salman Manzoor2, Shen Wang1, William Weigand2, Zhenhua Yu1, Guang Yang1, Zhenyi Ni1, Xuezeng Dai1, Zachary C. Holman2 and Jinsong Huang1; 1University of North Carolina at Chapel Hill, United States; 2Arizona State University, United States

Perovskite/silicon tandem solar cells have the potential to break the single-junction efficiency limit of silicon cells and further drive down the cost of silicon photovoltaics. To date, the reported monolithic perovskite/silicon tandem cells are fabricated primarily on silicon cells with front-side-polished surface, which not only cause large reflection loss but also require a costly chemical-mechanical polishing process. Thermal evaporation-involved fabrication of perovskite/silicon tandem cells on textured silicon to reduce the reflection loss, but it sacrifices the advantage of solution processability of perovskites. Here, we develop a scalable blade-coating technique to deposit perovskite film on double-side-textured silicon cells with sub-micrometer pyramids. This new tandem architecture combines the advances of textured silicon photovoltaics and solution processed perovskite photovoltaics to increase the efficiency while reducing the cost of monolithic perovskite/silicon tandem cells. The sub-micrometer pyramids are rough enough to scatter light within silicon nearly as efficiently as large pyramids but smooth enough to solution-process a perovskite film. Blade-coated perovskite film planarizes the textured silicon cell. With a textured light-scattering layer added to top of tandem to reduce front-surface reflectance, a monolithic perovskite/silicon tandem cell with an efficiency of 26% is achieved on textured silicon cells.

5:35 AM S.EN01.08.05
Thermally Co-Evaporated Perovskites—from Small Areas Solar Cells to Mini-Modules
Jia Li, Hao Wang, Herlina Arianita Dewi, Nripan Methews, Subodh Mhaisalkar and Annalisa Bruno; Energy Research Institute @Nanyang Technological University, Singapore

The rapid improvement in perovskite solar cells’ (PSCs) power conversion efficiency (PCE) has prompted the interest to adapt the perovskite technology in the production lines. Capitalizing on existing industrial processing methods will facilitate technology transfer from lab-scale research into mass production, thereby accelerating commercialization. In this work, we have proven the scalability of high quality thermally co-evaporation MAPbI3 active layers in perovskite solar cells up to 4 cm² and mini-modules up to 50 cm², being able to guarantee minimal PCE losses. With a combined strategy of active layer engineering based on deposition optimization, effective surface, and interfacial treatments and light-dispersion minimization, we demonstrate PSCs and mini-modules (active area 21 cm²) achieving PCEs > 20% and ~19% respectively. The un-encapsulated devices were able to retain ~ 90% of the initial PCE under continuous illumination at 1 sun (AM 1.5G) without active sample cooling. Looking towards both tandem applications and building-integrated photovoltaics (BIPV), we have also demonstrated thermally evaporated perovskite semi-transparent modules and semi-transparent PSCs. Colorful thermally evaporated semitransparent PSCs show a consistent PCE of ~16% for a set of colors ranging in the whole visible range. These results demonstrate the compatibility of perovskite technology with existing industrial processes and their potential for the next generation photovoltaics.
perovskite technologies is impeded by the usage of high-boiling point, hazardous solvents, lab-scale processing techniques, and nitrogen environment processing, which significantly increases the cost. Here we propose a low- boiling point, less toxic solvent that enables to process the high-quality perovskite films at a high relative humidity (RH) and ambient atmospheric conditions. Our deposition route enables precursor dissolution and further on spin- or blade-coating, intermediate film phase is obtained. When the intermediate film is exposed to methyamine (MA) gas flow, the film immediately converts to MAPbI$_3$ perovskite. This method enabled deposition at moisture levels which span from 50 to 80 % RH. Incorporating the film in a low temperature processed inverted device structure, achieved stabilized PCEs up to 14%. Furthermore, the deposition is proved compatible with both spin- and blade-coating methods, to ensure scalability of the process. This method renders promising scalable, humidity robust, less hazardous, ambient atmosphere and low-temperature processing perovskite device fabrication.

5:10 AM S.EN01.09.02
Enhancing Photovoltaic Performance of Aromatic Ammonium Based Two-Dimensional Organic-Inorganic Hybrid Perovskites via Tuning CH⋯π Interaction Liang Yan, Jun Hu, Ninghao Zhou, Andrew Moran and Wei You; University of North Carolina at Chapel Hill, United States

Phenethylammonium (PEA) based 2D perovskite is an interesting example of 2D perovskites, serving as the gateway towards further introduction of functional conjugated organic cations into 2D perovskites for a variety of applications, for example, photovoltaics. However, the efficiency of photovoltaic devices based on PEA 2D perovskites only achieved ~ 7% for $\langle n\rangle=3$, significantly lower than what have been achieved for other cations based 2D perovskites. Here we show that, by introducing propyl ammonium (C3A) into the PEA based 2D perovskites, the device efficiency can be improved to ~10% for 1:1 C3A:PEA based 2D perovskites ($\langle n\rangle=3$). Further investigation discloses that, tuning the CH⋯π interaction (between C3A and PEA or between two PEA) can have multiple beneficial impacts on such modified 2D perovskites, including (a) removal of undesirable $n^{-1}$ phase, (b) lowering the density of trap states, and (c) achieving rather large crystalline grains. Additionally, when substituting with 50% C3A, other aromatic ammonium cations based 2D perovskites ($\langle n\rangle=3$) also witness similar efficiency enhancement in their photovoltaic devices, boasting the general use of such method. Our results highlight that, the strategic tuning of non-covalent interactions (such as the CH⋯π interaction) is a viable and important method in further developing 2D perovskites for photovoltaics.

5:20 AM S.EN01.09.03
Formulating Simultaneous Quasi Core-Shell Structure and Heterojunction for Improving Efficiency and Stability of Low-Bandgap Perovskite Solar Cells Can Li and Wallace C. Choy; University of Hong Kong, China

The highest power conversion efficiency of perovskite solar cells has reached 25.2% which is approaching the Shockley-Queisser (S-Q) limit of single-junction devices. One solid strategy to break the S-Q limit is developing perovskite-perovskite tandem devices. The low-bandgap perovskite solar cells are ideal candidates as the rear subcell in the tandem device with the advantages of tunable bandgap, solution process and low cost. However, unlike Pb-based perovskites, it is still a challenge for realizing the targets of high performance and stability in mixed Pb-Sn perovskite solar cells owing to grain boundary traps and chemical changes in the perovskites. In this work, we propose the approach of in-situ tin(II) inorganic complex anti-solvent process for particularly tuning the perovskite nucleation and crystal growth process. Interestingly, by tuning the perovskite nucleation and crystal growth process through the tin(II) process, we uniquely form the quasi core-shell structure of Pb-Sn perovskite-tin(II) complex as well as heterojunction perovskite structure with energy offset at the same time for achieving the targets. The core-shell structure of Pb-Sn perovskite crystals covered by a tin(II) complex at the grain boundaries effectively passivates the trap states and suppresses the nonradiative recombination, leading to longer carrier life time. Equally important, the perovskite heterostructure with energy offset is intentionally formed at the perovskite top region for enhancing the carrier extraction and suppressing the bimolecular recombination. As a result, the mixed Pb-Sn low-bandgap perovskite device achieves a high power conversion efficiency up to 19.03% with fill factor over 0.8, which is among the highest fill factor in high-performance Pb-Sn perovskite solar cells. The perovskite device with the tin(II) process remains 92% of its initial PCE after stored in inert environment for 22 days. Remarkably, the device fail time under continuous light illumination is extended by over 18.5 folds from 30 h to 560 h beneficial from the protection of the quasi core-shell structure [1].


5:30 AM S.EN01.09.04
Tuning the Bandgap of Cs₂AgBiBr₆ through Dilute Tin Alloying

Kurt P. Lindquist¹, Stephanie A. Mack², Adam H. Slavney¹, Linn Leppert², Aryeh Gold-Parker¹,², Jonathan F. Stebbins¹, Alberto Salleo¹, Michael F. Toney⁵, Jeffrey B. Neaton²,³,⁶ and Hemamala Karunadasa¹,⁵; ¹Stanford University, United States; ²Lawrence Berkeley National Laboratory, United States; ³University of California, Berkeley, United States; ⁴University of Bayreuth, Germany; ⁵SLAC National Accelerator Laboratory, United States; ⁶Institute at Berkeley, United States

The promise of lead halide hybrid perovskites for optoelectronic applications makes finding less-toxic alternatives a priority. The double perovskite Cs₂AgBiBr₆ (I) represents one such alternative, offering long carrier lifetimes and greater stability under ambient conditions. However, the large and indirect 1.95 eV bandgap hinders its potential as a solar absorber. Here, I will show that alloying I with Sn allows for substantial modulation of the optical absorption to absorb more sunlight in a composition free from highly toxic elements. I will then present a detailed analysis, having employed a host of experimental techniques, of the speciation and substitution pathways of Sn alloyed into I. Using this structural understanding, I will discuss the electronic consequences of Sn alloying in I as understood through band structure calculations. The understanding of heterovalent alloying in halide perovskites presented here opens the door to a wider breadth of potential alloying agents for manipulating their band structures in a predictable manner.

5:40 AM *S.EN01.09.05
Increasing the Complexity of Halide Perovskites

Kurt P. Lindquist¹, Michael Boles¹, Adam H. Slavney¹, Stephanie A. Mack², Jeffrey B. Neaton²,³ and Hemamala Karunadasa¹,⁴; ¹Stanford University, United States; ²University of California, Berkeley, United States; ³Lawrence Berkeley National Laboratory, United States; ⁴SLAC National Accelerator Laboratory, United States

Halide perovskites provide a flexible platform for tuning optoelectronic properties through changes in composition, connectivity, and dimensionality. I will present our recent studies on increasing the accessible electronic structures of this versatile family of materials by synthesizing mixed-metal perovskites. Through both stoichiometric and substoichiometric substitutions we can synthesize a variety of halide perovskites, including those with unprecedented lattices with unusual electronic structures.

5:55 AM S.EN01.09.06
Building from the Ground Up—Structural Manipulation in 2D Hybrid Halide Perovskites

Lingling Mao¹,², Constantinos Stoumpos², Mercouri G. Kanatzidis², Anthony K. Cheetham¹ and Ram Seshadri¹; ¹University of California, Santa Barbara, United States; ²Northwestern University, United States; ³University of Crete, Greece

Two-dimensional (2D) hybrid halide perovskites offer high chemical versatility, strong potential in optoelectronic applications, and technological improvements in stability and performance of solar cells. The 2D perovskite family has a general formula of (A')ₙ(A)ₙ₋₁BₙX₃n+1, where A' is a large organic spacing cation (monovalent m=2 or divalent m=1), A is a small monovalent cation, B is a metal and X is halide. Here, we report the highest layer thickness (n = 7) that has ever been crystallographically characterized, for the Dion-Jacobson (DJ) phase. The seven-layered DJ phase (4AMP)(MA)₆Pb₇I₂₂ (4AMP = 4-aminomethylpyperidinium) shows less distortion in the crystal structure compared with the Ruddlesden-Popper (RP) phase (BA)₇(MA)₆Pb₇I₂₂ (BA = butylammonium). The comparison of the DJ and RP perovskites at the n = 7 level reveals that structural details still influence the optical properties, which the DJ phase has a smaller band gap than the RP due to smaller structural distortion. Another family derived from three-dimensional double perovskite, namely the layered double perovskite halides are reported here using propylammonium (PA) cation, with a general formula of AₓMM'Xₘ (single-layered) and AₓA’M’M”Xₘ (two-layered) (A = PA, A’ = Cs, M = Ag, M’ = Bi, In and X = Cl, Br). This system has demonstrated a high versatility, in which the layer thickness can be tuned up to two, and the organic spacer can be varied from singly protonated cations to a di-cation (1,4-butanediammonium, BDA). The band gap of the materials shows a wide tunability, varying from 2.41 eV (PA₄AgBiBr₈) to 3.96 eV (PA₄AgInCl₈). The diverse structural menu in 2D hybrid perovskite provides a wide selection in exploring the structure-property relations for better optoelectronic materials.

6:05 AM S.EN01.09.07
Improved Photo-Stability through the Incorporation of Phenyl Ethyl Ammonium Cations into Mixed Cation Perovskites

Aditya S. Yerramilli, Banashree Gogoi, Yuanqing Chen and Terry Alford; Arizona State University, United States

Organic-Inorganic halide perovskites have attracted much attention in the last few years. A certified efficiency of 23.7% has made them very attractive in the pursuit of cheaper alternatives to Si-based devices. However, the stability of the device has been a challenge given the very high moisture susceptibility in perovskites. The introduction of large cations is known to...
induce two-dimensional graded perovskite structures, which improved phase and ambient stability. Very few reports have emerged in this regard that looks at the influence of introducing large cations into a mixed triple cation perovskite, on the overall properties of the device. In this work, we investigated the impact of incorporating Phenyl ethyl ammonium (PEA) into the mixed triple cation composition of FAMACsPb(I0.7Br0.3)3. For the 5% PEA in the quadruple composition, we observed improvements in the crystallinity and more uniform coverage with little to no pinholes through X-ray diffraction and electron microscopy studies. Device data showed increased V_{oc} from 0.8V to more than 1V for 5% PEA samples. Corresponding photoluminescence data also showed improvement in the intensity of absorption and charge carrier lifetimes.

6:15 AM S.EN01.09.08
The Impact of Stoichiometry on the Photophysical Properties of Ruddlesden-Popper Perovskites Herman Duim, Sampson Adjokatse, Simon Kahmann, Gert H. Ten Brink and Maria Antonietta Loi; University of Groningen, Netherlands

Low dimensional perovskites are attracting interest for a variety of opto-electronic applications, owing to their tunable optical properties and their excellent ambient stability. In particular, metal halide perovskites of the Ruddlesden-Popper (RP) type – in which inorganic sheets are separated by relatively long organic cations - can be considered as strongly confined quantum well system. As these materials can be cast directly from solution, they hold the promise of procuring flexible and cost-effective films through large-scale fabrication techniques. However, such films typically possess a large degree of heterogeneity across different length scales, the origin and consequences of which are currently not well understood.

In this work, the influence of the stoichiometry of the precursor solution on the microscopic properties of films of the RP perovskite (PEA)2PbI4 are therefore investigated. It is found that the stoichiometry plays an important role in determining the crystallinity, morphology and optical properties of the resulting thin films. Pronounced differences in photoluminescence intensities are shown to exist even in films that are cast from stoichiometric solutions and manifest themselves on a sub-granular level. Using temperature-dependent photoluminescence mapping, an activation energy of 0.4 eV was extracted for the emergence of these local variations in non-radiative recombination rates. The spatial variation in the distribution of trap states is attributed to local fluctuations in the stoichiometry. In line with this, the surface can successfully be passivated by providing an excess of PEAI to an as-cast film, enhancing the photoluminescence intensity as much as 85% without significantly altering the film’s morphology.

6:25 AM S.EN01.09.09
Spin Dependent Charge Transport through Two-Dimensional Chiral Hybrid Lead-Iodide Perovskites Haipeng Lu1, Jingying Wang2, Zeev V. Vardeny2 and Matthew C. Beard1; 1National Renewable Energy Laboratory, United States; 2The University of Utah, United States

Chiral-induced spin selectivity (CISS) occurs when the chirality of the transporting medium selects one of the two spin ½ states to transport through the media while blocking the other. Monolayers of chiral organic molecules demonstrate CISS but are limited in their efficiency and utility by the requirement of a monolayer in order to preserve the spin selectivity. Here we demonstrate CISS in a system that integrates an inorganic framework with a chiral organic sub-lattice inducing chirality to the hybrid system. Using magnetic conductive-probe atomic force microscopy we find that oriented chiral 2D layered Pb-iodide organic/inorganic hybrid perovskite systems exhibits CISS. The electron transport through the perovskite films depends on the magnetization of the probe tip and the handedness of the chiral molecule. The films achieve a highest spin-polarization transport of up to 86%. Magnetoresistance studies in modified spin-valve devices having only one ferromagnet electrode confirms the spin-dependent charge transport through the organic/inorganic layers.

6:35 AM S.EN01.09.10
Perovskite-Inspired 2D Antimony-Based Absorber Layers for Optoelectronic Applications Nadja Giesbrecht; University of Muenchen, Germany

The presence of lead in novel hybrid perovskite-based solar cells remains a significant issue regarding commercial applications due to toxicity and instability issues. Therefore, perovskite-inspired new lead-free compounds are sought-after as new candidates for photovoltaic applications. However, most of the suggested substitutions are either oxidation unsteady or suffer from indirect and wide bandgaps. Here, we demonstrate the first thin-film synthesis of MA$_3$Sb$_2$I$_9$ in the perovskite-like 2D polymorph with narrow and direct bandgaps and their application to solar cell devices. So far, MA$_3$Sb$_2$I$_9$ was reported to only crystallize in the zero-dimensional dimer structure with wide indirect bandgap properties. The formation of the 2D layered polymorph with its expected direct and narrow bandgap is more suitable for solar cell application. Using in situ XRD methods, we confirm the stability of the layered phase towards high temperature and moisture. We investigated the electronic
band structure and confirmed experimentally the presence of a semi-direct bandgap at around 2.1 eV. With the incorporation of a two-valent metal cation to the 2D antimony-based structure with the general structure formula $A_3Sb_2X_9$, the direct bandgap can be further narrowed down. The most known compound, $Cs_4CuSb_2Cl_{12}$, has a direct bandgap of around 1 eV with strong absorption and high stability towards temperature and polar solvents. However, the synthesis of highly crystalline material or thin-films is challenging. To overcome the limitation in the application of low-quality precipitants in optoelectronic devices, we introduce synthesis procedures requiring at least two-steps procedures. We synthesize single crystals larger than 500 µm, enabling their full characterization and application in optoelectronics. Our work shows that careful control of nucleation via processing conditions can provide access to promising perovskite-like phases for photovoltaic applications.

SESSION S.EN01.10: Beyond Solar Cells and New Materials
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
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5:00 AM *S.EN01.10.01
Recent Advances in Integrated Perovskite Optoelectronics Anna Lena Giesecke1, Piotr Cegielski1, Stephan Suckow1, Manuel Runke2, Neda Pournavoud2, Stefanie Neutzner3, Annamaria Petrozza3, Thomas Riedl2 and Max C. Lemme1,4; 1AMO GmbH, Germany; 2University of Wuppertal, Germany; 3Center for Nano Science and Technology, Italy; 4RWTH Aachen University, Germany

Metal-halide perovskites as semiconductors with a direct band-gap are ideal candidates for optoelectronic on-chip devices such as lasers. These materials can be deposited onto existing chips and processed using back-end-of-line compatible techniques broadening their functionality. Recently, top-down lithographic patterning processes have been established in spite of the chemical sensitivity of perovskites. The first integrated devices show lasing thresholds that can compete with other technologies. Other recent works demonstrate continuous wave lasing operation and raising hopes for electrically pumped device concepts in the future. At the same time, monolithic integration onto different photonic substrates is feasible. This makes the integrated perovskite devices unique and, in the near future, more versatile compared to existing concepts such as hybrid-integrated III-V lasers.

In this talk we will demonstrate our latest achievements in integration of optoelectronic devices. Fabrication processes and treatment of the perovskite material has to be optimized differently in order to obtain efficient light emitting devices in comparison with photovoltaic applications. We work on a silicon nitride photonic platform and integrate perovskite processes seamlessly in our photonic fabrication line. The overall performance of the integrated devices is strongly dependent on the morphology of the used materials. First attempts of reducing the perovskite’s surface roughness and increasing the lateral dimensions of crystallites show the perspective of lowering laser threshold by order of magnitude. Scattering losses can be mitigated and thus polarization of the generated laser light can be stabilized. All devices work at room temperature and are currently optically pumped. Different types of perovskites (i.e. MAPbI$_3$ and CsPbBr$_3$) are integrated onto silicon nitride photonic chips. The generated laser light can directly be used by the photonic circuit underneath the perovskite laser. The emission is characterized after outcoupling through a silicon nitride waveguide. Furthermore, a detailed study about the optical properties of the perovskite after patterning by photolithography is carried out in order to define design optimizations needed for the future light emitting devices.

Our work focusses strongly on reproducible, mass manufacturable fabrication processes. Long term device stability is a central challenge for newly developed material and devices geometries. Possible industrial applications such as datacom and sensor devices are discussed.

5:15 AM S.EN01.10.03
Electrospun Hybrid Perovskite Fibers—Flexible Networks of One-Dimensional Semiconductors for Light Harvesting Applications Christoph Bohr, Markus Pfeiffer, Senol Öz, Florian von Toperczek, Ashish Lepcha, Thomas Fischer, Markus Schütz, Klas Lindfors and Sanjay Mathur; University of Cologne, Germany

The interest in perovskite solar cells is growing rapidly due to their versatile applicability for energy harvesting systems. In a short period of time, devices already reached efficiencies up to 25%, making them comparable to established thin-film solar
cells like Cu(In,Ga)Se₂ or CdTe. The quantity of publications dealing with planar and rigid solar cells is growing tremendously; however, fibrous solar cells have not been in focus yet. Since the 1D structure provides a greater flexibility in comparison to planar systems, applications ranging from e-textiles/wearables to lightweight applications are feasible. Here, the single step fabrication of phase-pure organic-inorganic lead halide perovskite fibers by inert electrospinning technique is presented. Morphological, as well as optical/photonic properties have been studied and demonstrate first comprehensive data on electrospun organic-inorganic hybrid materials. Substitution of the absorbing layer in planar heterojunction solar cells with perovskite fibers resulted in a photoelectric response under simulated sunlight conditions. These flexible 1D hybrid perovskite fibers are potential elements for flexible optoelectronics and mark a starting point towards competitive fibrous solar cells.

5:25 AM S.EN01.10.05
**Thermal Management for Perovskite Light Emitting Diodes** Lianfeng Zhao, Kwangdong Roh and Barry P. Rand; Princeton University, United States

Hybrid organic-inorganic perovskite semiconductors have shown potential to develop into a new generation of light-emitting diode (LED) technology with high light quality and energy efficiency. However, device operational stability is the biggest challenge for perovskite LEDs to become a commercial reality. Here we show that elevated device temperature caused by Joule heating is a major factor contributing to EQE roll-off and device degradation. Several thermal management strategies have been used to reduce Joule heating and improve thermal dissipation, such as adopting a thinner perovskite layer and doped charge transport layers, using substrates with higher thermal conductivity and optimizing device geometry. These strategies have allowed us to demonstrate perovskite LEDs with a peak EQE of 19.9%, a record high radiance of 1200 Wsr⁻¹m⁻², much reduced EQE roll-off (maintained an EQE of 5% at 4000 mA/cm²) and improved operational stability.

5:35 AM S.EN01.10.07
**Origin of Luminescent Centers and Edge States in Low Dimensional Lead Halide Perovskites** Jiming Bao¹, Zhiming Wang², Liangzhi Deng³, Zhaojun Qin², Shen-yu Dai³, Shuo Chen¹, Lixin Xie¹, Chong Wang⁴, Chunzheng Wu⁵, Guang Yang¹, Guoying Feng², Viktor Hadjiev¹, Qingkai Yu¹, Yizhou Ni¹, Qiang Li⁶, Haiyan Wang⁷, Kamrul Alam¹, Francisco Robles Hernandez², Jie Jian⁸, Hector Calderon Benavides¹, Yan Yao¹, Yanan Wang¹, Xinhuai Su³ and Feng Lin²; ¹University of Houston, United States; ²University of Electronic Science and Technology of China, China; ³Sichuan University, China; ⁴Yunnan University, China; ⁵Texas State University, United States; ⁶Purdue University, United States; ⁷Instituto Politecnico Nacional, ESFM-IPN, UPALM, Mexico; ⁸Chang’an University, China

With only a few deep-level defect states having a high formation energy and dominance of shallow carrier non-trapping defects, the defect-tolerant electronic and optical properties of lead halide perovskites have made them appealing materials for high-efficiency, low-cost, solar cells and light-emitting devices. As such, recent observations of apparently deep-level and highly luminescent states in low-dimensional perovskites have attracted enormous attention as well as intensive debates. The observed green emission in 2D CsPb₂Br₅ and 0D Cs₄PbBr₆ poses an enigma over whether it is originated from intrinsic point defects or simply from highly luminescent CsPbBr₃ nanocrystals embedded in the otherwise transparent wide bandgap semiconductors. The nature of deep-level edge emission in 2D Ruddlesden-Popper perovskites is also not well understood. In this talk, I will analyze the experimental evidences that support the opposing interpretations and discuss challenges and root causes for the controversy. I will then present experimental approaches that can better correlate property with structure of a material and help resolve the controversies. Using combined Raman-photoluminescence under hydrostatic pressure in a diamond anvil cell, we prove that CsPbBr₃ nanocrystals are responsible for the bright green emissions in both 2D CsPb₂Br₅ and 0D Cs₄PbBr₆. Finally, I will show our preliminary understanding of the edge emission in 2D R-P perovskites.

References:


Solution-Assembled Blue Perovskite Light-Emitting Diodes Using Branched Smaller Spacer Cations as Additives
Martha J. Rivera-Medina and Maria Antonietta Loi; University of Groningen, Netherlands

Research on metal halide perovskites (MHP) has paved the way towards excellent optoelectronic materials, establishing them as a prime candidate for the forthcoming generation of large-area lighting and displays. Due to their high color purity, high radiative recombination rates, and bandgap tunability, MHP devices have been demonstrated to be in the lead for future LED applications. However, history repeats itself as for perovskite-based light-emitting diodes (PeLEDs) achieving an efficient performance for blue-emission remains a challenge. Compared to the green, red, and near-infrared, blue PeLEDs is lacking in terms of efficiency and luminance. Close attention should be paid towards the perovskite thin-film processing to ensure radiative recombination, especially in smaller grain-sized structure as in quasi-two-dimensional perovskites. Initially, these perovskites are tailored to an $n$ number of inorganic slabs surrounded by spacer cations, but during the formation of thin-films, heterogeneous values of $n$ coexist giving raised to different N-phase domains. It has been observed that by the addition of smaller organic molecules, one can suppress the formation of higher $N$ values maintaining the excitation in the higher bandgap structures ensuring blue emission even as energy-funnelling is favored toward low bandgap domains. In this work, we report fully-solution-processed blue-light-emitting devices. Our devices have incorporated branched smaller spacer cations as additives to our PEA$_2$(MA$_{x}$Cs$_{1-x}$)$_n$Pb$_n$Br$_{3n+1}$ perovskite films to hinder the formation of higher values of $N$, while prevailing an N-phase purity of 2 for $n$ values of 1.5, 2, 2.5 in solution. This composition gave rise to devices with a dominant emission wavelength of 483 nm with color purity of 66 % at a maximum operating applied voltage, and a low threshold voltage as low as 3V.

PASSIVATION OF MIXED CATION PEROVSKITES THROUGH THE ADDITION OF GUANIDINUM IODIDE LAYER
Aditya S. Yerramilli, Banashree Gogoi, Yuanqing Chen and Terry Alford; Arizona State University, United States

Recent research in perovskite solar cells shows efficiencies beyond 20%. There are, however, several concerns that limit them from realizing the full potential. Defects on the surface of the perovskite are the significant reasons for non-radiative recombination, limiting the performance of the device. Several surface treatments show evidence as potential solutions to overcome these defects. Surface passivation of the perovskites is a viable option to minimize the defects and promote better charge carrier extraction. Also, the introduction of large cations into the perovskite induces a two-dimensional layered structure. In this work, we report the deposition of GUAI on mixed cation, FAMACsPb(I$_0.7$Br$_{0.3}$)$_3$, as a means to induce passivation and suppress non-radiative recombination. Results reveal improvements in structural properties and morphology. The open-circuit voltages ($V_{oc}$) with values >1V is indication of improvement with the addition of GUAI on the mixed cation perovskite.

SYSTEMATIC SCREENING AND OPTIMIZATION OF CONTACTS TO WIDE-BANDGAP PEROVSKITE THROUGH EXTERNAL RADIATIVE EFFICIENCY AND SURFACE PHOTO-VOLTAGE MEASUREMENTS
Arthur Onno$^1$, Shalinee Kavadiya$^1$, Caleb Boyd$^{2,3}$, Michael D. McGeehan$^{2,3}$ and Zachary C. Holman$^1$; $^1$Arizona State University, United States; $^2$University of Colorado Boulder, United States; $^3$National Renewable Energy Laboratory, United States

To achieve maximal efficiency, a photovoltaic solar cell requires:
1. an excellent absorber, with high material quality and surface passivation to maximize its quasi-Fermi-level splitting under illumination (hereafter referred to as the implied or internal open-circuit voltage $iV_{oc}$), and
2. excellent electron and hole contacts, selective enough to maximize the extraction of the $iV_{oc}$ and achieve a high external open-circuit voltage $V_{oc}$.

Consequently, deviations of the $V_{oc}$ from the detailed-balance theoretical maximum is either due to limitations of the absorber itself—because of poor material quality or surface passivation, leading to non-radiative recombination—or of the contacts—
not selective enough, with a drop of the majority-carrier quasi-Fermi level across the corresponding contact.

Based on this, we use a combination of characterization techniques to systematically investigate and quantify what limits the $V_{oc}$ of wide-bandgap (1.68 eV) perovskite solar cells and screen contact schemes. First, we measure the external radiative efficiency (ERE)—also referred to as the photoluminescence quantum efficiency or yield (PLQE or PLQY)—of perovskite films and finished devices to determine their $iV_{oc}$. This voltage, which corresponds to the maximum voltage that could be extracted from the absorber if its contacts were perfect, is a metric of the material quality and the surface passivation of the absorber. Second, we measure the surface photo-voltage ($SPV$) of non-metallized devices. The $SPV$ indicates the total band bending in the device; that is, the sum of the band bending at the absorber/ETL and at the absorber/HTL interfaces. Therefore, it is a metric of the selectivity of the contacts: the higher the $SPV$, the higher the band bending and, consequently, the lower the majority-carrier quasi-Fermi level drop across each contact. Finally, we compare the $iV_{oc}$ with the $V_{oc}$. The ratio $V_{oc}/iV_{oc}$ is also a metric of the selectivity of the contact and follows the same trend as the $SPV$. By comparing these three metrics ($iV_{oc}$, $SPV$, and $V_{oc}/iV_{oc}$) between cells with different contact architectures, we can guide the cell optimization process.

In particular, bare perovskite films on glass exhibit a very high luminescence (ERE>1%), corresponding to an $iV_{oc}$ of 1300 mV, more than 150 mV above the $V_{oc}$ of the finished devices. Thus, the absorber material quality is not the limiting factor in the voltage of the final devices and contacts are responsible of this voltage deficit—either because of a poor surface passivation of the absorber, a poor selectivity, or a combination of both. Comparing NiO$_x$ and PTAA as hole transport layers, we show that using NiO$_x$ typically leads to a higher $iV_{oc}$ but lower $V_{oc}/iV_{oc}$ and $SPV$ than PTAA. Consequently, NiO$_x$ is more passivating but less selective than PTAA. Researchers working on NiO$_x$ contacts should consequently focus on improving its selectivity, for example through modification of its work function. Conversely, for PTAA contacts, optimization of the surface passivation should be prioritized, for example by engineering the perovskite/PTAA interface to reduce its defect density.

5:20 AM S.EN01.11.04
Investigating the $V_{oc}$ Deficit of Wide-Bandgap Perovskite Solar Cells Using Numerical Modeling Jared Friedl, Ramez Hosseinian Ahangharnejhad, Adam Phillips and Michael Heben; The University of Toledo, United States

The performance of perovskite solar cells continues to improve as progress is made in both the optimization of charge transport materials and the absorbers themselves. Mixed-halide perovskites (e.g. CH$_3$NH$_3$Pb(I$_{3-x}$Br$_x$)$_3$) are useful for their bandgap adjustment through change in chemical composition. The bandgap engineering of perovskites is of particular interest due to applications for tandem architectures in conjunction with lower-bandgap absorbers such as Si and CIGS. A notable observation in record-performance cells across the relevant bandgap range is the presence of a “bandgap deficit” for wider-bandgap perovskites. This has led to a number of studies that focus on reducing this deficit through modifying the energetics of perovskite bands at the interface with transport layers (TLs) or reducing the recombination at the perovskite/TL interfaces by incorporating passivation layers. The success of these approaches in reducing the deficit in performance with respect to thermodynamic limits points towards requirement of detailed analysis on the band alignment of perovskite/TL interfaces to realize the full potential of the device. Here we use 1-dimensional simulation of a perovskite solar cell with structure TiO$_2$/CH$_3$NH$_3$Pb(I$_{3-x}$Br$_x$)/Spiro-OMeTAD to observe the limiting factors of solar cell performance at wider bandgaps. We show that changing the bandgap of the absorber changes the band alignment at the absorber/TL interfaces, which results in increased band bending and recombination. By investigating the band positions of CH$_3$NH$_3$Pb(I$_{3-x}$Br$_x$) for intermediate values of $x$, we consistently find the optimal valence band offset to be +0.05 eV between the absorber and HTL and find differing optimal conduction band offsets for different absorber bandgaps. Most notably, the optimal CBO between the ETL and a 1.7 eV bandgap perovskite absorber is found to be -0.05 eV. A TiO$_2$ ETL and a Spiro-OMeTAD HTL form a -0.4 eV CBO and a -0.3 eV VBO, respectively, with the same absorber, significant deviations from their optimal alignments. We show that the downward trends in $V_{oc}$ and PCE for widening bandgaps can be greatly improved through optimizing band alignment of the charge transport layers alone, leading to the recommendation of alternative transport layers that better suit wider-bandgap absorbers.

5:30 AM S.EN01.11.05
Rapid and Scalable Monolithic Integration of Single-Source Laser Scribes in Perovskite Modules with Adaptive Architecture Austin Flick, Nicholas Rolston, William J. Scheideler and Reinhold H. Dauskardt; Stanford University, United States

Small area (~0.1cm$^2$) hybrid organolead-halide perovskite solar cells have made tremendous improvements in performance in recent years, approaching the efficiencies of single crystalline silicon cells. While scalable methods such as slot-die coating
and spray coating offer the possibility of high quality large-area perovskite deposition, resistive losses across the transparent front electrode highlight the need for series interconnected module designs. Our group has developed laser scribing mechanisms for the ablation of the electrodes and active material utilizing a single wavelength (1064nm) high-frequency pulsed laser at ultrafast processing speeds (>20cm/s). This process coupled with improved module design that allows for the study of individual cell performance along with that of the complete module enables high throughput for both perovskite module development and characterization.

Our work first introduces the primary ablation mechanisms of our single-wavelength laser: direct ablation and lift-off. We demonstrate the unique characteristics of these scribing methods as they interact with the front electrode and highlight the unique capability of our single-wavelength laser system to perform each scribe step: patternning the front electrode (P1) with direction ablation, scribing the series interconnection (P2) with the lift-off mechanism, and patternning the back electrode (P3) with the lift-off mechanism. The unique lift-off characteristics for the P2 scribe result in improved efficiencies via increased short-circuit current and fill factor compared to modules utilizing direct ablation mechanisms from other laser sources. The use of a single laser system for each scribe step also allows for high repeatability and accuracy, enabling a reduction in dead area to <600µm. We address performance losses due to the requisite dead area in conjunction with the resistive losses from the series interconnections and front electrode in order to motivate a module design with optimized cell and scribe geometries. The module design incorporates an adaptive architecture that enables complete characterization of both the entire module and its constituent cells. While laser-beam induced current (LBIC) measurements are valuable in evaluating the geometries, the module design incorporates an adaptive architecture that enables complete characterization of both the entire module and its constituent cells. While laser-beam induced current (LBIC) measurements are valuable in evaluating the perovskite uniformity, particularly for large-area scalable deposition methods, previous module architectures force most of the module into reverse bias throughout the scan, resulting in inaccurate current outputs and the need to scan each cell individually. Our adaptive architecture allows for the complete characterization of large-area modules with a single LBIC scan, enabling high throughput single device and complete module characterization.

5:40 AM *S.EN01.11.06
Cd-Less/Free Buffer Materials for >10% Efficiency Pure Sulphide CZTS Solar Cells Xiaojing Hao; Univ of New South Wales, Australia

The uptake in expected future markets at TW-scale of photovoltaics demands stable, abundant, non-toxic materials. In addition to traditional silicon wafer-based solar cells, thin film offers a much wider flexibility in aesthetic designing, choice of substrates and module sizes, as well as unlocking new applications through the use of flexible and light-weight substrates. These regards, Cu2ZnSnS4 (CZTS) solar cell has been regarded as a compelling alternative of the emerging photovoltaic materials. So far the certified highest power conversion efficiency of 11 % has been demonstrated for CZTS, where a layer of traditional CdS buffer material was applied. Considering the high toxicity issue of CdS, efforts have been put on partially or even fully removing the use of toxic Cd containing buffer materials. In this talk, our work on the Cd-less and Cd-free buffer based CZTS solar cells will be discussed. With SILAR-ZnCd1-xS, we demonstrated >10% efficiency CZTS solar cells by finely tuning the chemistry process of ZnCdS and CZTS absorber composition, where the self-organised nanoscale Zn(O)S at the initial growth process of ZnCd1-xS was found playing a key role in the heterojunction interface passivation and band alignment. For ALD-Cd-free Zn1-xSn1-xO buffer, we achieved >10% efficiency CZTS solar cells, which is also the first >10% efficiency fully environmentally-friendly kesterite solar cells and realised by adjusting the ratio of Zn and Sn for an optimised conduction band alignment with CZTS, and inserting ALD-Aluminum oxide (Al2O3) for heterojunction interface passivation. Our buffer materials engineering work showed that in addition to the heterojunction band alignment, combined effects from the composition of CZTS absorber (cation ratios of Cu/Zn/Sn), buffer synthesis process-induced sodium redistribution and surface modification of absorber, as well as heterojunction interface passivation play major roles in determining the final device performance.

5:55 AM S.EN01.11.07
Scalable Fabrication of Perovskites Solar Cell Using Two-Step Doctor-Blade Technique Zahrah S. Almutawah1, Ramez Hosseinian Ahangharnejhad1, Tamanna Mariam1, Kamala Khanal Subedi1, Adam Phillips1, Randy J. Ellingson1 and Michael Heben1; 1University of Toledo, United States; 2The University of Toledo, United States

Lead halide perovskites have attracted much interest as an emerging photovoltaic technology due to high device efficiency and low-cost preparation methods. The highest efficiency record of Perovskite Solar Cells is 23% for device area of <0.1 cm² fabricated by spin-coating. Currently, perovskite solar cells are transitioning from small area devices to large area devices that are compatible with manufacturing. Blade-coating is a promising deposition technique because it is low cost, environmentally friendly, and easily transferable to roll-to-roll processing. Many studies demonstrating high efficiency devices using this method have been performed; however, these studies use a single step to deposit perovskite, which is challenging to scale because of the required addition of an antisolvent during deposition. In our previous study we demonstrated a compact perovskite film with large grain sizes deposited with the two-step blade-coating method in air, and
we achieved solar cell with 15% efficiency for small area ~ 0.08 cm². The two-step deposition method is widely used as a route for fabricating high-quality small area perovskite films using spin-coating because of its full coverage and excellent reproducibility. However, this method has not been investigated for perovskites deposited using a scalable blade coating method. In this work we investigate the possibility of a fully scalable deposition scheme for fabricating n-i-p perovskite modules of perovskite film with the two-step process. PbI₂ layer were blade coated on substrates with a transparent conducting oxide and SnO₂ electron transport layer (ETL) deposited by atomic layer deposit (ALD). The films were converted to perovskite by blade coating with a MAI solution. Small area devices and minimodules will be completed and characterized. For minimodule fabrication, the bottom conducting electrode layer will be laser scribed to form isolated substrates for the individual sub-cells; a second scribe will remove the active material (ETL, perovskite and HTL) to allow for interconnections between the sub-cells; and in the final scribe will remove the top electrode to isolate the individual sub-cells and define the outer boundaries of the module. Encapsulation the completed devices and minimodules with an inert SiO₂ layer prepared by RF-sputtering will also be investigated as a method to increase the stability.
with new functionality. So far most of the work has focused on implementing passive optical components like lenses and polarizers, where the optical bandwidth of the implemented structures is limited. Several optoelectronic applications like image sensors, infrared camera, and solar cells require broadband properties, which cannot be provided by most optical metasurfaces. In this study, optical metasurfaces are used to improve the light incoupling and light trapping of perovskite solar cells. Herein, a pyramid shaped metal oxide film is prepared through metal organic chemical vapor deposition (MOCVD), which later converted into optical metasurfaces. Optical metasurfaces are consist of an array of sub wavelength zinc oxide nanowires, where the incident light is controlled by the optical metasurfaces. Templated growth electrodeposition technique is used to grow sub wavelength nanowires. As a first step, metasurfaces are utilized on top of the flat perovskite single junction solar cells, which allows enhancing the short-circuit current density by $>20\%$ as compared to flat solar cell. As a second step, metasurfaces are applied to the implementation of perovskite/perovskite tandem solar cell, where materials with optimum bandgap combinations are selected to realize high energy conversion efficiency. The proposed perovskite/perovskite tandem solar cell integrated with optical metasurfaces exhibits a matched short-circuit current density beyond 18 mA/cm$^2$ and an estimated energy conversion efficiency exceeding 30%. Finite-difference Time-Domain simulations are used to investigate the optics of perovskite single junction and perovskite/perovskite tandem solar cells. Detailed guidelines for the realization of optical metasurfaces and solar cell structure will be provided.

References

S.EN01.12.08
On the Potential of Metal Nickel-Oxide Films for Efficient Perovskite Solar Cells Mohammad I. Hossain$^1$, Md Wayesh Qarony$^1$, A K Mahmud Hasan$^2$, Md Shahiduzzaman$^3$, M A Islam$^4$, Nowshad Amin$^5$, Dietmar Knipp$^6$, M Akhtaruzzaman$^7$ and Yuen Hong Tsang$^8$; $^1$The Hong Kong Polytechnic University, Hong Kong; $^2$The National University of Malaysia, Malaysia; $^3$Kanazawa University, Japan; $^4$Universiti Tenaga Nasional, Malaysia; $^5$Stanford University, United States

An efficient hole transport material is crucial for realizing improved short-circuit current density and energy conversion efficiency of perovskite solar cells. In this study, Nickel-oxide (NiO$x$) thin-film was used as a potential hole transport layer for efficient perovskite solar cells. The NiO$x$ films were prepared by electron-beam physical vapor deposition (EBPVD) at low temperatures. Necessary material characterizations were carried out to ensure high quality films and spectroscopic ellipsometry measurements allowed to determine the complex refractive indices of deposited films. Optics and optimization of perovskite solar cells were investigated by three-dimensional finite-difference time-domain simulations, where complex refractive indices were used as the input parameters. Optical simulations provided a very good agreement with the experiments in terms of quantum efficiencies and short-circuit current densities of planar perovskite solar cells. Hence, an optimized device design has been proposed, which can enhance short-circuit current density and energy conversion efficiency by 20$\%$ and over 25$\%$, respectively in comparison to the planar perovskite solar cell. Such enhancement is due to improved light incoupling and light trapping, which allows realizing the estimated energy conversion efficiency beyond 22$\%$. The optimized device design is further applied to the implementation of perovskite-based tandem solar cells reaching energy conversion efficiency over 30$\%$. A detailed discussion of the proposed device structure will be provided to attain effective photon management.

S.EN01.12.09
Spray-Pyrolysis Deposition of TiO2 for Efficient Planar Perovskite Solar Cells Md Shahiduzzaman$^1$, Mohammad I. Hossain$^2$, Md Wayesh Qarony$^3$, M Akhtaruzzaman$^4$, Koji Tomita$^5$, Yuen Hong Tsang$^6$ and Tetsuya Taima$^7$; $^1$Kanazawa Institute of Technology, Japan; $^2$The Hong Kong Polytechnic University, Hong Kong; $^3$The National University of Malaysia, Malaysia; $^4$Tokai University, Japan

A pin-hole free and uniformly distributed compact hole-blocking/electron-transport layer (ETL) is an essential requirement for reaching high power conversion efficiency (PCE) of planar perovskite solar cells (PSCs). In addition, the preparation of a hole-blocking layer has to be simple so that it reduces production costs and enables future commercialization of PSCs. Herein, high-performance planar PSCs were fabricated by employing spray pyrolysis deposition of TiO$_2$ compact ETL, where necessary material characterizations ensure obtaining high-quality films. The influence of TiO$_2$ layer thickness on the photovoltaic performance of the resulting devices was investigated by varying the precursor solution concentration from 0.15 M to 0.40 M. The photovoltaic performance is maximized for the 0.35 M TiO$_2$ precursor solution concentration, which allows realizing a PCE of 16.55$\%$ with short-circuit current density ($J_{sc}$) of 21.3 mA/cm$^2$, open-circuit voltage ($V_{oc}$) of 1.08
V, and fill factor (FF) of 72% from the champion device. Furthermore, three-dimensional (3D) finite-difference time-domain (FDTD) simulations were performed to investigate the mechanism of device operation from the optical point of view. Optical simulations were precisely used to model, design, and optimize the perovskite solar cells, where results from simulations provided a good agreement with experimental results which further reveal the correlation of the spray pyrolysis deposited TiO2 thickness on the photovoltaic performance of PSCs. A detailed discussion of the proposed efficient planar PSC will be provided.

References

S.EN01.12.11
Optical Analysis of All-Perovskite Planar Tandem Solar Cells Ahmed Mortuza Saleque1, Mohammad I. Hossain1, Ahmed Safayet1, Ilhom Saidjafarzoda2, Necmi Biyikli2, Md Wayesh Qarony1 and Yuen Hong Tsang1; 1The Hong Kong Polytechnic University, Hong Kong; 2University of Connecticut, United States

Perovskite material systems have recently attracted substantial research attention as solar energy materials owing to their excellent inherent optoelectronic properties, while the manufacturing costs are assumed to be very low. In the past decade, the energy conversion efficiency of perovskite single-junction solar cell has reached over 24%. According to the detailed balance theory, the energy conversion efficiency of tandem solar cell can go beyond 45% if the optimum bandgap materials are selected. The energy conversion efficiency of perovskite/silicon tandem solar cells has already reached to 28%, however, details of fabrication methods and device structures are not yet available. In this study, all-perovskite planar tandem solar cells are investigated, where a wide bandgap (1.72 eV) perovskite is used as a top cell absorber and a low bandgap (1.16 eV) perovskite for the bottom cell. An optimized device design is investigated to realize a high efficiency planar all-perovskite tandem solar cell, where materials used for the contacts have a comparable refractive index to the perovskite absorbers. Herein, atomic layer deposited experimentally realized metal oxide is used to prepare the contacts. Three-dimensional finite-difference time-domain optical simulations are utilized to investigate the optics and optimize individual layers in the solar cell structure. The proposed planar all-perovskite tandem solar cell exhibits a short-circuit current density of 17.6 mA/cm2 at matched condition, which allows estimating the energy conversion efficiency exceeding 29%. It is assumed that the proposed planar highly efficient all-perovskite tandem solar cell can be fabricated by solution-processed method at low cost. A detailed guideline on how to determine the solar cell design will be discussed.

S.EN01.12.15
From Fully Self-Consistent Electro-Optical Simulations to New Resonant Photovoltaic Devices Pyry Kivisaari, Toufik Sadi and Jani Oksanen; Aalto University, Finland

Thin-film photovoltaic devices are emerging as a serious alternative to conventional silicon solar cells. Thin films enable for example utilizing resonant modes to decrease the amount of material required for the device, and to design the solar cell for special operational circumstances. On the other hand, thin films could enable designing solar cells from unconventional earth-abundant materials, many of which have favorable light absorption properties but insatisfactory electrical conductivity. However, to enable studying the prospects of new thin-film photovoltaic devices in detail, it would be extremely beneficial to have a modeling tool that enables studying their optical and electrical properties fully self-consistently. To this end, we have recently developed an interference radiative transfer-drift-diffusion (IRTDD) model for arbitrary thin-film device structures. The IRTDD model is especially well suited to study photon recycling and luminescent coupling in direct connection with electron-hole distributions affected by both illumination and bias voltage. It constructs a fully self-consistent solution between the fluctuational electrodynamics framework of photon dynamics and the drift-diffusion formalism of charge carrier dynamics. Therefore it also directly includes interference effects, such as Fabry-Perot resonances and emission enhancement. In this work, we use the IRTDD model to reproduce the device characteristics of selected single- and multi-junction thin-film solar cells and connect them with the underlying local photon transport and generation-recombination processes that are obtained as a direct result of solving the combined equation system. We focus on photon recycling and luminescent coupling and how they affect the overall device characteristics of different thin-film structures under illumination and in dark current conditions. We also investigate possible ways to incorporate diffractive elements into the model, such as gratings on the device surface.

S.EN01.12.19
Titanium Disulfide (TiS$_2$) Dichalcogenide Thin Films as Inorganic Hole Transport Layer for Perovskite Solar Cells Synthesized from Ionic Liquid Electrodeposition Omar Asif, Farshad Azadian and Alok C. Rastogi; Binghamton University, The State University of New York, United States

The high efficiency organic-inorganic perovskite solar cells are generally fabricated as a multilayer structure in which the perovskite absorber layer is sandwiched between an electron transport and a hole transport thin film creating an interface on either side. So far different hole transport materials have been investigated of which the organic hole transport layers have delivered the highest efficiencies. However, these organic hole transport layers based on octakis(4-methoxyphenyl)-9,9'-spirob[9H-fluorene]-2,2',7,7'-tetramine (Spiro-OMeTAD) and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA) have displayed poor long term stability. Furthermore, their preparation involve expensive purification processes that hinders universal low-cost commercialization of perovskite solar cells. The alternative low-cost inorganic hole transport materials such as transition metal chalcogenides have been employed recently using the hot-injection method exhibiting superior device stability and high carrier mobility. However, hot-injection method has poor synthesis reproducibility and difficulty in scaling-up for large-scale production.

In this work we performed an ab initio study of facile inexpensive scalable syntheses of transition metal dichalcogenide (TiS$_2$) by electrodeposition from ionic liquids as a low-cost inorganic hole layer for perovskite solar cells. The TiS$_2$ thin films were electrodeposited from choline chloride–urea eutectic based ionic liquid electrolytes at 80°C with Na$_2$S$_2$O$_3$ as sulfur source. From the detailed cyclic voltametry studies, the deposition potential of TiS$_2$ was optimized at -0.79 V vs Pt. The as-deposited TiS$_2$ hole transport layer exhibited polycrystalline structure with preferential growth along (001), (100), (002), (102), (110), (111) planes. The Raman spectroscopy investigations of these films showed peaks around 225 cm$^{-1}$ and 330 cm$^{-1}$ which are attribute to the $E_g$ and $A_{1g}$ Raman modes respectively. The synthesized thin films demonstrated sharp optical bandgap edge along with bandgap tunability as the bandgap (direct) decreased from 1.53eV to 1.49eV, 1.40eV, and 1.34 eV with gradual change in deposition potential from -0.79V to -0.9V, -1.0V, and -1.1V vs Pt respectively. This aspect may have potential for alignment of valance band edge in facilitating the hole transport at the perovskite-TiS$_2$ interface. The absorption coefficient of the as-deposited TiS$_2$ thin films likewise shown a dependence of synthesis potential for visible-light range which is highly conducive for application as a hole transport layer in multilayer solar cell structure. The TiS$_2$ thin films were observed to be p-type as shown from the Hall Effect studies with a carrier mobility up to 14.4 cm$^2$V$^{-1}$s$^{-1}$. This paper will present a detailed study of the effect of the synthesis parameters on the optical and band-edge and its analysis for application as hole transport layer in perovskite solar cells.

S.EN01.12.20
Hole Transport Layer Free Carbon-Based Perovskite Solar Cells with SnO$_2$: Quantum Dots as Electron Transport Layer Vijayaraghavan Sankaranarayanan Nair, Jacob Wall and Feng Yan; University of Alabama, United States

Hybrid perovskite solar cells (PSCs) represent the hottest research topics due to its meteoric rise in its power conversion efficiency (PCE) to 25.2% since the first cell was fabricated in 2009 with PCE of ~ 3%. However, there is still a huge block in the form of stability and cost that hinders its path towards commercialization. The majority of the high-performance PSCs employ organic hole-transporting materials (HTMs) and precious metal as back contact (e.g. Au), which are expensive and operationally unstable. Through our work, we plan to tackle the stability and cost issues by employing cost-effective carbon as both the hole transport layer and back contact, thereby completely avoiding the organic hole HTMs. Carbon is a good replacement for the most commonly used precious metals such as gold and silver as a counter electrode as its work function (5.0 eV) is close to that of gold (5.1 eV). Our technique has the added advantage that it is suitable for the low-cost printing technology (e.g., roll-to-roll) as the material synthesis is done at low temperatures (<200 °C) and hence it gives rise to the possibility of fabricating flexible solar cell products. In this work, with SnO$_2$ quantum dots as an electron transport layer (ETL), and carbon as the counter electrode, we fabricated stable HTM-free planar heterojunction PSCs with the structure ITO/SnO$_2$/Cs$_{0.05}$FA$_{0.81}$MA$_{0.14}$PbI$_{2.55}$Br$_{0.45}$/Carbon. Our champion cell had an area of 0.08 cm$^2$ and recorded a PCE of 12.12% with an open-circuit voltage (V$\text{OC}$) of 1.07 V and a short-circuit current density (J$\text{SC}$) of 20.5 mA/cm$^2$. This low-cost and highly efficient HTL-free and carbon-based perovskite technology pave pathways to achieve affordable and stable perovskite thin-film solar cells.

S.EN01.12.23
Understanding the Effects of Moisture on Perovskite Solar Cells by Synchrotron-Based Characterization Tools Juanita Hidalgo$^{1,2}$, Nga Phung$^2$, Andres Felipe Castro Mendez$^2$, Dennis Jones$^1$, Barry Lai$^3$, Antonio Abate$^2$ and Juan Pablo Correa Baena$^2$; $^1$Georgia Institute of Technology, United States; $^2$Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; $^3$Argonne National Laboratory, United States

2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
Lead halide perovskite solar cell efficiencies have risen dramatically, reaching a certified 25.2%, promising as low-cost solar energy alternatives. However, perovskites are highly sensitive to temperature, moisture, oxygen, and UV light, presenting an obstacle to commercialization. Therefore, it is crucial to unravel the degradation mechanisms and the ways perovskites interact with water molecules. In the path to understand how water molecules are interacting with the material, a humid treatment was performed to perovskite solar cells with different precursor stoichiometries for hybrid organic-inorganic materials. By exposing the films for 48 hours in a high relative humidity environment, improvement in efficiency for the organic excess perovskite solar cells (highly efficient) was shown. Characterization was done from the material, to the device’s performance and using synchrotron advance X-ray methods to deepen in the properties of the perovskite. Synchrotron X-ray Fluorescence was realized in parallel to X-ray Beam Induced Current technique to exhibit a correlation between the elemental mapping and electrical behavior of the devices, in which heterogeneity upon moisture was observed.

S.EN01.12.27
Improved Efficiency and Stability of Inverted Planar Perovskite Solar Cell Devices by the Incorporation of an Additional Inorganic Hole Transport Layer Banashree Gogoi, Aditya S. Yerramilli, Yuanqing Chen and Terry Alford; Arizona State University, United States

The use of poly (3,4-ethylenedioxythiophene): poly(styrene sulfonate) sulfonic acid (PEDOT: PSS) as the hole transport layer (HTL) has been commonly reported in the field of perovskite solar cells during recent years. However, these devices suffer from stability issues due to the acidic and hygroscopic characteristics of PEDOT: PSS; therefore, rendering it as an inefficient option for large scale fabrication and commercialization. In this work, we have incorporated an additional layer of CuI along with PEDOT: PSS for efficient hole transport and stability. We have investigated different concentrations of CuI in acetonitrile and prepared devices with the inverted planar architecture of ITO/CuI/PEDOT: PSS/Perovskite/PCBM/Al. From our investigation, we found that 10mg/ml of CuI is the optimum concentration for better device performance as it showed an increase in efficiency by 28% and current density by 31% when compared to the devices with only PEDOT: PSS as the hole transport layer. In addition, the CuI devices also showed better stability under controlled atmospheres.

S.EN01.12.31
Synergistic Effect of Cooperating Solvent Vapor Annealing for High-Efficiency Planar Inverted Perovskite Solar Cells Ahra Yi1, Sangmin Chae2, Hanbin Lee1 and Hyo Jung Kim1; 1Pusan National University, Korea (the Republic of); 2University of California, Santa Barbara, United States

Solvent vapor annealing (SVA) is an effective post-treatment process to improve the quality of crystals and grains in metal halide perovskite films. Whereas SVA has been successfully adopted for the fabrication of perovskite films via the conventional two-step method, its adaptation to the simple single-step perovskite film deposition method has been limited because of the rapid transition of the precursor to the perovskite structure. In the present study, we demonstrate highly efficient and stable single-step-based inverted perovskite solar cells fabricated with perovskite films prepared using dimethyl sulfoxide (DMSO) and water as a combined solvent in an SVA treatment. The treatment with DMSO alone resulted in the growth of large grains (~900 nm) in the lateral direction at the surface region; however, voids and defects were observed in the vertical direction at the bottom interfacial region of the CH3NH3PbI3 layer, which resulted in poor device properties. Interestingly, the combined DMSO–water induced vertical growth of almost single grains and the healing effect of water improved the grain quality. As a result, we fabricated co-SVA CH3NH3PbI3 devices with a power conversion efficiency (PCE) of 19.52%. This PCE, which is much higher than that of pristine devices, was attributed to reduced nonradiative recombination. In addition, co-SVA solar cells displayed remarkable stability and their universality in various types of perovskite materials was demonstrated. We anticipate that our proposed process and mechanism will be widely used in the future development of perovskite-based devices.

S.EN01.12.34
Fabrication of a Coupled Lead Free Perovskite Oxide and Halide Layered Device—Towards Applications in Wearable Flexible Health Monitoring Devices Mandeep Singh1, Kristina Diaz1, Mark Kovalenko1, Baltripat Singh1, Saquib Ahmed2, Soumyasanta Laha1 and Sankha Banerjee1; 1California State University, Fresno, United States; 2Buffalo State College, United States

Lead Perovskite oxide and halide based devices are especially promising when their applications in biomedical wearables. The advantages of using a perovskite oxide and halide layer for a coupled active layer include but are not limited to broad a light absorption spectrum, tunable band gaps, long charge carrier diffusion, enhanced electron mobility and low fabrication cost. The current work involves the design, fabrication, and simulation of a layered BaTiO3-PMMA-Graphene perovskite oxide and a Tin iodide coupled active layer structure for application as signal transducers and amplifiers in led based
wearable and flexible biomedical health monitoring devices. The goal of the project is to develop a configuration that is non-toxic as well as stable in natural open air environments with a specific resistance to moisture. This design incorporates the use of organic and inorganic materials, as well as the efficient use of the perovskite crystalline structure that is produced by using the properties of the active layer. Different economical hole transport layers has also been explored to evaluate the impacts on opto-electronics, photon-to-current conversion efficiencies, variation in electron mobility and interfacial properties such as contact resistance and surface energy. The stacking structure is further modulated within the cell by progressively including a recombination-inhibiting thin BaTiO3-PMMA-Graphene layer with the FTO, followed by an electron-transport layer (various oxides) and a combination of CuO/Cu as the hole transport layer and back contact electrode. This work is intended to build up to a broader project of selecting the most optimal low-toxicity perovskite coupled layer for biomedical devices.

Vapor Processes for Perovskite Thin-Films Formation and Recrystallization

Isidora Susic, Michele Sessolo, Francisco Palazon and Henk J. Bolink; Instituto de Ciencia Molecular- Universidad de Valencia, Spain

Metal halide perovskites are a class of novel semiconductors, with tuneable band gap, high absorption coefficients, large charge diffusion length, and for these reasons are widely studied as absorbers in photovoltaics devices. One of the biggest challenge to achieve high-performing perovskite solar cells is the control over the perovskite film morphology. High crystallinity, low defect density, together with the formation of uniform films are important requirements in order to ensure efficient charge collection and minimize non-radiative recombination. The control over crystallization by solution techniques is challenging, due to the several parameters concurring in the film formation. For this reason, we explored solvent-free routes for the formation and post-treatment/recrystallization of perovskite thin films. Methylammonium lead iodide (MAPI) films were obtained by conversion of vacuum-deposited PbI2 films with vapours of methylammonium iodide in a vacuum oven. With this technique, we deposited MAPI films, which are typically homogeneous and flat, composed by fine (< 100 nm) grains. Furthermore, we introduce the methylamine gas post-treatment to tune the film morphology of the sequentially deposited perovskite films. Upon controlled exposure to methylamine, the perovskite film is partially recrystallized, obtaining films with different and enhanced crystallinity. In particular, by tuning the temperature and gas concentration, we are able to substantially increase the average grain size. We will present extensive morphological and structural characterization, as well as the latest advances in solar cells obtained with solvent-free, vapour treated perovskite thin films.

SYMPOSIUM S.EN02

Caloric Materials for Sustainable Cooling Applications
November 21 - December 1, 2020

Symposium Organizers
Franca Albertini, Consiglio Nazionale delle Ricerche IMEM-CNR
Gian Guzman-Verri, University of Costa Rica
Manfred Kohl, Karlsruhe Institute of Technology
Qiming Zhang, The Pennsylvania State University

* Invited Paper

SESSION S.EN02.06: Live Lightning/Flash I: Electrocaloric and Elastocaloric
Session Chairs: Manfred Kohl and Qiming Zhang
Monday Morning, November 30, 2020
S.EN02

8:00 AM S.EN02.01.01
Giant Temperature Span in Electrocaloric Heat Exchangers Alvar Torello Massana$^{1,2}$, Youri Nouchokgwe$^{1,2}$, Pierre Lheritier$^1$, Tomoyasu Usui$^1$, Sakyo Hirose$^3$ and Emmanuel Defay$^1$; $^1$Luxembourg Institute of Science and Technology, Luxembourg; $^2$University of Luxembourg, Luxembourg; $^3$Murata Manufacturing Co., Ltd., Japan

Cooling devices based on caloric materials have emerged as promising candidates to become the next generation of coolers. In recent years, several Electrocaloric (EC) heat exchangers have been proposed [1-5], covering different kinds of mechanisms and working principles. However, little has been told about the numerical modelling of these devices and their potential impact on improving the experimental performance. In this work, the authors highlight and prove how finite elements method could exploit and optimize EC heat exchangers. The simulations presented consisted of 2D-representations of a lead scandium tantalate multilayers capacitors (PST MLC) 22mm x 10.4mm x 1mm parallel-plates based active regenerator being developed at LIST and are used to explore new prototype’s configurations. Interestingly, results showed that by simplifying the complexity of the design and modifying the length and thickness of the parallel plates, the temperature span of the device could increase already from 1 to 9 degrees. By guidance of this outcome, the proposed new prototype’s configurations were tested in the laboratory. The maximum experimental temperature difference measured was of 9.45 degrees, which is several factors larger than the value obtained before the investigation of the numerical modelling. Furthermore, new modifications will be tested in the following months. According to our predictions, we expect to improve our actual maximum value even further.

8:09 AM.

8:10 AM S.EN02.01.03
Direct Measurements of Electrocaloric Materials Efficiency Emmanuel Defay$^1$, Youri Nouchokgwe$^1$, Alvar Torello$^1$, Pierre Lheritier$^1$, Wook Jo$^2$ and Sakyo Hirose$^3$; $^1$Luxembourg Institute of Science and Technology, Luxembourg; $^2$School of Materials Science and Engineering, Korea (the Republic of); $^3$Murata Manufacturing Co. Ltd., Japan

Electrocaloric (EC) materials exhibit adiabatic temperature change or isothermal entropy when triggered with electric field. Their dimensionless materials efficiency, called EC materials efficiency, is the ratio between the heat generated and the electrical work needed to trigger the EC effect. By direct measurements of heat using infra-red (IR) camera, Differential Scanning Calorimetry (DSC), and electrical work we report quantitative results of the efficiency of Lead Scandium Tantalum (PST). These measurements are done on two different PST samples: thick bulk ceramic and thick multi-layer capacitors (MLCs). In both cases, we observed an adiabatic temperature change $\Delta T_{ad}$ of 2.4 K at room temperature. For this $\Delta T_{ad}$, we report an efficiency of 35 and 85 respectively for MLCs and bulk. We present a comparative study on energy efficiency of different caloric materials, worked out indirectly in previous articles [1-2]. We reveal a maximum efficiency of 101 for PST (EC). Our study gives insights into the efficiency of EC materials and shows that PST is an excellent candidate for future efficient EC cooling devices.


8:19 AM.

8:20 AM *S.EN02.01.14
The Development of Electrocaloric Multilayer Capacitors Sakyo Hirose$^1$, Tomoyasu Usui$^1$, Bhavi Nair$^2$, Gian G. Guzman-Verrir$^{3,3}$, Xavier Moya$^2$ and Neil D. Mathur$^2$; $^1$Murata Manufacturing Co., Ltd., Japan; $^2$University of Cambridge, United Kingdom; $^3$Universidad de Costa Rica, Costa Rica

Since the discovery of giant electrocaloric (EC) effects [1-2], much effort has been made to explore new EC materials and develop prototypes EC cooling systems with high energy efficiency. However, the development of EC cooling systems has been one step behind magnetocaloric (MC) and elastocaloric (eC) cooling systems because few EC materials show comparable temperature change with MC materials. Moreover, EC working bodies with a large enough active volume and high breakdown strength have not been available.

Given this background, we have focused on developing EC multilayer capacitors (MLCs) based on various ferroelectric materials. MLCs are considered to be the ideal working bodies because a large electric field can be applied to thin EC layers without arcing, the active volume can be increased by laminating many thin EC layers, and existing MLC technologies are sufficient for mass production. The numerous internal electrodes permit EC effects to be driven by much larger electric fields than bulk ceramics, provided that the MLCs are of high quality.

Here we report EC effects driven by large electric fields in MLCs based on $\text{BaTiO}_3$ (BTO), $(1-x)\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$-
PbTiO$_3$ (PMN-PT), (Pb,Ba)ZrO$_3$ (PBZ), (Pb,La)(Zr,Ti)O$_3$, and Pb(Sc,Ta)O$_3$ (PST) [3]. In 19-layer MLCs with layer thicknesses of 36-40 μm, fields exceeding 15 V μm$^{-1}$ yield adiabatic temperature changes of 2.7 K for 0.9PMN-0.1PT at 380 K [4], 3.8 K for PBZ at 430 K, and 5.1 K for PST at 300 K [5]. For MLCs of PST, process optimization and reduced EC layer thickness (18 μm) increases the breakdown strength to over 45 V μm$^{-1}$, which exceeds the 29 V μm$^{-1}$ that could be applied to MLCs of PST with thicker EC layers (38 μm) [5]. Our high quality MLCs should aid the development of prototype EC cooling systems that will be competitive with respect to their MC and eC counterparts.

References

8:29 AM.

8:30 AM *S.EN02.01.05
Solar Thermal Source for Passive Water Desalination and Cooling Driven by Capillarity and Salinity Gradients Matteo Morciano$^{1}$, Matteo Alberghini$^{1}$, Matteo Fasano$^{1}$, Eliodoro Chiavazzo$^{1}$ and Pietro Asinari$^{1,2}$; $^{1}$Politecnico di Torino, Italy; $^{2}$Istituto Nazionale di Ricerca Metrologica, Italy

Nowadays energy-intensive and expensive processes are mainly used to desalinate contaminated water and supply cooling capacity. Developing more sustainable, robust and cost-effective technologies (e.g. powered by renewable energy or waste heat) for generating clean water and cooling effect is a crucial need. This necessity is particularly important and severe in rural countries due to the lack of infrastructure and investments.

The abundant solar thermal source, which is now mainly employed to provide domestic hot water, could have a significant impact in achieving such targets, thanks to a wider engineering exploitation of innovative materials and technologies. [1,2,3] In this respect, passive distillation and cooling technologies – where all processes occur without mechanical moving parts – can make an important contribution. Unfortunately, state-of-the-art passive devices operating under one sun (that is, below 1 kW m$^{-2}$) still require efficiency enhancement, durability increase, and cost reduction to scale from lab to fab. [4,5,6] The passive technologies for solar water desalination and cooling developed at the Multi-Scale Modeling Laboratory of Politecnico di Torino (www.polito.it/small) are presented.

First, a fully passive, multistage and low-cost solar thermal device able to produce freshwater from seawater is conceived, prototyped and tested under both laboratory and outdoor conditions. The device does not require any mechanical moving parts by exploiting the capillarity of hydrophilic materials. Under realistic conditions, a distillate flow rate of almost 3 L m$^{-2}$ h$^{-1}$ from seawater at less than one sun is demonstrated. Theoretical models, under the same conditions, also suggested that the concept has the potential to further doubling the observed distillate rate, namely up to 6 L m$^{-2}$ h$^{-1}$. [7] Long-term operations of the passive distiller are then improved by optimizing the structure of evaporators towards enhanced salt-rejecting performance. [8] Finally, the passive distiller is optimized to recovery the low-temperature heat, to co-generate electricity and distilled water at the same time. [9]

Second, a passive device exploiting similar phenomena as i) capillarity of hydrophilic materials and the ii) salinity difference between multiple evaporators and condensers is experimentally demonstrated to provide cooling capacity up to 100 W m$^{-2}$. [10] The implemented prototype works at ambient pressure, employs environmentally friendly water solutions, and consists of several identical stages where the cooling effect comes from a cascade of evaporation-condensation processes driven by vapor pressure gradient. The experimentally validated model predicts that cooling capacities above 200 W m$^{-2}$ could be possibly achieved with a proper design optimization of the current lab-scale prototype.

F. Signorato, M. Morciano, L. Bergamasco, M. Fasano, P. Asinari. submitted
Ni, G., Zandavi, S.H., Javid, S.M., Boriskina, S.V., Cooper, T.A. and Chen, G., Energy & Environmental Science, Vol. 11,
8:40 AM *S.EN02.03.01
Latest Development in Compression-Based Elastocaloric Cooling Materials and Systems Ichiro Takeuchi; University of Maryland, United States

In this talk, we will discuss our latest work on development of elastocaloric materials as well as cooling prototype systems. We have used additive manufacturing to engineer NiTi-based composites with extremely small hysteresis in stress-strain curves. Additive manufacturing allows flexible design topology of metallic refrigerants which also act as heat exchangers. The small hysteresis results in substantially enhanced materials coefficient of performance as well as long fatigue life needed for applications. On the systems front, we have demonstrated active regeneration schemes for systems with cooling capacity up to 100s of watts using commercially available NiTi tubes. The largest temperature span we have achieved for a single stage compressive regenerators is 23 K. This work is carried out in collaboration with H. Hou, J. Cui, R. Ott, A. Stebner, D. Catalini, R. Radermacher, and Y. Hwang, N. Emaikwu, and S. Qian,

8:50 AM *S.EN02.01.09
Electrocaloric Effects in Relaxor Ferroelectrics from Atomistic Simulations Zhijun Jiang1,2,3, Sergei Prokhorenko2, Yousra Nahas2, Sergey Prosandeev2, Dawei Wang4, Jorge Iniguez5, Hongjun Xiang1,6 and Laurent Bellaiche2; 1Fudan University, China; 2University of Arkansas, United States; 3Ludong University, China; 4Xi'an Jiaotong University, China; 5Luxembourg Institute of Science and Technology, Luxembourg; 6Collaborative Innovation Center of Advanced Microstructures, China

The electrocaloric (EC) effect characterizes the change in temperature induced by a change in electric field [1], with the electrocaloric coefficient being defined as $\alpha = \frac{\partial T}{\partial E} |_{S}$, where T is the temperature, E is the electric field and S is the entropy. It is expected that the EC effect has the potential to be an efficient solid-state cooling devices for a broad range of applications [2,3]. Up to now, fewer investigations about EC effects have been performed in relaxor ferroelectrics [4-8]. Here we study EC effect in Ba(Zr0.5Ti0.5)O3 (BZT) and PbMg1/3Nb2/3O3 (PMN) relaxor ferroelectrics. We use the first-principles-based effective Hamiltonian approach combined with Monte Carlo that has been recently developed for BZT and PMN solid solutions [9,10] to investigate the EC effects.

In the lead-free BZT systems, we investigated the electrocaloric effects subject to electric fields of different magnitude and all oriented along the pseudo-cubic [001] direction. It is found that, for any temperature, $\alpha$ exhibits a non-monotonic behavior with field that consists of small values at low fields, followed by an increase up to a maximum before decreasing for larger fields. Below the Burns temperature, this maximum of $\alpha$ is demonstrated to be correlated to a very specific microscopic feature. Finally, equalities that are derived from a simple Landau model reproduce and further help to understand the anomalous behavior of $\alpha$ with field and temperature in BZT, for any temperature above $T_m$ where the dielectric response can exhibit a peak. Our simulations also confirm that indirect and direct approaches yield similar results of the $\alpha$ EC coefficient for any temperature above the $T_m$ temperature but differ from each other for temperature below $T_m$, because of the non-ergodicity adopted by BZT at these low temperatures.

We also employed the effective Hamiltonian of Ref. [10] to shed some light on electrocaloric effects in PMN. It is particularly striking that such Hamiltonian can qualitatively reproduce not only the peculiar electric field-versus-temperature phase diagram but also the optimization of the EC coefficient near the critical point in this rather complex system. The fact that the recently developed Landau-like model, predicting that the EC coefficient is simply related to the product of temperature and the field derivative of the square of the polarization [7], also describes well the EC behavior of PMN as a function of electric field and temperature is also promising for phenomenological modelization of complex inhomogeneous systems. We therefore hope that our studies [7,8] lead to a broader knowledge of EC effects in ferroelectrics.

This work is supported by the National Natural Science Foundation of China (Grants No. 11804138 and No. 11825403), Shandong Provincial Natural Science Foundation (Grant No. ZR2019QA008), China Postdoctoral Science Foundation (Grant No. 2018M641905), and Shanghai Super Postdoctoral Incentive Program. We also thank the DARPA Grant No. HR0011-15-2-0038 (MATRIX program) and ARO grant W911NF-16-1-0227.
References:

SESSION S.EN02.07: Live Lightning/Flash II: Barocaloric and Magnetocaloric
Session Chairs: Franca Albertini and Gian Guzman-Verri
Tuesday Afternoon, December 1, 2020
S.EN02

1:45 PM S.EN02.02.01
Barocaloric Effects in Fluorinated Polymers Jiyeob Kim¹, Pol Lloveras² and Xavier Moya¹; ¹University of Cambridge, United Kingdom; ²Universitat Politècnica de Catalunya, Spain

We present barocaloric studies of ferroelectric polymers of poly(vinylidene fluoride-trifluoroethylene) [PVDF-TrFE]. These copolymers are well known because of their giant electrocaloric response, but here we study pressure-driven thermal changes. PVDF-TrFE polymers undergo first-order phase transition with very large latent heats and volume changes, near room temperature. These three properties make them ideal materials for barocalorics.

1:55 PM *S.EN02.02.02
Practical Considerations for Barocaloric Cooling Enric Stern Taulats¹, Juan M. Bermúdez-García¹,², Guillaume F. Nataf¹ and Xavier Moya¹; ¹University of Cambridge, United Kingdom; ²University of A Coruna, Spain

Barocaloric materials are blossoming, with recent reports of thermal changes that compare to those observed in commercial refrigerant fluids [1-3]. The viability of future barocaloric chillers will rely on properties that go beyond the magnitude of the pressure-driven barocaloric effects. On the one hand, the challenge of effective transmission of hydrostatic pressure needs to be addressed in order to guarantee homogeneous stress distribution in the active material, and therefore optimal caloric performance. On the other hand, heat extraction needs to occur at rates that can match the practical cycling frequencies. Here, I will discuss key aspects of pressure transmission and heat transfer in barocaloric devices, and present a guide for barocaloric materials to match applications requirements.


2:05 PM *S.EN02.02.03
Colossal Reversible and Irreversible Barocaloric Effects in Plastic Crystals Araceli Aznar¹, Pol Lloveras¹, Maria Barrio¹, Philippe Negrier², Antoni Planes³, Lluis Mañosa³, Neil D. Mathur⁴, Xavier Moya¹ and Josep-Lluís Tamarit¹; ¹Universitat Politècnica de Catalunya, Spain; ²Université de Bordeaux, France; ³Universitat de Barcelona, Spain; ⁴University of Cambridge, United Kingdom
The massive use of vapor-compressor-based coolers poses a serious global environmental problem due to a relatively small efficiency and the use of hydrofluorocarbons with huge greenhouse potential [1]. These devices are based on controlling the exchange of latent heat involved in liquid-vapor transitions by means of hydrostatic pressure. Alternative technologies based on driving solid-state first-order phase transitions using magnetic, electric and uniaxial stress fields avoid the use of harmful fluids and promise higher efficiencies [2], but they are limited by a relatively small magnitude of the latent heat associated with such transitions compared to evaporation. Here we show that pressure-driven caloric (i.e. barocaloric) effects at phase transitions in some plastic crystals is comparable to that in hydrofluorocarbons due to the emergence of strong molecular orientational disorder [3,4]. We also discuss the reversible barocaloric response that is obtained upon cyclic application and removal of pressure as this is key for technological implementation. In particular, we characterize reversible effects in terms of magnitude, temperature spans, and minimum required pressure. We determine that, while some of the plastic crystals under analysis are unfeasible for applications due to irreversibility within a large pressure range, others demonstrate colossal barocaloric effects that are reversible at low pressures [3,4] and therefore show aptitudes that should promote the future development of environmentally-friendly solid-state barocaloric cooling devices.


2:15 PM *S.EN02.02.04

Giant Barocaloric Effect at the Spin Crossover Transition of a Molecular Crystal Steven P. Vallone1,2, Anthony N. Tantillo1,2, António dos Santos1, Jamie J. Molaison2, Rafal Kulmaczewski2, Antonin Chapoy3, Pezhman Ahmadi1, Malcolm A. Halcrow4 and Karl Sandeman1,2; 1Brooklyn College of CUNY, United States; 2CUNY, United States; 3Oak Ridge National Laboratory, United States; 4University of Leeds, United Kingdom; 5Heriot-Watt University, United Kingdom

Abstract body: Spin crossover occurs in compounds where the crystal field splitting of d-orbitals associated with a magnetic moment is of the order of $k_B T$. As a result, a change of state from low spin (LS) to high spin (HS) can occur at the so-called spin crossover temperature, $T_{SCO}$. Crucially for caloric applications, the change of state from LS to HS can be either continuous or first order, and it can occur at temperatures up to and beyond room temperature. This makes SCO transitions of interest for caloric cooling applications. Since SCO compounds are paramagnets or diamagnets, the largest caloric effects will be barocaloric rather than magnetocaloric.

In this presentation, we provide the first direct experimental demonstration of a giant, low pressure barocaloric effect (BCE) and outline future research directions for the development and optimization of the BCE associated with spin crossover.

2:35 PM *S.EN02.04.02

Thermal Control Elements for Caloric Technologies Andrej Kitanovski; University of Ljubljana, Slovenia

The refrigeration and air conditioning consumes about 17% of the overall electricity used worldwide, and will drastically increase in the next 30 years. The vast majority of these systems utilize vapour-compression technology, which is actually and unfortunately still associated with the existing refrigerants and their environmental impact. Since they contribute to the 7.8 % of global greenhouse gas emissions, large efforts are invested in finding appropriate future working substances. However, the options for new, environmentally friendly refrigerants are very limited. Another important step in decreasing the energy consumption is through the energy efficient refrigeration and air conditioning. The large scale vapour compression systems operate with their upper limit of about 60% of the second law efficiency. However they suffer by the low 20% efficiency especially in small appliances. The above issues represent the driver for the quest for energy efficient and environmentally friendly refrigeration and air-conditioning, which is pronounced more than ever. Among the available best alternatives to existing technologies is the caloric energy conversion. This is due to the potentially very high energy efficiency and use of environmentally friendly and safe solid-state working substances. Most of today’s caloric devices apply so-called active regeneration, which involves the oscillation of the working fluid through the matrix of the caloric material – the caloric regenerator. However, the unavoidable, irreversible viscous and heat-transfer losses apply limits to the caloric device’s performance as well as its size. The quest for better caloric-device performance has led to the development of thermal control elements, which control the heat flux on different size and time scales. Here we describe the working principles of these elements: thermal switches, thermal diodes and thermal regulators. This is followed by the critical review.
of the research activities and applications of thermal control elements in all types of caloric devices. It is shown that thermal control elements have the potential to substantially improve the power density of caloric devices. Finally, we present the target features and future research guidelines for these elements in the field of caloric technologies.

2:44 PM BREAK

2:45 PM *S.EN02.04.05
Prospects and Challenges—Additive Manufacturing of Magnetocaloric Regenerators Radhika Barua1, Dustin M. Clifford1, Ravil L. Hadimani1, Hong Zhao1, Surojit Gupta2, Matthew Kramer3 and Laura Lewis4; 1Virginia Commonwealth University, United States; 2University of North Dakota, United States; 3Ames Laboratory, United States; 4Northeastern University, United States

Cooling, manifested both as air conditioning and as refrigeration, is regarded as one of the most energy-intensive technologies in demand today. Magnetic refrigeration is an energy-efficient, sustainable, environmentally-friendly alternative to conventional vapor-compression cooling technology. There are a number of magnetic refrigerator device designs in existence today that are predicted to be highly energy efficient, on condition that the suitable working materials can be developed.1 This materials challenge has proven to be daunting due to issues associated with intricate synthesis/post-processing protocols and complications related to shaping the mostly brittle magnetocaloric alloys into thin-walled, channeled regenerator structures to facilitate efficient heat transfer between the solid refrigerant and the heat exchange fluid in an active magnetic regenerator (AMR) cooling device. To this end, research centered on fabrication of functionally-graded AlFe2B2 magnetic regenerators via sophisticated additive manufacturing (AM) methods will be presented in this talk. This ferromagnetic intermetallic boride has attracted considerable attention due to its low cost, promising thermal properties that promote effective heat transfer (specific heat capacity, \( C_p = 115 \) J/moleK; thermal conductivity, \( \kappa = 5.6 \) W/mK) and moderate room temperature magnetocaloric response (adiabatic temperature change, \( \Delta T_{ad} = 1 \) K and magnetic entropy change, \( \Delta S = 2.6 \) J/kgK at \( \mu_0 H_{app} = 2 \) T).2,3

In this work, powders of single phase AlFe2B2 were synthesized using multiple conventional routes: (i) drop-casting, followed by heat treatment at 1040 °C for 72 hours and then grinding to particulate form in air, (ii) reaction sintering at 900 °C for 24 hours, followed by etching in dilute HCl for 30 min and a (ii) molten salt-assisted solid state reaction at 600 °C for 36 hours. Experimental data indicate that irrespective of processing method, powders of dimensions ranging from 5 to 40 μm demonstrate comparable structural and magnetic properties (orthorhombic \( Cmmm \)-type crystal structure with unit cell volume, \( V = 92.6 \pm 0.4 \) Å; Curie temperature, \( T_c = 277 \pm 6 \) K) as well as similar magnetocaloric response (\( \Delta S = 2.6 \pm 0.3 \) J/kgK at \( \mu_0 H_{app} = 2 \) T). These precursor powders were used to 3D-print cylindrical AlFe2B2 samples using the established direct energy deposition AM method, laser enabled net shaping (LENS) and using an innovative magnetic-field assisted extrusion method whose prime novelty lies in the 3D ink formulation.4,5 Efforts to optimize the material and printing process parameters to maximize the magnetocaloric potential of AlFe2B2 will be discussed. Further, the feasibility of printing high-quality magnetocaloric device components with high surface area and complex porous architectures will be deliberated upon. Overall, this study provides strategies for realizing low-cost functionally graded magnetic regenerators, thus potentially eliminating one of the main barriers to commercialization of magnetic cooling technology.

SESSION S.EN02.01: Electrocaloric Materials and Systems
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN02

5:00 AM S.EN02.01.02
Giant Temperature Span in Electrocaloric Heat Exchangers

Alvar Torello Massana1,2, Youri Nouchokgwe1,2, Pierre Lheritier1, Tomoyasu Usui3, Sakyo Hirose1 and Emmanuel Defay1; 1Luxembourg Institute of Science and Technology, Luxembourg; 2University of Luxembourg, Luxembourg; 3Murata Manufacturing Co., Ltd., Japan

Cooling devices based on caloric materials have emerged as promising candidates to become the next generation of coolers. In recent years, several Electrocaloric (EC) heat exchangers have been proposed [1-5], covering different kinds of mechanisms and working principles. However, little has been told about the numerical modelling of these devices and their potential impact on improving the experimental performance. In this work, the authors highlight and prove how finite elements method could exploit and optimize EC heat exchangers. The simulations presented consisted of 2D-representations of a lead scandium tantalate multilayers capacitors (PST MLC) 22mm x 10.4mm x 1mm parallel-plates based active regenerator being developed at LIST and are used to explore new prototype’s configurations. Interestingly, results showed that by simplifying the complexity of the design and modifying the length and thickness of the parallel plates, the temperature span of the device could increase already from 1 to 9 degrees. By guidance of this outcome, the proposed new prototype’s configurations were tested in the laboratory. The maximum experimental temperature difference measured was of 9.45 degrees, which is several factors larger than the value obtained before the investigation of the numerical modelling. Furthermore, new modifications will be tested in the following months. According to our predictions, we expect to improve our actual maximum value even further.

5:10 AM S.EN02.01.03
Direct Measurements of Electrocaloric Materials Efficiency

Emmanuel Defay1, Youri Nouchokgwe1, Alvar Torello1, Pierre Lheritier1, Wook Jo2 and Sakyo Hirose3; 1Luxembourg Institute of Science and Technology, Luxembourg; 2School of Materials Science and Engineering, Korea (the Republic of); 3Murata Manufacturing Co. Ltd., Japan

Electrocaloric (EC) materials exhibit adiabatic temperature change or isothermal entropy when triggered with electric field. Their dimensionless materials efficiency, called EC materials efficiency, is the ratio between the heat generated and the electrical work needed to trigger the EC effect. By direct measurements of heat using infra-red (IR) camera, Differential Scanning Calorimetry (DSC), and electrical work we report quantitative results of the efficiency of Lead Scandium Tantalum (PST). These measurements are done on two different PST samples: thick bulk ceramic and thick multi-layer capacitors (MLCs). In both cases, we observed an adiabatic temperature change delta Tad of 2.4 K at room temperature. For this delta Tad, we report an efficiency of 35 and 85 respectively for MLCs and bulk. We present a comparative study on energy efficiency of different caloric materials, worked out indirectly in previous articles [1-2]. We reveal a maximum efficiency of 101 for PST (EC). Our study gives insights into the efficiency of EC materials and shows that PST is an excellent candidate for future efficient EC cooling devices.


5:20 AM S.EN02.01.04
The Development of Electrocaloric Multilayer Capacitors

Sakyo Hirose1, Tomoyasu Usui1, Bhasi Nair2, Gian G. Guzman-Verri3, Xavier Moya2 and Neil D. Mathur2; 1Murata Manufacturing Co., Ltd., Japan; 2University of Cambridge, United Kingdom; 3Universidad de Costa Rica, Costa Rica

Since the discovery of giant electrocaloric (EC) effects [1-2], much effort has been made to explore new EC materials and develop prototypes EC cooling systems with high energy efficiency. However, the development of EC cooling systems has been one step behind magnetocaloric (MC) and elastocaloric (eC) cooling systems because few EC materials show comparable temperature change with MC materials. Moreover, EC working bodies with a large enough active volume and high breakdown strength have not been available. Given this background, we have focused on developing EC multilayer capacitors (MLCs) based on various ferroelectric materials. MLCs are considered to be the ideal working bodies because a large electric field can be applied to thin EC layers without arcing, the active volume can be increased by laminating many thin EC layers, and existing MLC technologies are
sufficient for mass production. The numerous internal electrodes permit EC effects to be driven by much larger electric fields than bulk ceramics, provided that the MLCs are of high quality.

Here we report EC effects driven by large electric fields in MLCs based on BaTiO₃ (BTO), (1-x)Pb(Mg₀.₃₆Nb₂₀.₃₄)O₃-xPbTiO₃ (PMN-PT), (Pb,Ba)ZrO₃ (PBZ), (Pb,La)(Zr,Ti)O₃, and Pb(Sc,Ta)O₃ (PST) [3]. In 19-layer MLCs with layer thicknesses of 36-40 μm, fields exceeding 15 V μm⁻¹ yield adiabatic temperature changes of 2.7 K for 0.9PMN-0.1PT at 380 K [4], 3.8 K for PBZ at 430 K, and 5.1 K for PST at 300 K [5]. For MLCs of PST, process optimization and reduced EC layer thickness (18 μm) increases the breakdown strength to over 45 V μm⁻¹, which exceeds the 29 V μm⁻¹ that could be applied to MLCs of PST with thicker EC layers (38 μm) [5]. Our high quality MLCs should aid the development of prototype EC cooling systems that will be competitive with respect to their MC and eC counterparts.

References

5:35 AM *S.EN02.01.05
Solar Thermal Source for Passive Water Desalination and Cooling Driven by Capillarity and Salinity Gradients Matteo Morciano¹, Matteo Alberghini¹, Matteo Fasano¹, Eliodoro Chiavazzo¹ and Pietro Asinari¹,²;¹Politecnico di Torino, Italy; ²Istituto Nazionale di Ricerca Metrologica, Italy

Nowadays energy-intensive and expensive processes are mainly used to desalinate contaminated water and supply cooling capacity. Developing more sustainable, robust and cost-effective technologies (e.g. powered by renewable energy or waste heat) for generating clean water and cooling effect is a crucial need. This necessity is particularly important and severe in rural countries due to the lack of infrastructure and investments.

The abundant solar thermal source, which is now mainly employed to provide domestic hot water, could have a significant impact in achieving such targets, thanks to a wider engineering exploitation of innovative materials and technologies. [1,2,3] In this respect, passive distillation and cooling technologies – where all processes occur without mechanical moving parts – can make an important contribution. Unfortunately, state-of-the-art passive devices operating under one sun (that is, below 1 kW m⁻²) still require efficiency enhancement, durability increase, and cost reduction to scale from lab to fab. [4,5,6] The passive technologies for solar water desalination and cooling developed at the Multi-Scale Modeling Laboratory of Politecnico di Torino (www.polito.it/small) are presented.

First, a fully passive, multistage and low-cost solar thermal device able to produce freshwater from seawater is conceived, prototyped and tested under both laboratory and outdoor conditions. The device does not require any mechanical moving parts by exploiting the capillarity of hydrophilic materials. Under realistic conditions, a distillate flow rate of almost 3 L m⁻² h⁻¹ from seawater at less than one sun is demonstrated. Theoretical models, under the same conditions, also suggested that the concept has the potential to further doubling the observed distillate rate, namely up to 6 L m⁻² h⁻¹. [7] Long-term operations of the passive distiller are then improved by optimizing the structure of evaporators towards enhanced salt-rejecting performance. [8] Finally, the passive distiller is optimized to recovery the low-temperature heat, to co-generate electricity and distilled water at the same time. [9]

Second, a passive device exploiting similar phenomena as i) capillarity of hydrophilic materials and the ii) salinity difference between multiple evaporators and condensers is experimentally demonstrated to provide cooling capacity up to 100 W m⁻². [10] The implemented prototype works at ambient pressure, employs environmentally friendly water solutions, and consists of several identical stages where the cooling effect comes from a cascade of evaporation-condensation processes driven by vapor pressure gradient. The experimentally validated model predicts that cooling capacities above 200 W m⁻² could be possibly achieved with a proper design optimization of the current lab-scale prototype.

F. Signorato, M. Morciano, L. Bergamasco, M. Fasano, P. Asinari. submitted
Recent Progress on Compliant Electronic and Electromechanically Responsive Materials and Device Explorations

Qibing Pei; University of California, Los Angeles, United States

The emergence of devices that combine rubbery elasticity with electronic, optoelectronic, and mechanically transductive properties offers exciting new opportunities for applications, but brings significant materials challenges. This presentation will describe our latest results in the materials efforts in developing highly compliant conductors, semiconductors, and dielectric polymers, as well as in the demonstration of integrated functional devices. Specific examples include a touch responsive sensors, a bistable electroactive polymer for tactile display, dielectric elastomer actuators, and compliant electrode for neural detection and stimulation.

Electrocaloric Effects in Relaxor Ferroelectrics from Atomistic Simulations

Zhijun Jiang¹,²,³, Sergei Prokhorenko², Yousra Nahas², Sergei Prokofeenko², Dawei Wang⁴, Jorge Iniguez⁵, Hongjun Xiang⁵,⁶ and Laurent Bellaiche²; ¹Fudan University, China; ²University of Arkansas, United States; ³Ludong University, China; ⁴Xi'an Jiaotong University, China; ⁵Luxembourg Institute of Science and Technology, Luxembourg; ⁶Collaborative Innovation Center of Advanced Microstructures, China

The electrocaloric (EC) effect characterizes the change in temperature induced by a change in electric field [1], with the electrocaloric coefficient being defined as $\alpha = \frac{\partial T}{\partial E} \bigg|_S$, where $T$ is the temperature, $E$ is the electric field and $S$ is the entropy. It is expected that the EC effect has the potential to be an efficient solid-state cooling devices for a broad range of applications [2,3]. Up to now, fewer investigations about EC effects have been performed in relaxor ferroelectrics [4-8]. Here we study EC effect in Ba(Zr0.5Ti0.5)O3 (BZT) and PbMg1/3Nb2/3O3 (PMN) relaxor ferroelectrics. We use the first-principles-based effective Hamiltonian approach combined with Monte Carlo that has been recently developed for BZT and PMN solid solutions [9,10] to investigate the EC effects.

In the lead-free BZT systems, we investigated the electrocaloric effects subject to electric fields of different magnitude and all oriented along the pseudo-cubic [001] direction. It is found that, for any temperature, $\alpha$ exhibits a non-monotonic behavior with field that consists of small values at low fields, followed by an increase up to a maximum before decreasing for larger fields. Below the Burns temperature, this maximum of $\alpha$ is demonstrated to be correlated to a very specific microscopic feature. Finally, equalities that are derived from a simple Landau model reproduce and further help to understand the anomalous behavior of $\alpha$ with field and temperature in BZT, for any temperature above $T_m$ where the dielectric response can exhibit a peak. Our simulations also confirm that indirect and direct approaches yield similar results of the $\alpha$ EC coefficient for any temperature above the $T_m$ temperature but differ from each other for temperature below $T_m$, because of the non-ergodicity adopted by BZT at these low temperatures.

We also employed the effective Hamiltonian of Ref. [10] to shed some light on electrocaloric effects in PMN. It is particularly striking that such Hamiltonian can qualitatively reproduce not only the peculiar electric field-versus-temperature phase diagram but also the optimization of the EC coefficient near the critical point in this rather complex system. The fact that the recently developed Landau-like model, predicting that the EC coefficient is simply related to the product of temperature and the field derivative of the square of the polarization [7], also describes well the EC behavior of PMN as a function of electric field and temperature is also promising for phenomenological modelization of complex inhomogeneous systems. We therefore hope that our studies [7,8] lead to a broader knowledge of EC effects in ferroelectrics.

This work is supported by the National Natural Science Foundation of China (Grants No. 11804138 and No. 11825403), Shandong Provincial Natural Science Foundation (Grant No. ZR2019QA008), China Postdoctoral Science Foundation (Grant No. 2018M641905), and Shanghai Super Postdoctoral Incentive Program. We also thank the DARPA Grant No. HR0011-15-2-0038 (MATRIX program) and ARO grant W911NF-16-1-0227.

References:
SESSION S.EN02.02: Barocaloric Materials and Systems

On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN02

5:00 AM S.EN02.02.01
Barocaloric Effects in Fluorinated Polymers Jiyeob Kim¹, Pol Lloveras² and Xavier Moya¹; ¹University of Cambridge, United Kingdom; ²Universitat Politècnica de Catalunya, Spain

We present barocaloric studies of ferroelectric polymers of poly(vinylidene fluoride-trifluoroethylene) [PVDF-TrFE]. There copolymers are well known because of their giant electrocaloric response, but here we study pressure-driven thermal changes. PVDF-TrFE polymers undergo first-order phase transition with very large latent heats and volume changes, near room temperature. These three properties make them ideal materials for barocalorics.

5:10 AM *S.EN02.02.02
Practical Considerations for Barocaloric Cooling Enric Stern Taulats¹, Juan M. Bermúdez-García¹,², Guillaume F. Nataf¹ and Xavier Moya¹; ¹University of Cambridge, United Kingdom; ²University of A Coruna, Spain

Barocaloric materials are blossoming, with recent reports of thermal changes that compare to those observed in commercial refrigerant fluids [1-3]. The viability of future barocaloric chillers will rely on properties that go beyond the magnitude of the pressure-driven barocaloric effects. On the one hand, the challenge of effective transmission of hydrostatic pressure needs to be addressed in order to guarantee homogeneous stress distribution in the active material, and therefore optimal caloric performance. On the other hand, heat extraction needs to occur at rates that can match the practical cycling frequencies. Here, I will discuss key aspects of pressure transmission and heat transfer in barocaloric devices, and present a guide for barocaloric materials to match applications requirements.


5:25 AM *S.EN02.02.03
Colossal Reversible and Irreversible Barocaloric Effects in Plastic Crystals Araceli Aznar¹, Pol Lloveras¹, Maria Barrio¹, Philippe Negrier², Antoni Planes³, Lluís Mañosa³, Neil D. Mathur⁴, Xavier Moya³ and Josep-Lluís Tamarit³; ¹Universitat Politècnica de Catalunya, Spain; ²Université de Bordeaux, France; ³Universitat de Barcelona, Spain; ⁴University of Cambridge, United Kingdom

The massive use of vapor-compressor-based coolers poses a serious global environmental problem due to a relatively small efficiency and the use of hydrofluorocarbons with huge greenhouse potential [1]. These devices are based on controlling the exchange of latent heat involved in liquid-vapor transitions by means of hydrostatic pressure. Alternative technologies based on driving solid-state first-order phase transitions using magnetic, electric and uniaxial stress fields avoid the use of harmful fluids and promise higher efficiencies [2], but they are limited by a relatively small magnitude of the latent heat associated with such transitions compared to evaporation. Here we show that pressure-driven caloric (i.e. barocaloric) effects at phase
transitions in some plastic crystals is comparable to that in hydrofluorocarbons due to the emergence of strong molecular orientational disorder [3,4]. We also discuss the reversible barocaloric response that is obtained upon cyclic application and removal of pressure as this is key for technological implementation. In particular, we characterize reversible effects in terms of magnitude, temperature spans, and minimum required pressure. We determine that, while some of the plastic crystals under analysis are unfeasible for applications due to irreversibility within a large pressure range, others demonstrate colossal barocaloric effects that are reversible at low pressures [3,4] and therefore show aptitudes that should promote the future development of environmentally-friendly solid-state barocaloric cooling devices.


5:40 AM *S.EN02.02.04
Giant Barocaloric Effect at the Spin Crossover Transition of a Molecular Crystal Steven P. Vallone1,2, Anthony N. Tantillo1,2, António dos Santos3, Jamie J. Molaison1, Rafał Kulmaczewski4, Antonin Chapoy5, Pezhman Ahmadi5, Malcolm A. Halcerw4 and Karl Sandeman1,2; 1Brooklyn College of CUNY, United States; 2CUNY, United States; 3Oak Ridge National Laboratory, United States; 4University of Leeds, United Kingdom; 5Heriot-Watt University, United Kingdom

Abstract body: Spin crossover occurs in compounds where the crystal field splitting of d-orbitals associated with a magnetic moment is of the order of k_B T. As a result, a change of state from low spin (LS) to high spin (HS) can occur at the so-called spin crossover temperature, T_{SCO}. Crucially for caloric applications, the change of state from LS to HS can be either continuous or first order, and it can occur at temperatures up to and beyond room temperature. This makes SCO transitions of interest for caloric cooling applications. Since SCO compounds are paramagnets or diamagnets, the largest caloric effects will be barocaloric rather than magnetocaloric.

In this presentation, we provide the first direct experimental demonstration of a giant, low pressure barocaloric effect (BCE) and outline future research directions for the development and optimization of the BCE associated with spin crossover.

SESSION S.EN02.03: Elastocaloric Materials and Systems
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN02

5:00 AM *S.EN02.03.01
Latest Development in Compression-Based Elastocaloric Cooling Materials and Systems Ichiro Takeuchi; University of Maryland, United States

In this talk, we will discuss our latest work on development of elastocaloric materials as well as cooling prototype systems. We have used additive manufacturing to engineer NiTi-based composites with extremely small hysteresis in stress-strain curves. Additive manufacturing allows flexible design topology of metallic refrigerants which also act as heat exchangers. The small hysteresis results in substantially enhanced materials coefficient of performance as well as long fatigue life needed for applications. On the systems front, we have demonstrated active regeneration schemes for systems with cooling capacity up to 100s of watts using commercially available NiTi tubes. The largest temperature span we have achieved for a single stage compressive regenerators is 23 K. This work is carried out in collaboration with H. Hou, J. Cui, R. Ott, A. Stebner, D. Catalini, R. Radermacher, and Y. Hwang, N. Emaikwu, and S. Qian,
5:00 AM *S.EN02.04.02

Thermal Control Elements for Caloric Technologies Andrej Kitanovski; University of Ljubljana, Slovenia

The refrigeration and air conditioning consumes about 17% of the overall electricity used worldwide, and will drastically increase in the next 30 years. The vast majority of these systems utilize vapour-compression technology, which is actually and unfortunately still associated with the existing refrigerants and their environmental impact. Since they contribute to the 7.8% of global greenhouse gas emissions, large efforts are invested in finding appropriate future working substances. However, the options for new, environmentally friendly refrigerants are very limited. Another important step in decreasing the energy consumption is through the energy efficient refrigeration and air conditioning. The large scale vapour compression systems operate with their upper limit of about 60% of the second law efficiency. However they suffer by the low 20% efficiency especially in small appliances. The above issues represent the driver for the quest for energy efficient and environmentally friendly refrigeration and air-conditioning, which is pronounced more than ever. Among the available best alternatives to existing technologies is the caloric energy conversion. This is due to the potentially very high energy efficiency and use of environmentally friendly and safe solid-state working substances. Most of today’s caloric devices apply so-called active regeneration, which involves the oscillation of the working fluid through the matrix of the caloric material – the caloric regenerator. However, the unavoidable, irreversible viscous and heat-transfer losses apply limits to the caloric device’s performance as well as its size. The quest for better caloric-device performance has led to the development of thermal control elements, which control the heat flux on different size and time scales. Here we describe the working principles of these elements: thermal switches, thermal diodes and thermal regulators. This is followed by the critical review of the research activities and applications of thermal control elements in all types of caloric devices. It is shown that thermal control elements have the potential to substantially improve the power density of caloric devices. Finally, we present the target features and future research guidelines for these elements in the field of caloric technologies.

5:15 AM *S.EN02.04.05

Prospects and Challenges—Additive Manufacturing of Magnetocaloric Regenerators Radhika Barua1, Dustin M. Clifford1, Ravi L. Hadimani1, Hong Zhao1, Surojit Gupta2, Matthew Kramer3 and Laura Lewis4; 1Virginia Commonwealth University, United States; 2University of North Dakota, United States; 3Ames Laboratory, United States; 4Northeastern University, United States

Cooling, manifested both as air conditioning and as refrigeration, is regarded as one of the most energy-intensive technologies in demand today. Magnetic refrigeration is an energy-efficient, sustainable, environmentally-friendly alternative to conventional vapor-compression cooling technology. There are a number of magnetic refrigerator device designs in existence today that are predicted to be highly energy efficient, on condition that the suitable working materials can be developed.1 This materials challenge has proven to be daunting due to issues associated with intricate synthesis/post-processing protocols and complications related to shaping the mostly brittle magnetocaloric alloys into thin-walled, channeled regenerator structures to facilitate efficient heat transfer between the solid refrigerant and the heat exchange fluid in an active magnetic regenerator (AMR) cooling device. To this end, research centered on fabrication of functionally-graded AlFe2B2 magnetic regenerators via sophisticated additive manufacturing (AM) methods will be presented in this talk. This ferromagnetic intermetallic boride has attracted considerable attention due to its low cost, promising thermal properties that promote effective heat transfer (specific heat capacity, \(C_p=115\) J/moleK; thermal conductivity, \(\kappa=5.6\) W/mK) and moderate room temperature magnetocaloric response (adiabatic temperature change, \(\Delta T_{ad}=1\) K and magnetic entropy change, \(\Delta S=2.6\) J/kgK at \(\mu_0H_{app}=2\) T).2,3

In this work, powders of single phase AlFe2B2 were synthesized using multiple conventional routes: (i) drop-casting, followed by heat treatment at 1040°C for 72 hours and then grinding to particulate form in air, (ii) reaction sintering at 900°C for 24 hours, followed by etching in dilute HCl for 30 min and a (ii) molten salt-assisted solid state reaction at 600°C for 36 hours. Experimental data indicate that irrespective of processing method, powders of dimensions ranging from 5 to 40 μm demonstrate comparable structural and magnetic properties (orthorhombic \(Cmmm\)-type crystal structure with unit cell volume, \(V=92.6±0.4\) Å; Curie temperature, \(T_C=277±6\) K) as well as similar magnetocaloric response (\(\Delta S=2.6±0.3\) J/kgK at \(\mu_0H_{app}=2\) T). These precursor powders were used to 3D-print cylindrical AlFe2B2 samples using the established direct energy deposition AM method, laser enabled net shaping (LENS) and using an innovative magnetic-field assisted extrusion method whose prime novelty lies in the 3D ink formulation.4,5 Efforts to optimize the material and printing process parameters to maximize the magnetocaloric potential of AlFe2B2 will be discussed. Further, the feasibility of printing high-quality magnetocaloric device components with high surface area and complex porous architectures will be deliberated upon. Overall, this study provides strategies for realizing low-cost functionally graded magnetic regenerators, thus potentially
eliminating one of the main barriers to commercialization of magnetic cooling technology.


SESSION S.EN02.05: Poster Session: Caloric Materials for Sustainable Cooling Applications
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020 5:00 AM - 8:00 AM S-EN02

S.EN02.05.06

**Computational Proxy Driven Identification of Magneto-Caloric Materials with Chemically Tunable Transition Temperature in the PbFCl Family**

Philip Murgatroyd, Kieran Routledge, John Claridge and Jonathan Alaria; University of Liverpool, United Kingdom

Conventional refrigeration based upon the vapor compression cycle is an inefficient process when compared to the efficiency of a Carnot engine operating between the same thermal reservoirs. A viable alternative is magnetic refrigeration, which utilizes adiabatic magnetization and demagnetization to create a cooling cycle analogous to that of the vapor compression cycle through the ‘magnetocaloric effect’. A viable compound for magnetic refrigeration at ambient temperature must present a large change in magnetic entropy, with minimum hysteresis and should be composed of earth abundant and non-toxic elements.

Recently a computational proxy was developed to identify new magnetocaloric materials whereby first principle structure relaxation is carried out with and without spin polarization to ascertain the degree of magnetic deformation.[1] By applying this method to ferromagnet in the PbFCl family we found magnetic deformation of around 2% which is similar to other magnetocaloric compounds. We therefore have focussed our experimental study on MnZnSb, which is reported to be an itinerant ferromagnet with a second order phase transition and Curie temperature about room temperature.[2] Detailed magnetization measurements were carried out and Arrott analysis yields a Curie temperature of 304K, with the system being described as a 3D itinerant ferromagnet from the critical exponents of the Arrott-Noakes equation. We find a reasonably large magnetic entropy change of 4.5 Jkg⁻¹K⁻¹ with a relative cooling power of 153 Jkg⁻¹; which is comparable to second order compounds with about room temperature transition temperatures. Heat capacity measurement shows an anomaly around the magnetic transition and together with the magnetometry can be used to calculate an adiabatic temperature change of 2 K under 2 T. Temperature dependant powder neutron diffraction was used to investigate the origin of the significant magnetic entropy change around the magnetic transition. By alloying this compound with transition metal such as Fe and Cr we found a linear relationship between the c/a ratio and the magnetic transition allowing for the tuning of the operating temperature of this material from 250 K to 320 K without being too detrimental to the magnetic entropy change.


S.EN02.05.07

**Effective Thermal Conductivity of Nickel-Polyurethane Composite Foams**

Rui Dai, Gokul Chandrasekaran, Jie Chen, Chayton Jackson, Yongming Liu, Beomjin Kwon and Qiong Nian; Arizona State University, United States

Foams offer extremely large surface area per unit mass, making them competitive material for heat exchangers and energy storage systems in automotive applications. Understanding the influence of foam characteristics, i.e., size, distribution and the concentration of pores, on their effective thermal conductivity is important when designing the foam-based devices. Herein, we present the effective thermal conductivity of 15μm-thick nickel (Ni) coated open-cell polyurethane (PU) foam (20 PPI, with ~174μm truss cross-section edge length) architectures measured by transient plane source (TPS) method. A calibration methodology for TPS method is developed to ensure an accuracy in measurements. The experiment results are
compared with theoretical models including a finite element model and effective medium theory. For modeling, an X-Ray tomography is used to accurately analyze the foam structures. We investigate how the foam characteristics, including the Ni coating thickness, coating defects, and angular alignment of the foam truss, modulate the effective thermal conductivity. Lastly, we discuss how the model assumptions are related to the discrepancy between the model predictions and measurements for the polymer-metal foams.

SESSION S.LP03.01: Live Poster Session: Energy, Storage and Conversion (S.EN02)
Session Chairs: Radhika Barua and Andrej Kitanovski
Tuesday Morning, December 1, 2020
8:00 AM - 10:00 AM
S.EN02

S.EN02.05.06
Computational Proxy Driven Identification of Magneto-Caloric Materials with Chemically Tunable Transition Temperature in the PbFCl Family
Philip Murgatroyd, Kieran Routledge, John Claridge and Jonathan Alaria; University of Liverpool, United Kingdom

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S.EN02.05.07
Effective Thermal Conductivity of Nickel-Polyurethane Composite Foams
Rui Dai, Gokul Chandrasekaran, Jie Chen, Chayton Jackson, Yongming Liu, Beomjin Kwon and Qiong Nian; Arizona State University, United States

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compared with theoretical models including a finite element model and effective medium theory. For modeling, an X-Ray tomography is used to accurately analyze the foam structures. We investigate how the foam characteristics, including the Ni coating thickness, coating defects, and angular alignment of the foam truss, modulate the effective thermal conductivity. Lastly, we discuss how the model assumptions are related to the discrepancy between the model predictions and measurements for the polymer-metal foams.

SYMPOSIUM S.EN05

Low-Cost Aqueous Rechargeable Battery Technologies
November 21 - December 1, 2020

Symposium Organizers
Joshua Gallaway, Northeastern University
Jaekook Kim, Chonnam National University
Matthew Lim, Sandia National Laboratories
Gautam Yadav, The City University of New York

Symposium Support
Bronze
Sandia National Laboratory-08811 Energy Storage

* Invited Paper

SESSION S.EN05.06: Live Lightning/Flash I: Low-Cost Aqueous Rechargeable Battery Technologies
Session Chairs: Joshua Gallaway and Matthew Lim
Monday Afternoon, November 30, 2020
S.EN05

1:45 PM INTRODUCTION AND ANNOUNCEMENTS

1:59 PM *S.EN05.03.02
Reaction Mechanisms for Long-Life Rechargeable Zn/MnO2 Batteries Yun Li1, Shanyu Wang1, James Salvador2, Jinpeng Wu3, Bo Liu4, Wanli Yang5, Jiong Yang5, Wenqing Zhang6, Jun Liu1 and Jihui Yang1; 1University of Washington, United States; 2General Motors R&D Center, United States; 3Stanford University, United States; 4Shanghai University, China; 5Lawrence Berkeley National Laboratory, United States; 6Southern University of Science and Technology, China

Rechargeable aqueous Zn/MnO2 batteries are promising for large-scale grid energy storage applications owing to their low cost, environmentally benign constituents, excellent safety, and relatively high energy density. Their usage, however, is largely hampered by the fast capacity fade. The complexity of the reactions has resulted in long-standing ambiguities of the chemical pathways in Zn/MnO2. In this talk, I will discuss our latest work on discerning the reaction mechanisms of rechargeable Zn/MnO2 batteries. We find that both H+/Zn2+ intercalation and conversion reactions occur at different voltages and that the rapid capacity fading can clearly be ascribed to the rate-limiting and irreversible conversion reactions at a lower voltage. By limiting the irreversible conversion reactions at ~1.26 V, we successfully demonstrated high power and long life that are superior to most of the reported Zinc-ion Batteries or even some lithium-ion batteries.

2:07 PM *S.EN05.03.03
Transition Metal Oxide Cathodes in Aqueous Zn Batteries—Electrochemistry and Mechanism Esther S. Takeuchi1,2, Kenneth Takeuchi1 and Amy Marschik1,2; 1Stony Brook University, The State University of New York, United
Rechargeable aqueous Zn batteries are being actively explored due to the high natural abundance and safety associated with Zn, along with the intrinsic nonflammability and the high ionic conductivity of the aqueous electrolyte. While the individual cell voltage is lower than lithium systems, the benefits may be significant for some application where low cost and nonflammability are key considerations.

Several cathode systems are under exploration for zinc based batteries. The most frequently explored cathode materials are oxides based on the transition metals manganese or vanadium where both layered and tunneled structural motifs have been utilized. The discharge mechanisms can be complex where there can be a combination of H⁺ insertion and Zn²⁺ insertion. Further, the mechanisms can be highly electrolyte dependent.

This presentation will discuss exploration of cathode materials used in Zn based aqueous batteries and their electrochemistry. Characterization methods used for the analysis include cyclic voltammetry, galvanostatic discharge, scanning electrochemical microscopy, x-ray diffraction, x-ray photoelectron spectroscopy, scanning electron microscopy with energy dispersive x-ray spectroscopy mapping, and x-ray micro-fluorescence spectroscopy will be highlighted.

2:23 PM *S.EN05.01.01
Nickel-Zinc Battery Characteristics and Manufacturability  
Eivind Listerud, Adam Weisenstein and Michael Gordon;  
ZAF Energy Systems, United States

The Nickel-Zinc battery has an energy density that fits in the gap between Lead-Acid and Li-Ion batteries. Given its nonflammability, environmental friendliness, and relatively low cost, it is an attractive candidate for grid-scale storage and industrial motive applications. With tailored electrodes for optimized rate capability, Nickel-Zinc is also suitable for applications like data center storage and heavy trucking. This presentation will give an overview of this rechargeable alkaline chemistry with an emphasis on large format designs (cell capacity > 120Ah) for a variety of applications. It will cover the strengths and weaknesses of this technology when compared to Lead-Acid and Li-ion. Data will show improved deep cycle performance and superior recharge capability over Lead-Acid. Long term float charge test results will also be discussed, as well as the safety of the chemistry and how this impacts sizing, cost, and management of large-scale energy storage systems. The presentation will also discuss recent advancements in manufacturability of both positive and negative electrodes that enables high rate production of large format Nickel-Zinc batteries. Manufacturing equipment traditionally used by the Lead-Acid industry has been shown to be suitable in the production of the electrodes used in Nickel-Zinc batteries. This will have a significant impact on manufacturing rate and cost and will allow Ni-Zn to be even more competitive in terms of price.

2:31 PM *S.EN05.01.07
High Energy Density Silver-Zinc Button Cells for Wearable Devices  
Xia Wei; ZPower, LLC, United States

The silver (Ag)-zinc (Zn) system has the highest theoretical specific (Wh/kg) and volumetric energy density (Wh/L) amongst all rechargeable batteries with the added benefit of safety and nonflammability compared to lithium-ion or lithium metal batteries, which makes it a good and ideal candidate for portable applications like hearing-aids, ear buds and other wearable devices. However, historically, the Ag-Zn battery has suffered from poor rechargeability and low energy utilization. At ZPower, we have tailored the chemistry and engineered a new Ag-Zn battery system, which is highly energy dense and rechargeable, thus making it possible to use it portable applications and giving more power to the consumer to allow them to contribute to a greener future.

As aforementioned, enhancing the capacity of the active materials is paramount for high energy density, which we achieved by developing proprietary additives and approaches. For divalent silver oxide (AgO) cathode, we developed an optimal method of processing the raw materials and novel proprietary conductive coatings for AgO, which allowed integrity control of material properties, faster charge, high capacity utilization and retention for many cycles. The optimal process was verified by experimenting processed AgO cathode under different fast charge rate, where the results showed that it improved the charge capabilities. The role of these coatings was further studied through charge algorithm cycling, where we found that it reduced AgO cathode’s impedance compared to the control tests and maintained its active surface area. More importantly, we found that the morphology of the proprietary conductive coatings played a crucial role in efficiently utilizing the AgO cathode’s capacity.

For the Zn anode, where it has a theoretical specific capacity of 820 mAh/g; however, Zn has a long history of poor rechargeability due to problems like shape change (zinc redistribution), dendrite formation and passivation. In the past,
previous researchers tried altering the Zn formulation to increase utilization; however, these attempts were not fruitful. We have engineered a new Zn anode that can access 94% of its theoretical capacity in a single primary discharge and 56% of its theoretical capacity rechargeably for over 300 cycles. We achieved this breakthrough by developing proprietary additives and methods that localize the Zn to the current collector and prevent dendrite formation. We showed that with incorporating these additives into Zn anode, it further helped mitigating shorting for 400 + cycles.

2:38 PM BREAK

2:43 PM *S.EN05.01.02
Development of Zn/MnO2 Alkaline Batteries for Grid Storage Timothy N. Lambert, Matthew Lim, Igor V. Kolesnichenko, David Arnot, Noah B. Schorr, Rachel L. Habing, Logan S. Ricketts, Elijah I. Ruiz and Babu Chalamala; Sandia National Laboratories, United States

For energy storage to become ubiquitous in the electric grid, safe, reliable low-cost electrochemical storage technologies manufactured at high volumes with low capital expenditures are needed. Alkaline batteries based on high capacity multi-electron conversion electrodes from low cost, abundant and safe materials, such as a Zn/MnO2 are a promising technology. These batteries have a theoretical specific energy rivaling that of Li-ion systems (Zn @820 mAh/g and MnO2 @617 mAh/g, with ~400 Wh/L) and costs reducible to <$50/kWh, when produced at scale (S. Banerjee et al.). While recent advances by Yadav et al. have demonstrated highly reversible Bi- and Cu-stabilized MnO2 electrodes that can achieve the full 2e- capacity of MnO2 in alkaline electrolyte, the ability to pair this electrode with Zn over 5000+ cycles, which equates to ~10-15 years of battery life, remains a difficult challenge.

Zn anodes suffer from irreversible shape change, the redistribution of active material, and passivation over repeated charge and discharge, limiting their achievable capacity and lifetime. Pre-saturating the electrolyte with zincate [Zn(OH)42-], which minimizes dissolution of Zn from the anode and reduces the rate of hydrogen evolution, has recently been shown to enhance cycle life for ~10-35% depth-of-discharge (DOD) Zn anodes by ~100-200% (M. Lim et al.); however, Zn(OH)42- saturated electrolyte is incompatible with high DOD MnO2, and exacerbates the formation of electrochemically inactive phases, such as ZnMn2O4 at the cathode. Hence, using zincate-blocking separators, able to entrap the zincate within the anode and effectively isolate the MnO2 cathode from Zn(OH)42- crossover, while maintaining hydroxide/cation conductivity, is one approach to improve the reversible cycling of a Zn/MnO2 cell at high DOD of both MnO2 and Zn.

Previously, our group has shown that a ceramic Na-ion super ionic conductor (NaSICON) membrane, which completely inhibits Zn(OH)42- crossover, increased cycle life in limited DOD batteries; however, its poor conductivity severely limited the rate capabilities and DOD of MnO2 (Duay et al.). More recently we have developed a series of permselective polymeric separators (Kolesnichenko et al.) and screened them using our newly-developed anodic stripping voltammetry crossover assay (Duay et al.) to identify those with Zn(OH)42- blocking ability. A primary discharge of MnO2 was used to demonstrate that a sustained 2nd e- discharge plateau, indicative of the absence of zinc species at the cathode, was observed only for Zn/MnO2 batteries that utilized our selective polymeric separators. Finally, application of these polymeric separators in rechargeable Zn/MnO2 batteries increased cycle life with higher coulombic efficiencies. Various aspects involved in improving the cycle life of Zn anodes at increased DOD, and of the application of our polymeric separators in isolating the MnO2 cathode from soluble zincate and their ability to enable higher DOD cycling in Zn, will be discussed.

This work was supported by the U.S. Department of Energy, Office of Electricity, and the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA-0003525. The views expressed herein do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

2:51 PM *S.EN05.01.03
From Concept through Product to Market—Rechargeable Zinc Manganese Dioxide Batteries Sanjoy Banerjee; Urban Electric Power, United States

Zinc (Zn) and manganese dioxide (MnO2) are key components of primary alkaline batteries which have dominated the market for decades. They have been demonstrated as promising electrochemical energy storage materials due to the high energy density, low cost, and outstanding safety characteristics. Transforming this non-rechargeable technology into a
rechargeable system would enable it as a revolutionary low-cost solution for grid-scale energy storage. However, the poor reversibility of the traditional Zn and MnO2 materials, especially at high depth of discharge, has limited the achievable energy density and cycle life of this rechargeable battery system. Recent developments in rechargeable Zn/MnO2 batteries achieved by the City University of New York Energy Institute (CUNY-EI) in partnership with Urban Electric Power, Inc. (UEP) has presented unique characteristics that could potentially disrupt existing technologies to access a $50BN market. In this talk, the challenges in developing and commercializing rechargeable Zn/MnO2 batteries for energy storage will be presented, from initial concept through the technical breakthroughs needed to commercialize and manufacture.

2:59 PM *S.EN05.01.05
Towards Higher Utilization of Electroactive Materials in Zn-MnO2 Alkaline Batteries Damon Turney1, Gautam G. Yadav1, Andrew Kiss1 and Sanjoy Banerjee1; 1The City University of New York, United States; 2Brookhaven National Laboratory, United States

Market price points for grid-scale energy storage range from $10– $200 per kWh depending on the application. These cost targets are not possible using lithium-ion technology. Fire safety is also a concern and prohibits lithium-ion in some locations. Lead-acid, Ni-MH, and Ni-Cd currently serve as alternatives, but are too expensive, bulky, and/or contain very toxic materials. Recent research from The City College of New York shows a rechargeable alkaline Mn-Zn battery that is very low cost, very safe fire, contains no toxic materials, and has moderately high energy density. Here we review what is currently known about the materials chemistry of this Mn-Zn battery and show new results of in-operando micro-XRD and XRD-imaging chemistry of the Mn electrode. New materials evolution pathways are identified using the in-operando data.

3:07 PM *S.EN05.01.10
The Case for Zinc Debra R. Rolison1, Brandon J. Hopkins1,2, Christopher N. Chervin1, Megan B. Sassin1, Jeffrey W. Long1 and Joseph F. Parker1; 1U.S. Naval Research Laboratory, United States; 2National Research Council Postdoctoral Associate, United States

Realizing a next-generation battery that meets or exceeds the system energy density of lithium batteries while capturing attributes beyond the reach of lithium batteries requires a balancing act. The elements that comprise aqueous, safer-than-lithium batteries need to be reasonably naturally abundant, can be acquired through low-risk supply chains, are nontoxic, and can be fabricated, modified, and assembled using green protocols. Zinc checks all those boxes and now that monolithic spongy zinc negative electrodes open new performance terrain—rechargeably cycled at high rate, to deep utilization of the metal—a broad class of rechargeable zinc-based aqueous batteries is finally possible. We perform the systems analysis to show that zinc anodes versus either MnO2 cathodes or air cathodes satisfy energy storage at low cost while meeting the sustainability sought for batteries beyond lithium.

3:30 PM CLOSING SUMMARY

SESSION S.EN05.07: Live Lightning/Flash II: Low-Cost Aqueous Rechargeable Battery Technologies
Session Chairs: Matthew Lim and Gautam Yadav
Tuesday Morning, December 1, 2020
S.EN05

8:00 AM INTRODUCTION AND ANNOUNCEMENTS

8:06 AM S.EN05.03.04
Aqueous Rechargeable Zinc Ion Batteries—Parasitic Reactions and Cycle Life Degradation Balaji Sambandam, Vaiyapuri Soundharrajan, Vinod Mathew, Muhammad H. Alfaruqi, Sohyun Park, Junji Piao and Jaekook Kim; Chonnam National University, Korea (the Republic of)

Since after a new concept of mild acidic aqueous rechargeable zinc-ion batteries (ARZIBs) was introduced in 2011, the technology has been establishing gradually. ARZIBs have proven to be the most eco-friendly energy storage systems (ESSs)
as they use zinc as the negative electrode (with a notable large theoretical capacity value of 820 mAh g⁻¹). Zinc is widely available in the Earth's crust and forms a non-toxic, low-cost aqueous electrolyte, thus ensuring low principal investment and high reliability and safety. Till to date, both manganese and vanadium oxides are widely utilized as cathode for this technology and well documented. However, all these oxides have their drawbacks accompanied with their life stability through long-term cycling, particularly at low current rates. The reason is: electrolyte pH change due to metal dissolution during electrochemical reaction, resulting a reversible parasitic reaction which seriously affects the cycling life of a cathode, depending on type of electrolyte being employed. Thus a most reversible product of zinc basic sulfate (ZBS, Zn₄(OH)₆SO₄·nH₂O), an insulating material, formed/dissolved on the cathode-electrolyte interface due to change of electrolyte pH resulting from metal dissolution, when ZnSO₄ utilized as an electrolyte. Irrespective of the cathode used, this side reaction related to ZBS formation is observed in most of the reported ARZIBs. As the reason, most of the reported studies demonstrate long cyclability in metal oxides-based electrodes at very high current drains. In other words, the application of high current drain increases cycle life-span as much as it can before the electrode demonstrates capacity fading due to metal dissolution. Through Operando analyses, this work establishes the parasitic reaction during electrochemical reaction and document its consequence on the cycle life of the aqueous battery. This will be discussed in detail.

8:14 AM S.ENV05.02.02
Understanding the Role and Consequence of the Mn²⁺ Additive in the Electrochemical Activity of a ZnMn₂O₄ Cathode in Aqueous Zinc-Ion Batteries Vinod Mathew, Vaiyapuri Soundharrajan, Saiful Islam, Balaji Sambandam, Seokhun Kim, Sungjin Kim, Zulkifli Zulkifli and Jaekook Kim; Chonnam National University, Korea (the Republic of)

The addition of Mn²⁺ additives in the electrolyte of aqueous zinc-ion batteries (ZIBs), in general, has shown to greatly improve the cyclability of the cathode, very recently. Despite a growing number of studies on this issue with respect to manganese-based cathodes, a complete understanding on the role of Mn²⁺ additive towards the electrochemical reaction in ZIBs has not yet been reached. In such a scenario, we studied the electrochemical activity of one such manganese-based cathode, ZnMn₂O₄ (ZMO) with zinc in a ZIB. Zinc manganate, as a ZIB cathode, is an intriguing choice due to its high theoretical capacity and voltage. We compared the electrochemical reaction of this ZMO nanorods cathode obtained through a simple co-precipitation process in the presence of a 0.1 M MnSO₄ (MS) solution as a full-time electrolyte, as an additive in zinc sulfate (ZMS) electrolyte (1 M ZnSO₄ + 0.1 M MnSO₄) and in its absence or a full-time zinc sulfate (ZS) electrolyte (1 M ZnSO₄), respectively. Systematic investigations including ex situ X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) studies revealed the reasons for the superior stability and high reversibility of ZMO in the ZMS electrolyte medium. The exceptional performance was facilitated by the the electrochemical equilibrium between Zn²⁺ and Mn²⁺ ions via a stable Zn²⁺ (de)insertion in the bulk, a reversible electro-deposition/dissolution of MnO₂ from the Mn²⁺ additive in the electrolyte onto (from) the surface of the cathode and the reversible Zn-insertion into the formed surface MnO₂ layer. This finding is significant as it is contrary to the conventional understanding that the addition of Mn²⁺ merely tends to prevent manganese dissolution thereby facilitating a stable cycle-life performance of the cathode in ZIBs.

8:30 AM S.ENV05.02.03
Hierarchical Porous Nickel-Doped Vanadium Dioxide (B) Nanobelts with Ultrahigh Rate Capability and Long Cycle Life for Aqueous Rechargeable Zinc-Ion Batteries Yi Cai and Rodney Chua; Nanyang Technological University, Singapore

Recently, aqueous rechargeable zinc-ion batteries (ARZIBs) have attracted great attention as compared to commercial lithium-ion batteries due to their unique advantages of high intrinsic safety (non-flammable water-based electrolyte) and low cost. [1-3] Over the past few decades, much progress has been focused on the exploration of suitable cathode materials. Among them, vanadium dioxide (B) has been considered as a potential cathode for ARZIBs owing to its unique double layers of V₄O₁₀ type with tunnels, which can facilitate rapid zinc-ions de/insertion processes. [4] However, the reported VO₂ (B) displays a high initial capacity but noticeable capacity fading and especially declines drastically at a high current rate. Compositing VO₂ (B) with an electrically conductive matrix has recently been introduced as an effective way to improve the power capability. However, it can only improve the external electric conductivity and the usage of expensive carbon (graphene) negates the cost advantage of vanadium oxides. Therefore, it is of great importance to construct novel VO₂ (B) electrode materials with excellent electrochemical performance. Herein, we report an alternative approach to designing and engineering a hierarchical porous Ni-doped vanadium dioxide (B)
nanobelts for ARZIBs. The as-synthesized samples were characterized by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy and transmission electron microscopy (TEM). The existence of Ni dopant was confirmed by the X-ray absorption near-edge structure studies (XANES) and X-ray photoelectron spectroscopy analysis. Electrochemical studies indicate that the Ni-doped VO₂ nanobelts electrode exhibits superior cycling stability and ultrahigh rate capability with long cycle life, which is significantly higher than that of the undoped VO₂ (B). This can be attributed to the utilization of Ni dopant to electrical wiring the electroactive material, the intrinsic conductivity of VO₂ can be effectively increased. In-operando XRD measurements coupled with ex-situ TEM micrographs taken at specific potentials were exploited to gain a further understanding into the structural evolution upon cycling and ions storage mechanism. The results of the study can potentially open the doors for the widespread application of constructing other elemental doping materials as cathodes with high rate capability and long cycle life for aqueous rechargeable batteries.

References:

8:38 AM OPEN DISCUSSION

8:54 AM *S.EN05.02.07
Flexible Zinc Ion Batteries Chunyi Zhi; City University of Hong Kong, Hong Kong

Prussian blue analogue (PBA)-type metal hexacyanoferrates have been considered as significant cathode materials for aqueous rechargeable zinc batteries (ZBs) due to the open face centered cubic framework, multiple active sites, and environmental benign. However, these PBA-type cathodes, such as cyanogroup iron hexacyanoferrate (FeHCF), suffer from ephemeral lifespan (≤1000 cycles), inferior rate capability (1A g⁻¹), and low operating voltage (ca. 1.2 V). This is because the redox active sites of multivalent iron (Fe(III/II)), which dominates its electrochemical activities, can only be very limited activated and thus utilized. The limited activity is attributed to the spatial resistance caused by the compact cooperation interaction between Fe and the surrounded six cyanogroup per unit, and the inferior conductivity. In this paper, surprisingly, we found high-voltage-scanning can effectively activate the C-coordinated Fe (redox active sites) in FeHCF cathode in ZBs. The activation spurred the increase of capacity at a high operating voltage plateau of ca. 1.5 V. Thanks to this activation, the Zn-FeHCF hybrid-ion battery achieved a record-breaking cycling performance of 5000 (82% capacity retention) and 10000 cycles (73% capacity retention), respectively, together with a superior rate capability of maintaining 53.2% capacity at super-high current density of 8 A g⁻¹ (ca. 97 C). To the best of our knowledge, this is the best cycling performance among all the Zn-PBA batteries up to now. As for the mechanism, the reversible distortion and recovering of crystalline structure caused by the (de)insertion of zinc and lithium ions was revealed. The developed strategy of applying a high-voltage-scan to trigger a greatly enhanced overall electrochemical performance of FeHCF can be easily extended to other PBA materials and other battery systems. We believe this work represents a substantial advance on PBA electrode materials and may essentially promote application of PBA materials.

9:09 AM BREAK

9:14 AM *S.EN05.04.01
Minimal Overhead Storage Technology—Living Forever By Dying Everyday Daniel Steingart; Princeton University, United States

In this work we seek to reduce cost and increase cycle life of a grid scale system by de-emphasizing the requirements for shelf life and short circuit prevention. We show a reconfiguration of the zinc-bromine system creates a system that may "live forever by dying everyday" by eliminating much of the balance-of-plant and exploiting the physical properties of the bromine and zinc. This "solution" also creates new questions. In a system that can safely short circuit at any point, what defines state
of charge and state of health? At what point is the battery now "dead"? Is this actually a useful system? The system will be illustrated and current answers to these questions will be discussed.

9:30 AM *S.EN05.04.02
Organic Electrode Materials for Aqueous Batteries—A Mechanistic Study Ye Zhang and Yan Yao; University of Houston, United States

I will present how quinone based organic materials can be designed to address the short cycle life challenges in aqueous batteries -- the structural and chemical instability of anode electrode plays a critical role. Quinone-based organic crystals can store multiple protons with high reversibility, which makes them promising candidates for the anode materials for aqueous batteries. However, the understanding of molecular structures and packing motifs on proton storage and proton-induced phase transition process is currently lacking. Recently we utilized the synchrotron-based X-ray surface scattering technique to probe the tetrachloro-p-benzoquinone (TCBQ) single crystal surface structure change during H⁺ insertion in operando. TCBQ underwent a two-phase reaction during the proton insertion process as the crystal planes of protonated TCBQ (H₂TCBQ) formed step-by-step on the crystal surface. Quinone-based polymers have also demonstrated superior performance in aqueous Na⁺, Ca²⁺, and Zn²⁺ batteries. We will also present mechanistic studies using in-situ techniques such as EQCM-D, FT-IR, and optical imaging that provide insights on how to optimize ion-solvent-polymer interactions in aqueous batteries to further improve cycle life.

9:38 AM S.EN05.02.08
Flexible Quasi-Solid-State Zinc-Ion Rechargeable Batteries for Subzero Temperature Applications Ying Wang and Yehong Chen; Louisiana State Univ, United States

The emerging zinc ion rechargeable batteries show high potential in the fast expanding market of electrochemical energy storage devices owing to their intrinsic safety and low cost, as they use aqueous electrolytes and zinc anodes that are stable and come from abundant sources, while current popular lithium ion batteries employ flammable organic electrolytes. Therefore, it would be very appealing to utilize zinc ion batteries in environments where safety is very crucial, such as ocean or space systems. However, it is challenging to use zinc ion battery in extremely cold environments due to its aqueous electrolyte. Herein we have prepared new flexible quasi-solid-state zinc ion battery consisting of anti-freezing gum-based electrolyte, high-capacity ammonium vanadate cathode and zinc foil anode, for subzero temperature applications. High concentration zinc salts are used to depress the freezing point and maintain the ionic conductivity of the quasi-solid-state electrolyte. The as-prepared battery cells exhibit a reversible capacity of 275mAh/g at 0.2 A/g at room temperature and 170mAh/g at 0 degreeC. When cycled at 0.5 A/g, the cell delivers an initial discharge specific capacity of 155mAh/g and maintains 119mAh/g after 100 cycles at 0 degreeC, and at -20 degreeC it shows an initial discharge capacity of 122mAh/g and a final capacity of 93mAh/g after 100 cycles. The capacity retention becomes higher when cycled at higher rate. As such, the high-performance quasi-solid-state zinc ion batteries with good mechanical flexibility can find potential wide applications in wearable devices and cold environments.

9:46 AM *S.EN05.04.05
Functionality Design of Nanoparticles via Surface Modification and Templated Synthesis Elena Shevchenko; Argonne National Laboratory, United States

Surface modification of nanoparticles with organic molecules and metal cations is a powerful tool to direct their assembly and catalytic properties. The composition of the inorganic cores determines the ability of nanoparticle to be modified. We will discuss the effect of surface modification and purification on catalytic and photocatalytic properties of the metal and semiconducting nanoparticles. We will also demonstrate that functional materials can be obtained using templated synthesis. The sequential infiltration synthesis which involves diffusion-controlled penetration and subsequent chemisorption of inorganic precursor molecules inside polar domains of the block-copolymer template is proposed as an efficient chemical-physical approach to design highly porous all inorganic single and multi-component nanostructures. We will show that this approach can be efficiently used for the fabrication of films with a low refractive index that enables the design of single-layer and broad-band graded-index anti-reflective coatings (ARCs). The fine-tuning of the refractive index can be achieved via control over the characteristics of the block copolymer templates, and the number of infiltration cycles. We will show that modification of the block-copolymer template with cations of different elements prior to the gas-phase infiltration cycles enables the fabrication of multicomponent structures consisting of highly accessible thermally stable functional centers randomly distributed in the highly porous host matrix.
SESSION S.EN05.01: Alkaline Zinc Batteries
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN05

5:00 AM *S.EN05.01.01
Nickel-Zinc Battery Characteristics and Manufacturability  Eivind Listerd, Adam Weisenstein and Michael Gordon; ZAF Energy Systems, United States

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5:15 AM *S.EN05.01.02
Development of Zn/MnO2 Alkaline Batteries for Grid Storage  Timothy N. Lambert, Matthew Lim, Igor V. Kolesnichenko, David Arnot, Noah B. Schorr, Rachel L. Habing, Logan S. Ricketts, Elijah I. Ruiz and Babu Chalamala; Sandia National Laboratories, United States

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Zn anodes suffer from irreversible shape change, the redistribution of active material, and passivation over repeated charge and discharge, limiting their achievable capacity and lifetime. Pre-saturating the electrolyte with zincate [Zn(OH)4]^2-, which minimizes dissolution of Zn from the anode and reduces the rate of hydrogen evolution, has recently been shown to enhance cycle life for ~10-35% depth-of-discharge (DOD) Zn anodes by ~100-200% (M. Lim et al.); however, Zn(OH)4^2- saturated electrolyte is incompatible with high DOD MnO2, and exacerbates the formation of electrochemically inactive phases, such as ZnMn2O4 at the cathode. Hence, using zincate-blocking separators, able to entrap the zincate within the anode and effectively isolate the MnO2 cathode from Zn(OH)4^2- crossover, while maintaining hydroxide/cation conductivity, is one approach to improve the reversible cycling of a Zn/MnO2 cell at high DOD of both MnO2 and Zn.

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Zn/MnO2 batteries that utilized our selective polymeric separators. Finally, application of these polymeric separators in rechargeable Zn/MnO2 batteries increased cycle life with higher coulombic efficiencies. Various aspects involved in improving the cycle life of Zn anodes at increased DOD, and of the application of our polymeric separators in isolating the MnO2 cathode from soluble zincate and their ability to enable higher DOD cycling in Zn, will be discussed.

This work was supported by the U.S. Department of Energy, Office of Electricity, and the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed herein do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

5:30 AM *S.EN05.01.03  
From Concept through Product to Market—Rechargeable Zinc Manganese Dioxide Batteries Sanjoy Banerjee; Urban Electric Power, United States

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5:45 AM *S.EN05.01.05  
Towards Higher Utilization of Electroactive Materials in Zn-MnO2 Alkaline Batteries Damon Turney1, Gautam G. Yadav1, Andrew Kiss2 and Sanjoy Banerjee1; 1The City University of New York, United States; 2Brookhaven National Laboratory, United States

Market price points for grid-scale energy storage range from $10– $200 per kWh depending on the application. These cost targets are not possible using lithium-ion technology. Fire safety is also a concern and prohibits lithium-ion in some locations. Lead-acid, Ni-MH, and Ni-Cd currently serve as alternatives, but are too expensive, bulky, and/or contain very toxic materials. Recent research from The City College of New York shows a rechargeable alkaline Mn-Zn battery that is very low cost, very safe fire, contains no toxic materials, and has moderately high energy density. Here we review what is currently known about the materials chemistry of this Mn-Zn battery and show new results of in-operando micro-XRD and XRD-imaging chemistry of the Mn electrode. New materials evolution pathways are identified using the in-operando data.

6:00 AM *S.EN05.01.07  
High Energy Density Silver-Zinc Button Cells for Wearable Devices Xia Wei; ZPower, LLC, United States

The silver (Ag)-zinc (Zn) system has the highest theoretical specific (Wh/kg) and volumetric energy density (Wh/L) amongst all rechargeable batteries with the added benefit of safety and non-flammability compared to lithium-ion or lithium metal batteries, which makes it a good and ideal candidate for portable applications like hearing-aids, ear buds and other wearable devices. However, historically, the Ag-Zn battery has suffered from poor rechargeability and low energy utilization. At ZPower, we have tailored the chemistry and engineered a new Ag-Zn battery system, which is highly energy dense and rechargeable, thus making it possible to use it portable applications and giving more power to the consumer to allow them to contribute to a greener future.

As aforementioned, enhancing the capacity of the active materials is paramount for high energy density, which we achieved by developing proprietary additives and approaches. For divalent silver oxide (AgO) cathode, we developed an optimal method of processing the raw materials and novel proprietary conductive coatings for AgO, which allowed integrity control of material properties, faster charge, high capacity utilization and retention for many cycles. The optimal process was verified by experimenting processed AgO cathode under different fast charge rate, where the results showed that it improved the
charge capabilities. The role of these coatings was further studied through charge algorithm cycling, where we found that it reduced AgO cathode’s impedance compared to the control tests and maintained its active surface area. More importantly, we found that the morphology of the proprietary conductive coatings played a crucial role in efficiently utilizing the AgO cathode’s capacity.

For the Zn anode, where it has a theoretical specific capacity of 820 mAh/g; however, Zn has a long history of poor rechargeability due to problems like shape change (zinc redistribution), dendrite formation and passivation. In the past, previous researchers tried altering the Zn formulation to increase utilization; however, these attempts were not fruitful. We have engineered a new Zn anode that can access 94% of its theoretical capacity in a single primary discharge and 56% of its theoretical capacity rechargeably for over 300 cycles. We achieved this breakthrough by developing proprietary additives and methods that localize the Zn to the current collector and prevent dendrite formation. We showed that with incorporating these additives into Zn anode, it further helped mitigating shorting for 400 + cycles.

6:15 AM *S.EN05.01.10
The Case for Zinc Debra R. Rolison1, Brandon J. Hopkins1,2, Christopher N. Chervin1, Megan B. Sassin1, Jeffrey W. Long1 and Joseph F. Parker1; 1U.S. Naval Research Laboratory, United States; 2National Research Council Postdoctoral Associate, United States

Realizing a next-generation battery that meets or exceeds the system energy density of lithium batteries while capturing attributes beyond that of lithium batteries requires a balancing act. The elements that comprise aqueous, safer-than-lithium batteries need to be reasonably naturally abundant, can be acquired through low-risk supply chains, are nontoxic, and can be fabricated, modified, and assembled using green protocols. Zinc checks all those boxes and now that monolithic spongy zinc negative electrodes open new performance terrain—rechargeably cycled at high rate, to deep utilization of the metal—a broad class of rechargeable zinc-based aqueous batteries is finally possible. We perform the systems analysis to show that zinc anodes versus either MnO2 cathodes or air cathodes satisfy energy storage at low cost while meeting the sustainability sought for batteries beyond lithium.

SESSION S.EN05.02: Zinc-Ion Batteries—Cathodes
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN05

5:00 AM S.EN05.02.02
Understanding the Role and Consequence of the Mn²⁺ Additive in the Electrochemical Activity of a ZnMn₂O₄ Cathode in Aqueous Zinc-Ion Batteries Vinod Mathew, Vaiyapuri Soundharrajan, Saiful Islam, Balaji Sambandam, Seokhun Kim, Sungjin Kim, Zulkifli Zulkifli and Jaekook Kim; Chonnam National University, Korea (the Republic of)

The addition of Mn²⁺ additives in the electrolyte of aqueous zinc-ion batteries (ZIBs), in general, has shown to greatly improve the cyclability of the cathode, very recently. Despite a growing number of studies on this issue with respect to manganese-based cathodes, a complete understanding on the role of Mn²⁺ additive towards the electrochemical reaction in ZIBs has not yet been reached. In such a scenario, we studied the electrochemical activity of one such manganese-based cathode, ZnMn₂O₄ (ZMO) with zinc in a ZIB. Zinc manganate, as a ZIB cathode, is an intriguing choice due to its high theoretical capacity and voltage. We compared the electrochemical reaction of this ZMO nanorods cathode obtained through a simple co-precipitation process in the presence of a 0.1 M MnSO₄ (MS) solution as a full-time electrolyte, as an additive in zinc sulfate (ZMS) electrolyte (1 M ZnSO₄ + 0.1 M MnSO₄) and in its absence or a full-time zinc sulfate (ZS) electrolyte (1 M ZnSO₄), respectively. Systematic investigations including ex situ X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) studies revealed the reasons for the superior stability and high reversibility of ZMO in the ZMS electrolyte medium. The exceptional performance was facilitated by the the electrochemical equilibrium between Zn²⁺ and Mn²⁺ ions via a stable Zn²⁺ (de)insertion in the bulk, a reversible electron-deposition/dissolution of MnO₂ from the Mn²⁺ additive in the electrolyte onto/from the surface of the cathode and the reversible Zn-insertion into the formed surface MnO₂ layer. This finding is significant as it is contrary to the conventional understanding that the addition of Mn²⁺ merely tends to prevent manganese dissolution thereby facilitating a stable cycle-life performance of the cathode in ZIBs.
Hierarchical Porous Nickel-Doped Vanadium Dioxide (B) Nanobelts with Ultrahigh Rate Capability and Long Cycle Life for Aqueous Rechargeable Zinc-Ion Batteries

Yi Cai and Rodney Chua; Nanyang Technological University, Singapore

Recently, aqueous rechargeable zinc-ion batteries (ARZIBs) have attracted great attention as compared to commercial lithium-ion batteries due to their unique advantages of high intrinsic safety (non-flammable water-based electrolyte) and low cost. [1-3] Over the past few decades, much progress has been focused on the exploration of suitable cathode materials. Among them, vanadium dioxide (B) has been considered as a potential cathode for ARZIBs owing to its unique double layers of V₄O₁₀ type with tunnels, which can facilitate rapid zinc-ions de/insertion processes. [4] However, the reported VO₂(B) displays a high initial capacity but noticeable capacity fading and especially declines drastically at a high current rate. Compositing VO₂(B) with an electrically conductive matrix has recently been introduced as an effective way to improve the power capability. However, it can only improve the external electric conductivity and the usage of expensive carbon (graphene) negates the cost advantage of vanadium oxides. Therefore, it is of great importance to construct novel VO₂(B) electrode materials with excellent electrochemical performance.

Herein, we report an alternative approach to designing and engineering a hierarchical porous Ni-doped vanadium dioxide (B) nanobelts for ARZIBs. The as-synthesized samples were characterized by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy and transmission electron microscopy (TEM). The existence of Ni dopant was confirmed by the X-ray absorption near-edge structure studies (XANES) and X-ray photoelectron spectroscopy analysis. Electrochemical studies indicate that the Ni-doped VO₂ nanobelts electrode exhibits superior cycling stability and ultrahigh rate capability with long cycle life, which is significantly higher than that of the undoped VO₂(B). This can be attributed to the utilization of Ni dopant to electrical wiring the electroactive material, the intrinsic conductivity of VO₂ can be effectively increased. In-operando XRD measurements coupled with ex-situ TEM micrographs taken at specific potentials were exploited to gain a further understanding into the structural evolution upon cycling and ions storage mechanism. The results of the study can potentially open the doors for the widespread application of constructing other elemental doping materials as cathodes with high rate capability and long cycle life for aqueous rechargeable batteries.

References:

Flexible Zinc Ion Batteries

Chunyi Zhi; City University of Hong Kong, Hong Kong

Prussian blue analogue (PBA)-type metal hexacyanoferrates have been considered as significant cathode materials for aqueous rechargeable zinc batteries (ZBs) due to the open face centered cubic framework, multiple active sites, and environmental benign. However, these PBA-type cathodes, such as cyanogroup iron hexacyanoferrate (FeHCF), suffer from ephemeral lifespan (≤1000 cycles), inferior rate capability (1A g⁻¹), and low operating voltage (ca. 1.2 V). This is because the redox active sites of multivalent iron (Fe(III/II)), which dominates its electrochemical activities, can only be very limited activated and thus utilized. The limited activity is attributed to the spatial resistance caused by the compact cooperation interaction between Fe and the surrounded six cyanogroup per unit, and the inferior conductivity. In this paper, surprisingly, we found high-voltage-scanning can effectively activate the C-coordinated Fe (redox active sites) in FeHCF cathode in ZBs. The activation spurred the increase of capacity at a high operating voltage plateau of ca. 1.5 V. Thanks to this activation, the Zn-FeHCF hybrid-ion battery achieved a record-breaking cycling performance of 5000 (82% capacity retention) and 10000 cycles (73% capacity retention), respectively, together with a superior rate capability of maintaining 53.2% capacity at super-high current density of 8 A g⁻¹ (ca. 97 C). To the best of our knowledge, this is the best cycling performance among all the Zn-PBA batteries up to now. As for the mechanism, the reversible distortion and recovering of crystalline structure caused by the (de)insertion of zinc and lithium ions was revealed. The developed strategy of applying a high-voltage-scan to trigger a greatly enhanced overall electrochemical performance of FeHCF can be easily extended to other PBA materials and other battery systems. We believe this work represents a substantial advance on PBA electrode materials and may essentially
Flexible Quasi-Solid-State Zinc-Ion Rechargeable Batteries for Subzero Temperature Applications

Ying Wang and Yehong Chen; Louisiana State Univ, United States

The emerging zinc ion rechargeable batteries show high potential in the fast expanding market of electrochemical energy storage devices owing to their intrinsic safety and low cost, as they use aqueous electrolytes and zinc anodes that are stable and come from abundant sources, while current popular lithium ion batteries employ flammable organic electrolytes. Therefore, it would be very appealing to utilize zinc ion batteries in environments where safety is very crucial, such as ocean or space systems. However, it is challenging to use zinc ion battery in extremely cold environments due to its aqueous electrolyte. Herein we have prepared new flexible quasi-solid-state zinc ion battery consisting of anti-freezing gum-based electrolyte, high-capacity ammonium vanadate cathode and zinc foil anode, for subzero temperature applications. High concentration zinc salts are used to depress the freezing point and maintain the ionic conductivity of the quasi-solid-state electrolyte. The as-prepared battery cells exhibit a reversible capacity of 275mAh/g at 0.2 A/g at room temperature and 170mAh/g at 0 degreeC. When cycled at 0.5 A/g, the cell delivers an initial discharge specific capacity of 155mAh/g and maintains 119mAh/g after 100 cycles at 0 degreeC, and at -20 degreeC it shows an initial discharge capacity of 122mAh/g and a final capacity of 93mAh/g after 100 cycles. The capacity retention becomes higher when cycled at higher rate. As such, the high-performance quasi-solid-state zinc ion batteries with good mechanical flexibility can find potential wide applications in wearable devices and cold environments.

Reaction Mechanisms for Long-Life Rechargeable Zn/MnO2 Batteries

Yun Li¹, Shanyu Wang¹, James Salvador², Jinfeng Wu¹, Bo Liu¹, Wanli Yang², Jiong Yang², Wenqing Zhang³, Jun Liu¹ and Jihui Yang¹; ¹University of Washington, United States; ²General Motors R&D Center, United States; ³Stanford University, United States; ⁴Shanghai University, China; ⁵Lawrence Berkeley National Laboratory, United States; ⁶Southern University of Science and Technology, China

Rechargeable aqueous Zn/MnO₂ batteries are promising for large-scale grid energy storage applications owing to their low cost, environmentally benign constituents, excellent safety, and relatively high energy density. Their usage, however, is largely hampered by the fast capacity fade. The complexity of the reactions has resulted in long-standing ambiguities of the chemical pathways in Zn/MnO₂. In this talk, I will discuss our latest work on discerning the reaction mechanisms of rechargeable Zn/MnO₂ batteries. We find that both H⁺/Zn²⁺ intercalation and conversion reactions occur at different voltages and that the rapid capacity fading can clearly be ascribed to the rate-limiting and irreversible conversion reactions at a lower voltage. By limiting the irreversible conversion reactions at ~1.26 V, we successfully demonstrated high power and long life that are superior to most of the reported Zinc-ion Batteries or even some lithium-ion batteries.

Transition Metal Oxide Cathodes in Aqueous Zn Batteries—Electrochemistry and Mechanism

Esther S. Takeuchi¹,²; Kenneth Takeuchi¹ and Amy Marschilok¹,²; Stony Brook University, The State University of New York, United States; ²Brookhaven National Laboratory, United States

Rechargeable aqueous Zn batteries are being actively explored due to the high natural abundance and safety associated with Zn, along with the intrinsic nonflammability and the high ionic conductivity of the aqueous electrolyte. While the individual cell voltage is lower than lithium systems, the benefits may be significant for some application where low cost and nonflammability are key considerations. Several cathode systems are under exploration for zinc based batteries. The most frequently explored cathode materials are oxides based on the transition metals manganese or vanadium where both layered and tunnelled structural motifs have been utilized. The discharge mechanisms can be complex where there can be a combination of H⁺ insertion and Zn²⁺ insertion.
Further, the mechanisms can be highly electrolyte dependent. This presentation will discuss exploration of cathode materials used in Zn based aqueous batteries and their electrochemistry. Characterization methods used for the analysis include cyclic voltammetry, galvanostatic discharge, scanning electrochemical microscopy, x-ray diffraction, x-ray photoelectron spectroscopy, scanning electron microscopy with energy dispersive x-ray spectroscopy mapping, and x-ray micro-fluorescence spectroscopy will be highlighted.

5:30 AM S.EN05.03.04
Aqueous Rechargeable Zinc Ion Batteries—Parasitic Reactions and Cycle Life Degradation Balaji Sambandam, Vaiyapuri Soundharrajan, Vinod Mathew, Muhammad H. Alfaruqi, Sohyun Park, Junji Piao and Jaekook Kim; Chonnam National University, Korea (the Republic of)

Since after a new concept of mild acidic aqueous rechargeable zinc-ion batteries (ARZIBs) was introduced in 2011, the technology has been establishing gradually. ARZIBs have proven to be the most eco-friendly energy storage systems (ESSs) as they use zinc as the negative electrode (with a notable large theoretical capacity value of 820 mAh g⁻¹). Zinc is widely available in the Earth's crust and forms a non-toxic, low-cost aqueous electrolyte, thus ensuring low principal investment and high reliability and safety. Till to date, both manganese and vanadium oxides are widely utilized as cathode for this technology and well documented. However, all these oxides have their drawbacks accompanied with their life stability through long-term cycling, particularly at low current rates. The reason is: electrolyte pH change due to metal dissolution during electrochemical reaction, resulting a reversible parasitic reaction which seriously affects the cycling life of a cathode, depending on type of electrolyte being employed. Thus a most reversible product of zinc basic sulfate (ZBS, Zn₄(OH)₆SO₄.nH₂O), an insulating material, formed/dissolved on the cathode-electrolyte interface due to change of electrolyte pH resulting from metal dissolution, when ZnSO₄ utilized as an electrolyte. Irrespective of the cathode used, this side reaction related to ZBS formation is observed in most of the reported ARZIBs. As the reason, most of the reported studies demonstrate long cyclability in metal oxides-based electrodes at very high current drains. In other words, the application of high current drain increases cycle life-span as much as it can before the electrode demonstrates capacity fading due to metal dissolution.

Through Operando analyses, this work establishes the parasitic reaction during electrochemical reaction and document its consequence on the cycle life of the aqueous battery. This will be discussed in detail.

5:00 AM *S.EN05.04.01
Minimal Overhead Storage Technology—Living Forever By Dying Everyday Daniel Steingart; Princeton University, United States

In this work we seek to reduce cost and increase cycle life of a grid scale system by de-emphasizing the requirements for shelf life and short circuit prevention. We show a reconfiguration of the zinc-bromine system creates a system that may “live forever by dying everyday” by eliminating much of the balance-of-plant and exploiting the physical properties of the bromine and zinc. This "solution" also creates new questions. In a system that can safely short circuit at any point, what defines state of charge and state of health? At what point is the battery now “dead”? Is this actually a useful system? The system will be illustrated and current answers to these questions will be discussed.

5:15 AM *S.EN05.04.02
Organic Electrode Materials for Aqueous Batteries—A Mechanistic Study Ye Zhang and Yan Yao; University of Houston, United States

I will present how quinone based organic materials can be designed to address the short cycle life challenges in aqueous batteries -- the structural and chemical instability of anode electrode plays a critical role. Quinone-based organic crystals can store multiple protons with high reversibility, which makes them promising candidates for the anode materials for aqueous batteries. However, the understanding of molecular structures and packing motifs on proton storage and proton-induced...
phase transition process is currently lacking. Recently we utilized the synchrotron-based X-ray surface scattering technique to
probe the tetrachloro-p-benzoquinone (TCBQ) single crystal surface structure change during H\(^+\) insertion in operando. TCBQ
underwent a two-phase reaction during the proton insertion process as the crystal planes of protonated TCBQ (H\(_2\)TCBQ)
formed step-by-step on the crystal surface. Quinone-based polymers have also demonstrated superior performance in aqueous
Na\(^+\), Ca\(^{2+}\), and Zn\(^{2+}\) batteries. We will also present mechanistic studies using in-situ techniques such as EQCM-D, FT-IR, and
optical imaging that provide insights on how to optimize ion-solvent-polymer interactions in aqueous batteries to further
improve cycle life.

5:30 AM *S.EN05.04.05
Functionality Design of Nanoparticles via Surface Modification and Templated Synthesis Elena Shevchenko; Argonne
National Laboratory, United States

Surface modification of nanoparticles with organic molecules and metal cations is a powerful tool to direct their assembly
and catalytic properties. The composition of the inorganic cores determines the ability of nanoparticle to be modified. We
will discuss the effect of surface modification and purification on catalytic and photocatalytic properties of the metal and
semiconducting nanoparticles. We will also demonstrate that functional materials can be obtained using templated synthesis.
The sequential infiltration synthesis which involves diffusion-controlled penetration and subsequent chemisorption of
inorganic precursor molecules inside polar domains of the block-copolymer template is proposed as an efficient chemo-
physical approach to design highly porous all inorganic single and multi-component nanostructures. We will show that this
approach can be efficiently used for the fabrication of films with a low refractive index that enables the design of single-layer
and broad-band graded-index anti-reflective coatings (ARCs). The fine-tuning of the refractive index can be achieved via
control over the characteristics of the block copolymer templates, and the number of infiltration cycles. We will show that
modification of the block-copolymer template with cations of different elements prior to the gas-phase infiltration cycles
enables the fabrication of multicomponent structures consisting of highly accessible thermally stable functional centers
randomly distributed in the highly porous host matrix.

SESSION S.EN05.05: Poster Session: Low-Cost Aqueous Rechargeable Battery Technologies
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday
Morning, November 21, 2020
5:00 AM - 8:00 AM
S-EN05

S.EN05.05.09
Realizing Superior Energy Output for Aqueous Rechargeable Zn-Ion Batteries Using Na2V6O16.3H2O Cathode Vaiyapuri Soundharrajan, Balaji Sambandam, Sohyun Park, Moonsu Song, Sunhyeon Park and Jaekook Kim; Chonnam National University, Korea (the Republic of)

Arguably, aqueous rechargeable Zn-ion Batteries (ARZIBs) are currently the most efficient energy storage device (ESD) for
eco-friendly grid-scale applications, as associated with organic batteries such as lithium and sodium-ion batteries. However,
for the long-standing storage requests the present cathode materials used in the ARZIBs are not sufficient; due to the poor
rate capability and fast capacity fading issues. In the present study, a stable and robust Na2V6O16.3H2O (NVO) Cathode is
introduced for ARZIBs, which found to satisfy the above-said uncertainties by delivering superior electrochemical Zn storing
capability. In situ synchrotron X-ray diffraction technique is used to establish the Zn storage mechanism in NVO cathode
during the Zn (de)insertion stage. The constructed ARZIBs using NVO cathode and metallic Zinc anode in the presence of
low-cost ZnSO4 electrolyte delivers high specific energy of 90 Wh kg\(^{-1}\) at a specific power of 15.8 KW kg\(^{-1}\), and superior
cycling stability (80% capacity retention after 1000 cycles) at 40\(^{\circ}\)C (1c=361 mAh g\(^{-1}\)), illuminating the material rewards for
an eco-friendly ambiances.

S.EN05.05.11
Potassium-Pillared V\(_2\)O\(_5\).\(_n\)H\(_2\)O Nanorods with Exposed Layer Structure as High-Performance Cathode Materials for Low-Cost Aqueous Rechargeable Zinc-Ion Batteries Saiful Islam, Muhammad Alfaruqi, Vinod Mathew, Sohyun Park, Jun Lee, Moonsu Song and Jaekook Kim; Chonnam National University, Korea (the Republic of)

Research interest in aqueous rechargeable zinc-ion batteries (ARZIBs) is growing enormously because of their low-cost and
ecofriendly cell components. However, designing high-performance cathode materials towards practical application of ARZIBs remains a great challenge. In this contribution, groundbreaking work on the potassium-pillared V$_2$O$_5$·nH$_2$O (K$_{0.5}$V$_2$O$_5$·nH$_2$O) nanorod with exposed layer structure as high-performance cathode for ARZIB is presented. The storage mechanism of the K$_{0.5}$V$_2$O$_5$·nH$_2$O cathode in ARZIB is systematically elucidated using a combined of in operando synchrotron X-ray diffraction, ex situ synchrotron X-ray absorption spectroscopy, ex situ TEM analyses, and first-principle calculations. The K$_{0.5}$V$_2$O$_5$·nH$_2$O cathode exhibits a remarkable discharge capacity of 439 and 286 mAh g$^{-1}$ at current densities of 50 and 3000 mA g$^{-1}$, respectively. Furthermore, it recovers 96% of the capacity after 1500 cycles at 8000 mA g$^{-1}$. Impressively, the Zn/K$_{0.5}$V$_2$O$_5$·nH$_2$O battery offers a specific energy of 121 Wh kg$^{-1}$ at a high specific power of 6480 W kg$^{-1}$. The superior performance of the cathode is attributed to its unique exposed layer structure with high surface energy, high conductivity, and low migration barrier. This study provides an insight for designing high-performance cathode materials for ARZIBs and other electrochemical systems.

S.EN05.05.12
Improving Performance of Zn Ion Battery by 3D Engineering of Zn Anodes
Sanket D. Bhoyate, Irsalan Cockerill, Marcus L. Young and Wonbong Choi; University of North Texas, United States

Batteries play significant role in powering modern electronic devices. Li-ion batteries are widely used in such applications. However, there are several factors such as scarcity of Li metal, major safety issues, cost and life cycle that can affect the long-term applicability of Li-batteries. Recently, aqueous Zn-ion batteries have caught research attention due to their characteristic properties such as intrinsic safety, low cost and high theoretical volumetric capacity desired for safer energy storage system. Due to high molecular weight of Zn metal, the active weight utilization of Zn anode plays major role in designing commercial batteries. Inefficient use of Zn ions from anodes can result in inferior battery performance. The active utilization of Zn anodes can be improved by decreasing the unwanted weight from Zn anodes and increasing electrochemically active surface area. In this study, we used additive manufacturing assisted technique to fabricate 3D Zn anode. Our results suggest, that 3D Zn anode show higher rate capability at high charge-discharge current as compared to commercial Zn foil. The higher performance owes to the porous surface area of designed 3D Zn anode and can be used for high-performance battery application.

SESSION S.LP03.02: Live Poster Session: Energy, Storage and Conversion (S.EN05, S.EN06, S.EN09 and S.EN11)
Session Chairs: Joshua Gallaway, Jaekook Kim and Damon Turney
Tuesday Afternoon, December 1, 2020
5:15 PM - 7:15 PM
S.EN05

S.EN05.05.09
Realizing Superior Energy Output for Aqueous Rechargeable Zn-Ion Batteries Using Na$_2$V$_6$O$_16$.3H$_2$O Cathode
Vaiyapuri Soundharrajan, Balaji Sambandam, Sohyun Park, Moonsu Song, Sunhyeon Park and Jaekook Kim; Chonnam National University, Korea (the Republic of)

Arguably, aqueous rechargeable Zn-ion Batteries (ARZIBs) are currently the most efficient energy storage device (ESD) for eco-friendly grid-scale applications, as associated with organic batteries such as lithium and sodium-ion batteries. However, for the long-standing storage requests the present cathode materials used in the ARZIBs are not sufficient; due to the poor rate capability and fast capacity fading issues. In the present study, a stable and robust Na$_2$V$_6$O$_16$.3H$_2$O (NVO) Cathode is introduced for ARZIBs, which found to satisfy the above-said uncertainties by delivering superior electrochemical Zn storing capability. In situ synchrotron X-ray diffraction technique is used to establish the Zn storage mechanism in NVO cathode during the Zn (de)insertion stage. The constructed ARZIBs using NVO cathode and metallic Zinc anode in the presence of low-cost ZnSO$_4$ electrolyte delivers high specific energy of 90 Wh kg$^{-1}$ at a specific power of 15.8 KW kg$^{-1}$, and superior cycling stability (80% capacity retention after 1000 cycles) at 40C (1c=361 mAh g$^{-1}$), illuminating the material rewards for an eco-friendly ambiances.

S.EN05.05.11
Potassium-Pillared V$_2$O$_5$.nH$_2$O Nanorods with Exposed Layer Structure as High-Performance Cathode Materials for Low-Cost Aqueous Rechargeable Zinc-Ion Batteries
Saiful Islam, Muhammad Alfaruqi, Vinod Mathew, Sohyun Park, Jun Lee, Moonsu Song and Jaekook Kim; Chonnam National University, Korea (the Republic of)
Research interest in aqueous rechargeable zinc-ion batteries (ARZIBs) is growing enormously because of their low-cost and eco-friendly cell components. However, designing high-performance cathode materials towards practical application of ARZIBs remains a great challenge. In this contribution, ground-breaking work on the potassium-pillared V$_2$O$_5$.nH$_2$O (K$_{0.5}$V$_2$O$_5$.nH$_2$O) nanorod with exposed layer structure as high-performance cathode for ARZIB is presented. The storage mechanism of the K$_{0.5}$V$_2$O$_5$.nH$_2$O cathode in ARZIB is systematically elucidated using a combined of in operando synchrotron X-ray diffraction, ex situ synchrotron X-ray absorption spectroscopy, ex situ TEM analyses, and first-principle calculations. The K$_{0.5}$V$_2$O$_5$.nH$_2$O cathode exhibits a remarkable discharge capacity of 439 and 286 mAh g$^{-1}$ at current densities of 50 and 3000 mA g$^{-1}$, respectively. Furthermore, it recovers 96% of the capacity after 1500 cycles at 8000 mA g$^{-1}$. Impressively, the Zn/K$_{0.5}$V$_2$O$_5$.nH$_2$O battery offers a specific energy of 121 Wh kg$^{-1}$ at a high specific power of 6480 W kg$^{-1}$. The superior performance of the cathode is attributed to its unique exposed layer structure with high surface energy, high conductivity, and low migration barrier. This study provides an insight for designing high-performance cathode materials for ARZIBs and other electrochemical systems.

**S.EN05.05.12**

**Improving Performance of Zn Ion Battery by 3D Engineering of Zn Anodes**

Sanket D. Bhoyate, Irsalan Cockerill, Marcus L. Young and Wonbong Choi; University of North Texas, United States

Batteries play significant role in powering modern electronic devices. Li-ion batteries are widely used in such applications. However, there are several factors such as scarcity of Li metal, major safety issues, cost and life cycle that can affect the long-term applicability of Li-batteries. Recently, aqueous Zn-ion batteries have caught research attention due to their characteristic properties such as intrinsic safety, low cost and high theoretical volumetric capacity desired for safer energy storage system. Due to high molecular weight of Zn metal, the active weight utilization of Zn anode plays major role in designing commercial batteries. Inefficient use of Zn ions from anodes can result in inferior battery performance. The active utilization of Zn anodes can be improved by decreasing the unwanted weight from Zn anodes and increasing electrochemically active surface area. In this study, we used additive manufacturing assisted technique to fabricate 3D Zn anodes. Our results suggest, that 3D Zn anode show higher rate capability at high charge-discharge current as compared to commercial Zn foil. The higher performance owes to the porous surface area of designed 3D Zn anode and can be used for high-performance battery application.

**S.EN06.04.02**

**Zinc Oxide Nanostructures Synthesized by a Simple Hot Water Treatment Method for Photocatalytic Degradation of Organic Pollutants in Water**

Ranjitha Hariharalakshmanan, Busra Ergul, Nawzat S. Saadi, Khalidah Al-Mayalee and Tansel Karabacak; University of Arkansas at Little Rock, United States

The use of zinc oxide (ZnO) nanostructures as a photocatalyst for the degradation of organic pollutants in water has received significant attention over the recent years. However, synthesis methods for producing ZnO nanomaterials are generally costly, complicated, and hazardous to the environment. In this work, we demonstrate the synthesis of zinc oxide nanostructures by a simple hot water treatment (HWT) method and the photocatalytic activity of the hence produced nanomaterials. HWT is a one-step, low-cost, eco-friendly, and scalable nanostructure growth method. By HWT, various metal oxide nanostructures can be produced simply by the interaction of metals with hot water without the need for any chemical additives in the solution. Growth of metal oxide nanostructures by HWT involves the formation of metal oxides and their release from the surface of the metal into water, the migration of the metal oxides in water and their re-deposition at a different part of the metallic surface, which initiates the growth of nanostructures. In this study, we used zinc powder and plates for producing the ZnO nanostructures by HWT in DI water at 75 °C. Scanning electron microscopy images and X-ray diffraction were utilized to verify the formation of ZnO nanostructures. Zinc plates produced a suspension of ZnO nanostructures in water, while on the other hand Zn powder resulted in a predominantly core-shell geometry of Zn particle-core and ZnO nanostructures-shell also mixed in water. We used these nanostructures + water suspensions for our photocatalytic degradation studies. Methylene blue was used as a model organic pollutant. We mixed the ZnO nanostructure suspension with methylene blue and exposed it to UV light. The degradation of methylene blue was observed by measuring its absorbance values using a UV-Visible spectrophotometer over a period of four hours. We observed a 20% decrease in the concentration of methylene blue in four hours when nanostructured Zn/ZnO core-shell powder suspension was used, and a 30% decrease was achieved when ZnO nanostructure-only suspension was used. Methylene blue alone was also exposed to UV light for the same period as a control experiment and we did not observe any significant decrease in its concentration. These preliminary results indicate that hot water treatment method presents a very simple, cost-effective, scalable, and eco-friendly alternative for the synthesis of zinc oxide nanostructures for photocatalytic water treatment applications.
Mitigating atmospheric CO₂ concentration is a great challenge for the twenty-first century. It can be done only by capturing and converting CO₂ into useful fuels with the help of catalysts. Knowledge of the reaction mechanism in CO₂ hydrogenation reactions is key to the rational design of highly efficient catalysts. Here, we investigate the CO₂ conversion into methanol on Rh intercalated Graphene/SiC using density functional theory calculations and kinetic Monte Carlo simulations. The adsorption energy, bonding configuration, bond lengths, and vibrational frequencies of all the surface intermediates involved in the reaction mechanisms are studied. Present results on methanol production suggest that the hydrogenation of CO₂ to CO occurs via the reverse-water-gas shift (CO₂ + H₂ → CO + H₂O) reaction rather than formate (HCOO⁻) or direct C−O bond cleavage pathways. The produced CO can either desorb or further react with hydrogen to produce CH₄ or CH₃OH since the adsorption energy of CO is low. The intermediates of the CO₂ pathway for methanol production includes *OCOH, CO, *CHO, *CHOH, and *H₂COH. The reaction barrier energy for each elementary steps involved in CO₂ hydrogenation will be discussed, and that can provide further insights into the reaction mechanism. Finally, we will also discuss how the energetics affects the kinetics of the reaction, such as the overall rates for CO₂ conversion and the production of CO, CH₃OH, and CH₄ under reaction condition.

Plasmonic photocatalysis offers the promise of using light as the energy source to drive a variety of thermal energy-intensive phonon-driven chemical reactions close to room temperature [1]. Industrially relevant heterogeneous catalytic reactions targeted by plasmonic photocatalysis include CO₂ reduction, water-splitting to generate H₂, hydrocarbon reforming, Fischer-Tropsch reactions, synthesis of azo dyes, nitrogen fixation, hydrogenation reactions, and the oxidative degradation of organic compounds. Plasmonic catalysis also offers unique chemical bond activation mechanisms that differentiate hot carrier-driven chemical reactions from routine carrier-driven catalysis [2].

Herein, we present the bottom-up synthesis of large area PhCs consisting of arrays of self-organized vertically oriented TiO₂ nanotubes (TNTAs) with periodically modulated diameters, grown by a charge controlled pulsed electrochemical anodization (CCPEA) technique. The CCPEA technique enables superior control over the optical resonances exhibited by TNTA PhCs, compared with galvanostatic & potentiostatic pulsed anodization processes. When TNTA PhCs with well-defined photonic stop-bands are decorated or embedded with nanoparticles (NPs) of Au, Ag, CuPt, TiN, etc, plasmonic photonic crystals result.

TNTAs partially embedded with Au NPs are shown to be excellent photoanodes for visible light-driven photoelectrochemical water-splitting in alkaline electrolytes. Embedding Au NPs in the nanotube walls as opposed to decorating them results in high extinction coefficient, high Q-factor, red-shifted plasmon resonances [3] that facilitate the injection of hot electrons formed by plasmon dephasing, into the conduction band of TiO₂ while residual hot holes oxidize water to O₂. The observation of photoelectrochemical quantum yields approaching 30 % for visible wavelengths indicates surprisingly efficient hot carrier harvesting. Likewise, TNTA PhCs decorated with Au NPs are also excellent photocatalysts for the vapor phase reduction of CO₂ into light hydrocarbons. TNTAs conformally coated with titanium nitride exhibit near-infrared resonances and appreciable photocatalytic activity [4]. The TNTA structure provides a high density of active surface sites for reactant adsorption, and its own optical properties (PhC and Mie scattering effects) [5] interact with the plasmons to influence the photocatalytic behavior.

REFERENCES

**S.EN06.04.10**
**Solar Fuel Production—Opportunities for Nanostructures** Zhiyang Zou; Nanjing University, China

The photocatalytic and photoelectrochemical reduction of water or CO₂ is an intriguing approach to producing sustainable solar fuels, and has attracted growing and intense interest. Nanostructuring of photocatalysts and photoelectrodes has been proven to be a strong strategy to dramatically improve overall solar-to-fuel conversion efficiencies. Another technological barrier for the practical implementation of solar fuel production is long-term material durability, which has recently been well addressed by using conformal coatings of protective layers onto the narrow band-gap semiconductors that are suitable for efficient solar-to-fuel conversions but photoelectrochemically unstable. These significant progresses may lead us to the practical implementation of solar fuel production. We focused on the exciting progresses achieved by using nanostructuring strategies, specifically regarding how the nanostructure influences the charge transport and separation. Special attention was paid to investigate how a nanoscale coating (overlay) passivates the surface states, thereby reducing the surface electron hole recombination, and how a nanoscale coating (protective layer) prevents the photocorrosion or photopassivation of the semiconductors with optimal band gaps. We hope that the design strategies using these nanostructures will offer new and greater opportunities for efficient solar fuel production to existing photocatalytic and photoelectrochemical systems.

**S.EN06.04.11**
**Low Temperature and Green Synthesis of Diethylenediamine Functionalized Reduced-GO Grafted on SiC for Photodegradation and Conversion of Organic Pollutants to Useful Fuels** Olusegun Abass; Nanyang Technological University, Singapore

Conventional photocatalysts based on metals and semiconductors are sometimes rigid and possesses stability issues when applied in the treatment of industrial wastewater. Thus, novel photocatalysts based on polymer/nanomaterial composites are attracting more interest. Although much effort has been devoted to acquire catalysts with high efficiency and long-term durability, this work puts forward a simple and green three-steps procedure for synthesis of diethylenediamine-modified reduced graphene oxide (DD-rGO) grafted on a magnesio-thermically produced silicon carbide (SiC) to achieve one-vessel conversion of organic pollutants into useful fuels such as methanol and ethanol under simulated solar irradiation. The mechanism behind the distinct reactivity and stability of the as-prepared photocatalyst was proposed. We expect that these entirely new nanocomposite structures will not only pave way for the development of highly efficient and stable photocatalyst systems but also have a wider impact in applications (such as water treatment) where catalysts stability is essential.

**S.EN06.04.13**
**Sodium Niobate (NaNbO3) Nanorods Coupled with RGO Nanocomposite for Enhanced Photoelectrochemical Water Splitting** Dheeraj Kumar and Neeraj Khare; Indian Institute of Technology Delhi, India

The utilization of fossil fuel subsidiaries, for example, coal, heavy oil, natural gas and petrol have transformed into global issue of environment concern. The use of energy is rapidly expanding with rising population in view of which there is a need of utilizing efficient green sustainable energy sources to fulfil the requirements of energy supply [1]. The solar light based energy can be converted and stored in the form of fuels, for instance, generation of hydrogen (H₂) by photoelectrochemical (PEC) water splitting appears to be a potential alternative to the fossil fuels [2]. PEC water splitting is one of the most attractive technology for H₂ generation using a semiconductor nanocomposite materials [3, 4]. In the present work, hydrothermally grown sodium niobate nanorods (NaNbO₃-NRs) has been successfully coupled with reduced graphene oxide (RGO) nanosheets by using reflux method. Furthermore, the potentiality of the synthesized nanostructures has been investigated for photoelectrochemical (PEC) water splitting. A ~4 fold enhancement in the photocurrent density is demonstrated by fabricated RGO/NaNbO₃-NRs nanocomposite photoanode than that of NaNbO₃-NRs photoanode under UV-visible light illumination. The enhancement in the PEC activity of RGO/NaNbO₃-NRs nanocomposite
is attributed to the more absorption of visible light of the solar spectra and increase the mobility of photogenerated charge carriers which improves the separation efficiency and reduces the recombination of charges. The possible mechanism responsible for the PEC water splitting have been proposed.

References

S.EN06.04.14
Non-Noble Metal Plasmonic Nanoparticles as Highly Efficient Light Absorber for Solar Steam Generation Fan Yang and Yadong Yin; University of California, Riverside, United States

Plasmonic nanoparticles have attracted great interest in harvesting solar energy due to their excellent capability in photothermal conversion. However, noble-metal-based plasmonic nanoparticles typically exhibit a narrow absorption peak, which limits their ability to fully utilize solar energy. Compared with conventional noble metal nanoparticles, transition metal nanoparticles show relatively broad resonance band, allowing absorption of a larger fraction of solar radiation. However, the application of these nanoparticles is limited due to their poor stability, especially in the presence of oxygen and water. In this presentation, we report the synthesis of Ni@C@SiO₂ core-shell nanoparticles that can be used as light absorbers. The stability of Ni nanoparticles is greatly enhanced by a layer of densified SiO₂. Moreover, by adding a carbon layer between Ni and SiO₂, the absorption peak of Ni can be expanded and red-shifted to maximize the overlapping between the absorption spectra of core-shell nanoparticles and the solar radiation spectra. The colloidal nature of the nanoparticles allows their easy processing into a thin film that can be attached to a floating melamine foam, producing an integrated solar steam generator. The three-layered core-shell nanoparticles exhibit an excellent photothermal property and high steam generation efficiency under solar illumination.

S.EN06.04.19
Photoelectrochemistry of Cobaloxime-Modified Gallium Phosphide and Gallium Arsenide Surfaces Nghi Nguyen, Brian L. Wadsworth, Edgar Reyes Cruz, Daiki Nishiori and Gary F. Moore; Arizona State University, United States

Photoelectrochemistry provides a strategy for creating fuels from sunlight. In this poster presentation, I will describe the chemistry of immobilizing polypyridyl coatings containing cobaloxime-type catalysts onto either GaP or GaAs surfaces. When wired in a three-electrode configuration with appropriate counter and reference electrodes, the hybrid constructs use light to power the production of hydrogen gas with near unity faradaic efficiency from aqueous solutions in the absence of sacrificial chemical reductants and with no electrochemical forward biasing. When operating at the equilibrium potential of the hydrogen evolution reaction under simulated 1-sun illumination, the modified-GaP and GaAs assemblies produce current densities of 1 and 10 mA cm⁻², respectively. Analyses of the wavelength-resolved external and internal quantum efficiencies show the modified-GaP assemblies are active over wavelengths ranging from 300 to 550 nm, and the modified-GaAs assemblies are active over wavelengths ranging from 300 to 870 nm. The cobaloxime-modified GaAs thus gives a higher rate of photoelectrochemical fuel production due to the improved spectral overlap of the semiconductor's absorption properties with the solar flux spectrum.

Human-engineered materials capable of generating fuels from sustainable energy sources provide an approach to satiating modern societies' energy demands, with minimal environmental impact. In this poster presentation, I will describe hybrid photoelectrosynthetic assemblies composed of gallium phosphide (GaP) functionalized with metalloporphyrin complexes of five different transition metal ions: Fe(III), Co(II), Ni(II), Cu(II), and Zn(II). Surface attachment of these metalloporphyrin complexes was achieved using a previously reported UV-induced photochemical grafting method. The photoelectrochemical properties of these heterogeneous-homogeneous materials will be contrasted with electrochemical properties of the isolated, homogeneous metalloporphyrins and other previously reported heterogeneous-homogeneous constructs.


Self-Assembling Effects of NiFe Hydroxide on 3D Nano-Morphology and Enhanced Oxygen Evolution Performance Li Ren, Jiaqi Wang, Fangfei Li, Yang Yang, Jingru Liu, Kuizhou Dou and Yongqiang Yu; Jilin University, China

Layered double hydroxide (LDH) has been proven to have excellent performance in water splitting reactions, especially toward the oxygen evolution reaction (OER). The morphology of NiFe LDH is one of the key factors in improving its electrochemical performance. However, the controlling factors and mechanisms of morphological evolution of the nanoflower-shaped NiFe LDH remain poorly understood. In this study, NiFe LDH nanoflowers were synthesized by hydrothermal method, and the morphology and structure of NiFe LDH crystals are carefully controlled during the synthetic stage. The results indicate that NiFe LDH primary nano flakes rapidly agglomerate to form a nucleus matrix at the initial stage. Subsequently, these nano flakes are laterally aggregated and connected orderly on the substrate to form nanoflowers, and the nano-petals are generated by a rotating and edge-to-edge orientation attachment (OA) mechanism. The morphological evolution occurred by staged three-dimensional OA process plays an essential role in the self-assembly of flower-like NiFe LDH crystals. The well-formed NiFe LHD nanoflowers, grown by 10 hours of hydrothermal treatment, exhibits excellent OER performance in alkaline electrolyte, which displays very low overpotential of 190 mV at the current density of 10 mA cm⁻² and small Tafel slope of 35 mV per decade (much better than RuO₂ catalyst). Furthermore, the prepared NiFe LDH still showed high stability after 10,000 cycles of cyclic voltammetry tests. This work provides new insights into the relationship between catalyst morphology and OER performance, and provides new fundamental understanding of hydrothermal synthetic process of NiFe LDH.
Some emerging alloys, such as Mg alloy, are susceptible to galvanic corrosion, consequently accelerating corrosion process and resulting in severe financial loss. The galvanic corrosion potential and current obtained by experimental polarization curves could differ a lot between different literature. Herein, we proposed a semi-empirical model based on the mixed potential theory and first principles calculation to analyze the galvanic corrosion of the metal alloys. Our model is further validated in the case of Mg-Ge alloys, which is composed of anode Mg matrix and cathode Mg2Ge second phase. The combination of the large anode equilibrium potential difference between Mg and Mg2Ge, and the Schottky barrier across the interface indicates that the Mg2Ge second phase can prevent the Mg grain from serving as the cathode and impede the electron transfer between the Mg grains. First principles calculations on the kinetics of hydrogen evolution reaction upon Mg2Ge reveal that the rate-determining step is the hydrogen adsorption, which is extremely energetically unfavored but an inevitable intermediate state. The estimated exchange current of the hydrogen evolution upon Mg2Ge is about 3 orders of magnitude smaller than that on pure Mg, depressing the hydrogen exchange current upon Mg2Ge and hence the galvanic corrosion of the Mg-Ge alloys. Moreover, some other Mg alloys, such as Mg-Zn and Mg-Sc, were also investigated, which is in close agreement with the experimental observations. Our model is capable of predicting the galvanic corrosion behavior and provide a promising perspective for designing better corrosion-resistant metal alloys.

Fuel cell technologies (FC) make hydrogen (H2) a promising fuel to produce electrical energy due to their great efficiency and minimal pollution emission. However, one problem is to optimize pure H2 production. On account of 96% global H2 production is performed by steam reforming (SR) (76% from natural gas), H2 purification process must be improved in SR plants to achieve a short-term hydrogen economy.

In order to avoid a cooling process from SR gas in a purification step, materials with high thermal stability and selective oxidation and chemisorption capability of CO must be developed. This work summarizes Li2MnO3 behavior as a selective CO oxidizing-captor to purify H2 from SR gas. Li2MnO3 was synthetized by the solid-state method and characterized by XRD, N2 adsorption-desorption and SEM. To evaluate CO chemisorption process in Li2MnO3, dynamic thermal analyses were performed using different gas flow compositions (CO, CO-O2, CO2, CO2-O2 and N2). These experiments showed that CO chemisorption is only produced in oxygen absence. Furthermore, CO2 chemisorption was not evidenced at any CO2 partial pressure.

Based on these results, isothermal experiments were performed between 550 and 700 °C into a CO atmosphere (N2 balanced). The isothermal products were identified as Li2CO3 and MnO by XRD. It must be pointed out that at temperatures lower than 625 °C Li2MnO3 was identified as well. These results demonstrated that CO is chemisorbed as Li2CO3. It may be produced by a surface CO oxidation step (into CO2) that involves the evolution from Li2MnO3 (Mn4+) into LiMnO2 (Mn3+) or even into MnO (Mn2+).

An interesting ~2% weight loss was observed at the beginning of all the isotherms (before weight gain started). In order to elucidate the process associated to this, several thermogravimetric and catalytic experiments were carried out. Their solid and gas products were identified by XRD and mass spectrometry, respectively. The catalytic experiments showed CO2 production at the same temperature range where Li2MnO3 weight loss take place. Moreover, after this ~2% weight loss occurs and before weight gain process would perform, the material composition was analyzed by XRD and ATR-FTIR, where Li2MnO3 was the only crystalline phase identified in addition to carbonates.

Based on these results, it may be pointed out that an oxidation step is performed at the material surface to oxidize CO into CO2, where some part of it is chemisorbed as Li2CO3, while the rest is released from the material’s surface. In addition, lithium diffusion from bulk to surface in Li2MnO3 may be triggered by oxygen vacancies formation (at surface) due to CO oxidation. This could explain wherefore chemisorption process was not performed in CO2 atmosphere or in oxygen presence. To further analyze Li2MnO3, dynamical and isothermal experiments were performed varying the CO-CO2 partial pressures. These results demonstrated that if CO2 is involved into the gas flow composition, the CO oxidation-capture process is displaced to higher temperatures and the total weight gain decreases as consequence of less superficial oxygen vacancies formation. Moreover, kinetic constants were calculated using the Jander-Zhang diffusion model, which can be related to ΔH° by the Eyring equation. Results showed that, in addition of CO2, kinetics diffusion become slower than those obtained into a CO atmosphere, although the ΔH° values decreased.

Finally, Li2MnO3 was dynamical tested on H2 and H2-CO atmospheres (Ar balanced). These experiments showed a preference oxidation of CO over H2. Nevertheless, ~10% of hydrogen was oxidized into water while CO was chemisorbed.
Evaluation of Boron Doped Reduced Graphene Oxide as IrO$_2$ Support for Efficient Oxygen Evolution Reaction

Prerna Joshi$^{1}$, Hsin-Hui Huang$^{2}$, Masanori Hara$^{1}$ and Masamichi Yoshimura$^{1}$; $^{1}$Toyota Technological Institute, Japan; $^{2}$Japan Fine Ceramics Center, Japan

With depleting fossil fuel reserves and increasing environmental problems, novel strategies have been developed based on renewable energies. A major source of renewable energy is water, which can produce hydrogen energy in large amounts. Electrochemical water splitting is an excellent way to produce hydrogen as an energy source. For generation of hydrogen at a specific rate, under ideal conditions, 1.23 V must be supplied to the water electrolyzers to allow hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in a feasible manner. In practice, OER is a complex reaction with slow kinetics and low overpotential, hence, precious metal catalysts such as iridium and ruthenium oxides (IrO$_2$, RuO$_2$) are used to reduce the overpotential for OER$^1$. However, their high cost and low natural abundance limit their extensive commercialization. One of the plausible approach can be the reduction of metal loading with the use of conductive support. For metal catalysts, the reduction in size of the catalysts (formation of nanoparticles (nps)) can help in increasing active surface area. Further, for conducting support, doped graphene can be used as a support because it can tune the electronic structure of catalysts to improve specific activity. In the current research, we have studied the electrochemical activity of IrO$_2$ nps catalyst supported on heteroatom-doped reduced graphene oxide (rGO) as the carbon support. Along with alteration of the electronic structure of the IrO$_2$ nps, heteroatom-doping of graphene$^2$ also promotes ion diffusion at the electrode-electrolyte interface, improving the overall performance of the catalyst.

Graphene oxide (GO) was prepared from synthetic graphite (Sigma Aldrich) by modified Hummers’ method$^3$. For boron doping, boric anhydride (B$_2$O$_3$, BA) was used as the precursor. Briefly, BA and GO were mixed together and ultrasonicated in water for 1 hour. The mixture was freeze dried and the obtained powder was pyrolysed at 1000 °C for 60 min in N$_2$ atmosphere. The pyrolysed sample was washed with boiling water and ethanol to yield boron-doped rGO (B-rGO). As the second step, IrO$_2$ nps were decorated onto B-rGO by hydrothermal synthesis at 150 °C for 4 h using H$_2$IrCl$_6$ as the Ir precursor. The synthesized materials were characterized for its chemical composition, morphology and electrocatalytic activity using various analytical techniques such as X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), cyclic voltammetry (CV) and linear sweep voltammetry (LSV).

XPS analysis of the synthesized catalyst, IrO$_2$-B-rGO revealed the presence of all constituent elements at their respective binding energies. The XPS spectra were deconvoluted to obtain the types of constituent C and B. Ir 4f peaks for IrO$_2$-B-rGO were obtained at lower binding energies than the unsupported IrO$_2$ powder confirming the change in electronic states of Ir due to boron doping. Further, EDX analysis indicated B to be present in ~2.0 wt% and Ir in 3.3, 7.1 and 19.6 wt%. TEM results exhibited the uniform dispersion of IrO$_2$ over the wrinkled B-rGO sheets with an average particle diameter of 1.5 nm. Electrochemical analysis in 0.5 M H$_2$SO$_4$ with Ir loading of ~140 µg cm$^{-2}$ on glassy carbon (GC) electrode showed that the onset potential was 1.41 V vs RHE for IrO$_2$-B-rGO which was ~90 mV lower than that of IrO$_2$ decorated on undoped rGO (IrO$_2$-rGO). Despite the low Ir content, higher current density was obtained for B-doped catalyst as compared to the IrO$_2$-rGO. Increase in current density for B-doped catalyst is attributed to charge redistribution in graphene lattice which alters the electronic states for Ir and provides additional active centres for catalysis.


Alkylphosphine as a Ligand for Shape-Controlled Synthesis of Metal Nanostructures

Shutang Chen and Gugang Chen; Honda Research Institute USA Inc., United States

Metal nanoparticles with high index facets and controllable shape have demonstrated excellent catalytic performance because of their unique surface chemistry. Generally, the selection of proper ligand plays an important role for the shape-control of nanoparticles. Here, different kinds of alkylphosphines with high temperature solution reduction method are adopted to synthesize metal nanostructures. With increasing chain length of alkylphosphines, different morphologies of copper nanoparticles were synthesized in a hydrophobic system, such as nanocubes, tetrahedron nanoparticles, nanowires, and nanosheets. All these copper nanostructures demonstrated excellent catalytic performance and selectivity to carbon dioxides reduction reaction. Such simple strategy is also extended to the design of other metal nanoparticles for their potential
applications in catalysis, sensor, and electronics.

**S.EN11.07.12**

**First Principles Investigation of the Influence of Magnetic Moment on Single Atom Earth-Abundant Transition Metal Catalysts for Integrated 3D Graphene Structures**

Chloe Groome and Regina Ragan; University of California, Irvine, United States

Single atom catalysis (SAC) represents a promising design for the next generation of robust catalysts. These systems, which are commonly single metal atoms stabilized on carbonaceous materials, maximize catalytic performance while simultaneously minimizing the use of expensive and scarce platinum-group metals (PGM). While it is accepted that the molecular environment of a SAC is of crucial consequence to the chemical activity, the exact catalytic sites and chemical pathways responsible have been a matter of some controversy. For industrially practical non-PGM SAC, optimizing the defect environment stabilizing the single metal atom is necessary for enhanced performance. We will present work using a first principles approach for materials discovery to investigate three less studied earth abundant transition metals (V, Mo, Ta) stabilized on single vacancy and pyridinic N-doped defect moieties on graphene substrates to understand the role of electronic transfer, spin state and steric effects on SAC. Our results of all investigated metals demonstrate single atom stability on graphene substrates with both defect moieties. By modeling carbon monoxide oxidation, a common benchmark reaction, facilitated by these defect stabilized SAC with climbing image-nudged elastic band (CI-NEB) calculations, we find that all activation energies for transition metals stabilized on the pyridinic N-doped graphene surface defect are ~0.8 eV or lower. These low activation energy barriers suggest that the CO oxidation reaction would proceed at room temperature with pyridinic N-dopants present in the defect environment. The CI-NEB calculations further illustrate that SAC of Ta and V on pyridinic N doped graphene significantly decrease the activation energy of CO oxidation by 27% and 44%, respectively. Bader charge analysis reveals that the electronic charge transfer is surprisingly similar across the two defect moieties investigated for all four earth-abundant transition metals. However, the pyridinic N-dopant introduces an additional magnetic moment of 0.53 µB on average. Plotting the density of states of CI-NEB transition states shows spin destabilization of O2 peaks near the Fermi level, suggesting that these imparted magnetic moments could be destabilizing the O2 bond and hence lowering activation energies for CO oxidation in some cases. We will present results suggesting that magnetic moment could play a significant role in enhancing catalytic performance of SAC on nitrogen doped graphene substrates, as well as more traditionally understood mechanisms such as charge transfer and steric effects. Computational design of materials is used to define processing conditions for three-dimensional porous graphene structures. Fabrication and characterization of macroscopic graphene structures with high surface area and architectures to facilitate mass transport will also be presented.

**S.EN11.07.09**

**Graphene- and CNT- Hybrids with Metallic and Metalorganic Framework Nanostructures as Reversible and Sustainable H₂ Storage Media**

Suresh Kuppireddy, Anish Varghese and Georgios Karanikolos; Khalifa University, United Arab Emirates

H₂ storage constitutes a barrier in decarbonizing the energy economy and expanding H₂ utilization into large scale. Design of novel nanostructured materials is currently a high research priority toward a permanent solution to this challenging problem, and development of safe, dense, solid state media to substitute cryogenic storage. In this work, we present in-situ grown hybrid nanostructures based on graphene and CNTs supporting metalorganic framework (MOF) and metallic (e.g. Mg) clusters and nanocrystallites exhibiting controlled microstructure, porosity, and interface characteristics. The resulting nanohybrids exhibit increased storage capacity, while the stability of the active sites is preserved through the presence and controlled coating by the graphitic layers.

**S.EN11.07.18**

**Studies in Pulsed Laser Deposition of FeWO₄ Thin Films**

Chandler W. Cotton, Braden L. Spiller, Sumner B. Harris and Renato P. Camata; The University of Alabama at Birmingham, United States

Complex metal oxides such as metal tungstates, niobates, cuprates, and vanadates, have long been considered as promising absorber materials for photoelectrochemical (PEC) cells. In particular, the recent demonstration of self-passivated bismuth (Bi)-containing FeWO₄ thin films with suitable photovoltage for coupling to a photocathode, suggests significant potential for FeWO₄-based photoanodes. In this study, we explore the growth of FeWO₄ thin films with the laser plasma control afforded by pulsed laser deposition (PLD). In PLD, thin film growth is mediated by a laser-generated plasma that exhibits rich chemistry and spatiotemporal phenomena. The chemical diversity, variety of gas backgrounds, and shockwave characteristics of the laser plume are highly conducive to kinetic control of materials synthesis. The laser-induced plasma allows wide tunability of plasma parameters. This includes control of the strong gradients of density and temperature that
We report an investigation of potential kinetic limitations to the rate of hydrogenation of magnesium diboride. The metals Pd, Fe and Ti, known to be proficient at H-H bond dissociation, were introduced into MgB₂ by ball milling. Pd and Fe are directly introduced as crystalline metals, whereas Ti metal was introduced via the reaction between TiF₅ and MgB₂ to form Ti metal and MgF₂. XRD, FTIR, XAS and TEM data show that the additives persist as metals in the MgB₂ solid, free from significant oxidation of the additive itself (i.e. TiO₂, Fe₂O₃, PdO) as well oxidation of the MgB₂ material (i.e. no MgO, B₂O₃). The Pd in the MgB₂ material consists of two morphological forms: Pd particles of a size ~ 2 – 25 nm diameter with a d-spacing essentially the same as bulk Pd, as well as a highly dispersed Pd component within the MgB₂ matrix. The Fe additive decorates the MgB₂ particles as small particles with sizes ranging from ~ 11 – 34 nm diameter with comparatively little atomic-scale dispersal of the Fe additive. TiF₅ reacts with MgB₂ to form Ti metal and MgF₂, with the Ti and the F smeared out within the MgB₂ base solid. Sieverts-acquired MgB₂ hydrogenation rates for the Pd, Fe and Ti modified MgB₂ are higher than for commercial MgB₂, but the improvement is very modest, about a factor of two at most. H-D exchange studies were conducted to confirm H-H bond breaking in these materials. The data shows that H-H bond breaking is slowest for the bulk MgB₂ material, but much faster for the Fe, Pd and Ti modified samples for which H-H bond breaking reaches equilibrium in about 20 minutes. This work shows that H-H bond dissociation is not limiting the rate of hydrogenation of MgB₂ because extensive H-H bond breaking is already occurring after only 20 minutes whereas the initial hydrogenation to ~0.8 weight percent hydrogen takes about 100 hours. The results also show that surface diffusion cannot be limiting the MgB₂ hydrogenation rate because surface diffusion, a requirement for HD generation, is occurring very rapidly. We speculate that it is the intrinsic stability of the B-B extended hexagonal ring structure in MgB₂ that hinders the hydrogenation of this material. This supposition was supported by B K-edge TFY XAS measurements of the materials, which showed spectroscopically that the B-B ring was intact in these systems throughout most of the material.
evolution reactions. MOF-derived cobalt oxide showed overpotential of 375 mV and 224 mV to achieve a current density of 10 mA/cm² for oxygen and hydrogen evolution processes, respectively. A significant improvement in electrocatalytic properties was observed with the electrode after sulfurization producing MOF-derived cobalt sulfide. MOF-derived cobalt sulfide displayed overpotential of 278 mV and 220 mV at 10 mA/cm² for oxygen and hydrogen evolution processes, respectively. Our results suggest that a facile method of sulfurization of the MOF-derived compound is a way to achieve high electrocatalytic activities for oxygen and hydrogen evolution reactions in the water-splitting process.

S.EN11.07.19

**Luminescent Solar Concentrators Based on Self-Contained Silicon Quantum Dots Films for Photovoltaic Applications**

*Rosendo Lopez-Delgado¹, Alejandra J. Cordova-Rubio², Roberto C. Carrillo-Torres² and Mario E. Alvarez-Ramos²; ¹Cátedras Conacyt - Universidad de Sonora, Mexico; ²Universidad de Sonora, Mexico*

The incorporation of energy harvesting systems into architectural elements of buildings is gaining attention as a new possible renewable energy technology for the production of electricity. Luminescent solar concentrators (LSC) represent a promising and cost-effective complement to existing semiconductor photovoltaic (PV) technologies that could be employed as semitransparent windows to contribute to the building’s energy consumption. Typically, an LSC consist of an optical waveguide that collect sunlight from a large-area window and concentrates the emission on the smaller-area edges. The emission is obtained from luminescent materials such as organic dyes, rare earth ions or semiconductor quantum dots in the LSC that absorbs the sunlight and, by a stokes shift, emit photons at wavelengths that are better suitable for absorption by the PV devices coupled at the edges of the LSC, reducing the costs of photovoltaic power generation.

Organic dyes have been the most commonly used luminophores for LSC applications mainly due to their high quantum yield and in some cases its low degradation rate, however, organic dyes no only tend to absorb and convert only a relatively small region of the solar spectrum, but also, they present a large spectral overlap between the absorption and emission regions, which increases the reabsorption losses and prevents the viability of fabrication of large-scale efficient devices. On the other hand, colloidal semiconductor nanoparticles or quantum dots (QDs) exhibit very attractive optical properties and have attracted a lot of attention as potential luminophores for LSC applications. Colloidal QDs are promising candidates since their properties mainly arises from the materials they are made, their size and their surface passivation. Also, QDs can be engineered to manipulate their energy bandgap and the stokes shift values to suppress effectively the reabsorption losses. Here, we report the fabrication of one-pot synthesized and self-contained photoluminescent films based on silicon quantum dots (SiQDs) and its employment on luminescent solar concentrators (SiQDLSC). Silicon quantum dots were synthesized from reduction of (3-aminopropyl) triethoxysilane (APTES) by sodium ascorbate. Besides the reduction of APTES into silicon quantum dots, a silicate matrix host is obtained, which is further employed as the support for the photoluminescent film in the fabrication of the LSC. The size of the synthetized SiQDs were measured by dynamic light scattering and electron microscopy techniques obtaining an average size of 3 nm. Both SiQDs and SiQDLSCs transmittance, absorbance and photoluminescent properties were characterized. The synthesized colloidal SiQDs exhibit an abrupt increase of optical absorption below 425nm extending to the ultraviolet region while emitting photons in a broad band extending from 450 to 600 nm with maximum intensity at 525 nm. SiQDLSC were fabricated in two sets of different dimensions: 1) 50x50x3mm and 2) 25x25x1mm. Set 1 shown a transmittance above 85% while set 2 exhibited above 90% transmittance over the visible region of the electromagnetic spectrum. Both sets shown the absorbance characteristics of the SiQDs decreasing the transmittance (increasing the absorbance) below 425 nm. Photoluminescent properties of the SiQDLSC were measured at the edges of the devices, obtaining broad bands of emission that were slightly blue shifted to around 500nm due to the expected oxidation of the SiQDs surfaces. However, the fabricated SiQDLSC preserve the desired stokes shift that is necessary to prevent reabsorption losses. These results demonstrate a feasible and very attractive method of fabrication of SiQD-based luminescent solar concentrators that presents good transmittance as well as the photoluminescent stokes shift effects desired for their incorporation as PV windows.

S.EN11.07.15

**3D Interface-Engineered Transition Metal Oxide/Carbon Hybrid Structures for Efficient Bifunctional Oxygen Electrocatalysis in Alkaline and Acidic Environments**

*Simranjit K. Grewal¹,2,3, Angela Andrade-Macedo¹, Ziqi Liu¹ and Dr. Min-Hwan Lee¹,²,³; ¹University of California, Merced, United States; ²NASA, United States; ³Lawrence Berkeley National Laboratory, United States*

Use of regenerative fuel cells (RFC) requires bifunctionality in oxygen electrocatalysis of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) to decrease weight and cost for efficient energy conversion. Many RFC based technologies have used noble metals such as Pt and its alloys (Pt/Ir or Pt/Ru) due to their efficient catalytic activity, selectivity and stability in harsh environments. However, their susceptibility to fast degradation during operation, as a result of catalyst agglomeration and poisoning, has driven research to find alternatives [1]. Non-precious transition metal oxides
(TMO) including Fe₃O₄, MnOₓ and Co₃O₄ have attracted significant attention as a potential candidates [2]. We utilized a composite structure where TiO₂, ZrO₂, or CeO₂ are deposited onto conductive 3D carbon structure such as graphene oxide (GO), metal-organic frameworks (MOFs) or a combination of activated carbon (AC) with GO/MOFs. The use of carbon structures is to leverage their high surface area and excellent electronic conductivity. However, GO contains oxygen based functional groups on the edges and wrinkles that provides an anchor for nanoparticle binding while its basal plane stays relatively non-reactive. To incur a catalytically active sites between the metal oxides and carbon, we functionalize the basal surface of carbon using phosphoric, hydrobromic and/or oxalic acids. After such treatment, various types of carbon structures were hydrothermally reacted with metal precursors (Ce(NO₃)₃ or ZrOCl₂) or nanoparticles (P25). For MOF structures, due their susceptibility towards degradation after the common step of pyrolysis, a thin film of metal oxides are used. However, to adhere the metal oxides properly onto the MOF, we leverage acid treatment similar to our treatment of GO.

The hydroxylated CeO₂/GO hybrids showed the best ORR and OER performance in both alkaline (0.1 M KOH) and acidic media (0.5 M H₂SO₄), in terms of onset/half-wave potential, electron transfer number, and current density (electrochemical performances) when comparing to the performance of Pt/C (for ORR) and IrO₂ (for OER). From a series of material/experimental analyses, a strong tethering of metal oxides upon the basal plane of GO prohibits restacking, and that the particle-carbon interfaces (as oppose to the particle or GO itself) dictates the performance and reaction route, as indicated in density functional theory calculations. In addition, a hybrid catalyst where TiO₂ nanodots are uniformly anchored on phosphorylated MOF by atomic layer deposition (ALD) showed an even better ORR and OER performance in 0.1 M KOH when compared the aforementioned CeO₂/GO hybrid. Materials characterization emphasizes a strong adhesion of metal oxides upon MOF structures, thus providing ample surface interactions for favorable reaction route is important. In addition, an activation of catalytic sites can be realized by a proper engineering of interfaces in each hybrid systems. Finally, we present a facile route of improving operational durability of TMO/carbon hybrids both in alkaline and acidic media: interfacing with an activated carbon after a proper acid treatment.

This project was funded by NASA Advanced STEM Training and Research (ASTAR) Fellowship.

References:
Monday Afternoon, November 30, 2020
S.EN06

5:15 PM INTRODUCTION AND ANNOUNCEMENTS

6:07 PM BREAK

6:11 PM S.EN06.02.05
Enhancing Solar Water Evaporation with Activated Carbon Sai Kiran Hota and Gerardo Diaz; University of California, United States

Thermal based desalination systems involve heating water and collecting the condensate. The use of solar energy to drive the desalination phenomena, utilizing the heat for enhancing water evaporation (steam generation) is attracting wide-spread attention. The process involves absorbing the spectral intensity of solar light and converting it to heat. This photo-thermal conversion can be enhanced by using a strong solar absorber diluted in water, which is a poor absorber of sun light. Among the solar absorbers, carbon materials have proven to enhance water desalination rate while being economical as compared to their plasmonic counterparts. Activated carbon is a carbon-rich source which has many applications such as toxic gas adsorption and industrial effluent treatment. Considering its optical quality, it has the potential to be a strong solar absorber for enhancing water evaporation rate. A series of characterization tests were performed on activated carbon. It showed 94.17% (granular) carbon composition with trace presence of hydrogen and oxygen through ultimate analysis. FT-IR analysis performed showed mostly C=C and aromatic C-H rings. Geometric (envelope) density of the sample was almost 710 kg/m³ with theoretical porosity of 0.663. The skeleton (true) density measured was 2106.9 kg/m³. The density measurements showed that activated carbon can be used as a solid dispersion in water. The granular particles sink to the bottom of the container and behave like a black bottom in enhancing water evaporation. The apparent zeta potential for nanoparticles was measured to be -47.9 mV, showing a good dispersion stability. Optical measurements showed that the absorbance of the activated carbon was 96.35%. The strength of absorbance increases with increasing concentration and can be attributed to increased extinction coefficient of the solar spectral intensity. This increases the fraction of solar absorption in the fluid dispersion system, leading to enhanced heat localization at higher concentrations. Outdoor experiments were performed to measure the mass loss of water utilizing activated carbon nanoparticle and granular activated carbon particles dispersed in DI water. The strong absorbance of the activated carbon led to increased water evaporation rate. Activated carbon particles are inexpensive compared to expensive plasmons such as copper or gold, and hence offer an economically viable solution for augmenting desalination of water.

6:22 PM OPEN DISCUSSION

7:09 PM CLOSING SUMMARY

SESSION S.EN06.06: Live Lightning/Flash II: Rational Designed Hierarchical Nanostructures for Photocatalytic System
Session Chairs: Roland Marschall and Zaicheng Sun
Tuesday Morning, December 1, 2020
S.EN06

11:30 AM INTRODUCTION AND ANNOUNCEMENTS

11:35 AM S.EN06.06.01
Dinuclear Heterogeneous Catalysts as a New Platform for Catalysis Dunwei Wang; Boston College, United States

The field of catalysis has been traditionally divided into subdisciplines of homogeneous and heterogeneous catalysis, where the former primarily studies catalytic processes by molecular structures and the latter chiefly deals with surface catalysis processes. Each subdiscipline enjoys a wealth of knowledge that underpins its own respective applications. For instance, researches on homogeneous catalysis have generated a wealth of knowledge on how to tailor the reaction selectivity and specificity at the atomic level for the production of high-value chemicals such as targeted drugs. The ease of separation and processing renders heterogeneous catalysts ideal for commodity chemical synthesis. However, how to take advantage of the
two orthogonal fields and apply knowledge learned in one field to accelerate the advancements of both has remained a critical challenge. It is within this context that recent years have witnessed a surge of research activities on atomically dispersed catalysts. A prominent example is the single atom catalysts (SACs). On the one hand, such catalysts can maximize the atomic efficiency of heterogeneous catalyst materials by minimizing the amount of materials, especially precious metals such as Pt or Pd, used; on the other hand, such catalysts are reminiscent of homogeneous catalysts in that their structures tend to be better defined than conventional heterogeneous catalysts. It, therefore, opens up an opportunity to bridge the gap between the two traditional subfields. Within this context, we have focused on developing and understanding heterogeneous catalysts with dinuclear metal centers. They are similar to SACs in that the catalytically active centers are well-defined; they present a critical difference by featuring two metal atoms at the active site. This key feature enables the studies of chemical reactions that may benefit from the presence of the second metal centers. Examples of such reactions include H$_2$O oxidation, CH$_4$ activation, and preferential CO oxidation. In all cases, we have observed a clear benefit of having a second metal center at the active site. For instance, in water oxidation, we observed that the presence of the second Ir atom facilitates the proton-coupled electron transfer process so as to lower the activation energies during the rate-determining step of O-O bond formation. Similarly, for CH$_4$ activation, we found that the presence of the second Ir center promotes C-C bond formation for the synthesis of C$_2$ products. The same effect was observed for PROX, as well, where the presence of the 2nd Ir metal center was found to enable both CO adsorption and O$_2$ activation. Our work opens a new door to the study of atomically dispersed catalysts for the chemical transformations of significant industrial relevance. We envision that similar studies will be readily expanded to other chemical processes or other catalysts systems or both.

11:47 AM *S.EN06.06.02
Rationally Designed Hierarchical Nano-Bio Assemblies for Artificial Photosynthesis Elena A. Rozhkova; Argonne National Laboratory, United States

The biological use of solar energy for the synthesis of fuels from water and carbon dioxide inspires researchers and engineers in their efforts to replace existing exhaustible energy sources with renewable energy technologies. Environmentally friendly schemes of photocatalytic visible-light hydrogen production known as artificial photosynthesis along with inorganic semiconductor material also utilize biological structures, such as enzymes, machineries of whole microorganism, capable of light-harvesting, water splitting, carbon dioxide and proton reduction. A natural membrane complex of retinal-containing proton pump bacteriorhodopsin (also known as purple membranes, PM) from the extremophile microbe has been attracting an attention of researchers owing to its minimalistic structure, exceptional robustness, excellent photophysical properties, and functional sophistication. This biological material can be assembled with inorganic nanomaterials, such as semiconductor or photonic particles, into artificial hierarchical structures and demonstrate functionality that spans far beyond its natural property. This talk will provide examples of catalytic systems based on natural proton pump for light-driven H$_2$ production, ATP synthesis and CO$_2$ reduction.

11:59 AM *S.EN06.06.03
Rational Design of Photoelectrocatalytic Materials for Artificial Photosynthesis Guiji Liu and Francesca Maria Toma; Lawrence Berkeley National Laboratory, United States

Due to the rapid depletion of fossil fuels and related environmental issues, developing technologies for producing renewable, clean fuels for our future is of great importance. Artificial photosynthesis via water splitting or CO$_2$ reduction offers an attractive and cost-effective route to achieve this goal. However, existing photoelectrocatalytic materials generally suffer from low activity or instability, thus greatly impeding the feasibility of artificial photosynthesis technologies. Herein, we present design strategies for the synthesis and integration of photoelectrocatalytic materials.

References
In Situ/Operando Study of Photocatalytic Materials Using Optical Liquid Cell Transmission Electron Microscopy
Khim Karki1, Pawan Kumar2,2, Antoine Verret2, Noah Glachman2, Rui Filipe Serra Maia2, Deep M. Jariwala2, Daan Hein Alsem1 and Eric A. Stach2; 1Hummingbird Scientific, United States; 2University of Pennsylvania, United States

The clean production of hydrogen from non-fossil energy sources is highly desirable for future energy needs and realization of hydrogen fuel cell vehicles. One way of producing green hydrogen is via photoelectrochemical splitting water into hydrogen by utilizing solar energy and/or highly active catalytic materials, both subjects of much research interests1-3. Particularly, the atomic scale mechanisms of the photocatalysts that facilitate the water splitting for efficient hydrogen generation are currently poorly understood. Further understanding of the role of various photocatalysts and the physics governing the active hydrogen evolution sites will allow for better and efficient design of photoelectrochemical devices.

We have developed a unique in situ/operando liquid cell transmission electron microscope (TEM) holder with photo-capable light source4 which can be used to study photocatalytic reactions in real time at nanometer length scales. Using some of the model materials such as Au nanoprisms and MoS2 flakes, we will present the correlation of I-V characteristics with water splitting and simultaneous structural changes at the catalytically active sites. The following photocatalysts used were chosen because the proposed mechanism for each exhibits a spatial dependence: plasmonically enhanced catalysis for Au nanoprisms and catalytically active edge sites for MoS2 flakes. For accurate quantitative information and reliability of materials interface in liquid, we will also present strategies for site-specific deposition/loading of sample materials in the desired electrodes of liquid cell chips for electroanalytical characterization and TEM imaging. The availability and utilization of photo stimuli in liquid cell TEM can provide important fundamental insights into the understanding of several other photoelectrochemical systems.

References:
1 Nowotny, J.; Sorrell, C. C.; Sheppard, L. R.; Bak, T. Int. J. Hydrogen Energy 2005, 30, 521
4 Funding for the development of the sample holder was provided by the Department of Energy, Office of Basic Energy Sciences, through SBIR Grant # DE-SC0015213

Si-Based Photoelectrodes Coupled with Earth-Abundant Transition Metal-Based Catalysts
Ho Won Jang; Seoul National University, Korea (the Republic of)

Harvesting solar energy for carbon-free hydrogen production via photoelectrochemical (PEC) water splitting is a promising pathway to meet the increased energy demands and deal with severe environmental pollution including climate change. Silicon is the second earth-abundant element and a narrow bandgap material which is found to be a prime candidate for water splitting photoelectrodes due to ease of high-quality wafers fabrication. Si can be doped with elements of different valence states to fabricate n-type or p-type semiconductors for photoanode and photocathode respectively. However, high light reflection, low photovoltage output due to its narrow bandgap, and severe photocorrosion in the electrolyte remain as serious limitations to manufacture efficient Si-based photoelectrodes.

In this talk, I will discuss the fabrication of Si-based photoelectrodes coupled with earth-abundant transition metal-based catalysts for efficient water splitting. We introduced two-dimensional (2D) transition metal dichalcogenides catalysts on p-type Si-photocathode for highly efficient PEC hydrogen production. 2D transition metal dichalcogenides such as MoS2 and WS2 are promising materials to replace noble metal catalysts due to their high density of catalytically active edge sites and large surface-to-volume ratio. Wafer-scale transferable transition metal dichalcogenides thin-film catalysts can provide a low onset potential and high photocurrent density. I will also talk about n-type Si photoanodes with high catalytic activity in transition metal-based catalysts synthesized via facile electrodeposition method for efficient water oxidation. Si photoanodes covered with water oxidation catalysts such as layered-double hydroxides, metal nanoparticles, and thin films exhibited high photoelectrochemical property and long-term stability.

Design Principles for Photocathodes for Solar Driven Carbon Dioxide Reduction
Joel W. Ager1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States
Solar photovoltaic (PV) and photoelectrochemical (PEC) energy conversion share the same fundamental requirements of photon absorption, charge separation, and selective carrier collection [1]. In addition, in order to produce storable chemical energy, PEC systems must drive multi-electron transfer reactions, i.e. water oxidation (OER, a 4 electron process) at the anode and hydrogen evolution (HER) or carbon dioxide reduction (CO$_2$R) at the cathode (2-18 electron processes) [2]. In a small number of cases it has been possible to have a single material perform all of the requisite steps and remain stable under operation: water oxidation photoanodes composed of TiO$_2$ or Fe$_2$O$_3$ are examples. However, in the majority of cases, it has been beneficial to construct multi-material PEC systems, with different components chosen for optimal light absorption, selective carrier collection/passivation, and catalysis.

In this context, the design of PEC systems for CO$_2$R will be discussed. While it is attractive to design semiconductor absorbers based on the position of their conduction band relative to the standard state redox potentials of a given CO$_2$ reaction, e.g. CO$_2$/CO, CO$_2$/HCOOH, CO$_2$/CH$_4$, etc., this analysis neglects the fact that these multi-electron reactions occur via a series of elementary proton coupled electron transfers, with each step having its own redox potential [3]. For this reason, either solid state or molecular CO$_2$R co-catalysts are usually integrated with the absorber in PEC CO$_2$R studies [4,5]. These concepts will be illustrated through the design and operation of Si-based CO$_2$R photocathodes. Adroit use of charge selective contacts allows for considerable flexibility in design. For example, in contrast to conventional photocathode designs which employ p-type absorbers, we used a back illumination geometry with an n-type Si absorber to permit the use of absorbing metallic catalysts which would otherwise block the light. Back and front interfaces were configured by ion implantation and by surface passivation to achieve carrier selectivity. Selectivity to C-C coupled products was achieved by using hierarchical Au- Ag-Cu nanostructures as electrocatalysts. The photovoltage, 550–600 mV under simulated 1-sun illumination, and photocurrents exceeding 30 mA cm$^{-2}$ confirm the carrier selectivity and passivation of the front and back interfaces. Under simulated diurnal illumination conditions, over 60% faradaic efficiency to C$_2$ hydrocarbon and oxygenate products (mainly ethylene, ethanol, propanol) is maintained for several days. By coupling photocathodes to series-connected semi-transparent halide perovskite solar cells, we demonstrated stand-alone, “no-bias,” CO$_2$ reduction with a 1.5% conversion efficiency to hydrocarbons and oxygenates [6].

As further examples of the PEC design space for CO$_2$R, use of nanowire geometries which would permit the use of front illumination and the prospects of achieving cascade CO$_2$R [7] on the PEC surface will be discussed.

Today, much research on water-splitting and fuel synthesis is directed at improving the efficiency of catalysts and their immobilisation on (photo)electrodes in order to be electroactive under aqueous conditions in photoelectrochemical (PEC) devices. In such hybrid configurations, metal oxide (MO) semiconductor materials hold the key to high efficiencies, as their facile preparation, stability in water and modular high surface-area architecture render them promising platforms. By greatly expanding in this area of research, our recent studies show that achieving a synergistic size parity between macromacrocatalysts and the substrate is a promising strategy to improve the electrocatalytic performance.

In this invited talk, I will present our rational development of macro-meso-porous inverse opal (IO) titanium dioxide and indium tin oxide electrodes, designed to host macromolecules – enzymes and polymeric catalysts – towards water-splitting and CO2 reduction. Our recent efforts allowed the development of semi-artificial photosynthetic systems that demonstrate how, using a dye-sensitised approach, natural archetypes – photosystem II, hydrogenase and formate dehydrogenase – can be interfaced with a synthetic organic dye to achieve unassisted solar-driven water-splitting into H2 and O2, and CO2-to-formate splitting. We took further advantage of the wide pore architecture to develop catalytic copolymeric architectures capable of electrocatalysing the reduction of CO2-to-CO. Capitalising on the multifunctional capabilities intrinsically delivered by copolymer scaffolds, this work also provided a seminal example of enhanced product selectivity achieved only by tuning the environmental surroundings of the molecular catalyst. The ability of IO electrodes to host and drive large, electrocatalytically active polymers was further demonstrated on silicon-based photoelectrodes, where selective, precious metal-free, solar-driven CO2 reduction was achieved in hydro-organic media.


1:25 PM CLOSING SUMMARY

SESSION S.EN06.01: Polycatalytic Materials

On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN06

5:00 AM S.EN06.01.03

Core-shell Magnetic Nanoparticles Functionalized with Copper(ii)-Loaded Dendrimer as Recoverable and Robust Magnetic-Nanoinitiator for Polymerization of Adhesive System Haruethai Kongcharoen and Pooi See Lee; Nanyang Technological University, Singapore

A cost effective synthesis route for tunable shapes and sizes of large scale monodisperse nanocrystals functionalized with copper-loaded dendrimer through a low-temperature thermal decomposition from iron (III) olate has been demonstrated for the first time as a recoverable and reusable heterogeneous magnetic-nanoinitiator for polymerization of adhesive system. Herein, the colloidal system comprised of methacrylate ester monomers, peroxide and core-shell magnetic nanoparticles functionalized with copper-loaded dendrimer are used for the polymerization of adhesives with the nanoinitiators. The effect of various morphologies of the magnetic particles such as spherical, cubic, hexagonal shape as a core of the nanoinitiators are investigated through the polymerization of anaerobic adhesive formulation. To enable the recoverability of nanoinitiators and achieve simultaneously control of the loading of Cu(II) of nanoinitiators, core-shell magnetic nanoparticles and dendrimer have been designed to initiate highly efficient and safe polymerization through redox radical initiated cationic polymerization reaction under mild condition. Moreover, core-shell magnetic nanoparticles functionalized copper-loaded dendrimer can be separated simply by either magnetic separation or centrifugation and reused for several times without any significant mass loss. The core-shell magnetic nanoparticles functionalized with copper-loaded dendrimer were characterized using transmission electron microscopy (TEM), Scanning electron microscopy (SEM-EDX), X-Ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FT-IR).
Even though the potential of hematite thin films for water splitting applications are widely accepted, researchers are still tackling the ‘rust challenge’. We report here on the influence of external magnetic fields applied parallel or perpendicular to the substrate during plasma enhanced chemical vapor deposition (PECVD) of hematite (α-Fe₂O₃) nanostructures and the accessibility of the very same through magnetic field assisted CVD of Fe(CO)₅. Hematite films grown from iron precursors showed pronounced changes in crystallographic textures depending upon whether PECVD was performed with or without the influence of external magnetic field and anisotropic film growth with higher exposure to water in case of mfCVD. In all cases, a superior photoelectrochemical (PEC) performance was obtained for hematite photoanodes synthesized under applied magnetic fields. Our experimental data on microstructure and functional properties of hematite films showed that magnetic fields have a significant effect on the crystallite size and texture with preferred growth and/or suppression of grains with specific texture in α-Fe₂O₃ films. Thereby, we are able to demonstrate magnetic field assisted gas phase depositions as new experimental playground for the ‘rust challenge’.

Solar photovoltaic (PV) and photoelectrochemical (PEC) energy conversion share the same fundamental requirements of photon absorption, charge separation, and selective carrier collection [1]. In addition, in order to produce storable chemical energy, PEC systems must drive multi-electron transfer reactions, i.e. water oxidation (OER, a 4 electron process) at the anode and hydrogen evolution (HER) or carbon dioxide reduction (CO₂R) at the cathode (2-18 electron processes) [2]. In a small number of cases it has been possible to have a single material perform all of the requisite steps and remain stable under operation: water oxidation photoanodes composed of TiO₂ or Fe₂O₃ are examples. However, in the majority of cases, it has been beneficial to construct multi-material PEC systems, with different components chosen for optimal light absorption, selective carrier collection/passivation, and catalysis. This context, the design of PEC systems for CO₂R will be discussed. While it is attractive to design semiconductor absorbers based on the position of their conduction band relative to the standard state redox potentials of a given CO₂ reaction, e.g. CO₂/CO, CO₂/HCOOH, CO₂/CH₄, etc., this analysis neglects the fact that these multi-electron reactions occur via a series of elementary proton coupled electron transfers, with each step having its own redox potential [3]. For this reason, either solid state or molecular CO₂R co-catalysts are usually integrated with the absorber in PEC CO₂R studies [4,5]. These concepts will be illustrated through the design and operation of Si-based CO₂R photocathodes. Adroit use of charge selective contacts allows for considerable flexibility in design. For example, in contrast to conventional photocathode designs which employ p-type absorbers, we used a back illumination geometry with an n-type Si absorber to permit the use of absorbing metallic catalysts which would otherwise block the light. Back and front interfaces were configured by ion implantation and by surface passivation to achieve carrier selectivity. Selectivity to C-C coupled products was achieved by using hierarchical Au- Ag-Cu nanostructures as electrocatalysts. The photovoltage, 550- 600 mV under simulated 1-sun illumination, and photocurrents exceeding 30 mA cm⁻² confirm the carrier selectivity and passivation of the front and back interfaces. Under simulated diurnal illumination conditions, over 60% faradaic efficiency to C₂⁺ hydrocarbon and oxygenate products (mainly ethylene, ethanol, propanol) is maintained for several days. By coupling photocathodes to series-connected semi-transparent halide perovskite solar cells, we demonstrated stand-alone, “no-bias,” CO₂ reduction with a 1.5% conversion efficiency to hydrocarbons and oxygenates [6]. As further examples of the PEC design space for CO₂R, use of nanowire geometries which would permit the use of front illumination and the prospects of achieving cascade CO₂R [7] on the PEC surface will be discussed.

Structure-Property Study of Titania-PMMA Based Nanoporous Core-Shell Fibers for Waste Water Treatment
Namrata Kanth, Weiheng Xu, Dharneedar Ravichandran and Kenan Song; Arizona State University, United States

Titanium dioxide (TiO₂), or titania, is a suitable choice for environmental remediation due to its photocatalytic advanced oxidation ability which can inactivate pathogens and decompose dyes. Current researches have been focusing on titania nanoparticles impregnated in polymers, due to higher active sites for contaminant adsorption, pore size control, and easy manufacturability. Low throughput rates, however, have far limited the adoption of titania-based water-treatment systems. Our research explored a scalable manufacturing technique and achieved morphology control of core-shell fibers incorporating titania nanoparticles. The novelty of this research is that it encompasses the benefits of remote ultraviolet (UV) light accessibility and porosity-enabled enhanced adsorption sites. The fibre core was composed of UV light transparent, flexible, and oxidation-resistant polymethyl methacrylate (PMMA) that served as an optical channel for UV light transmission and was prepared by melt spinning technique. The fibre shell was composed of a porous PMMA-titania nanoparticle composite prepared by dip-coating in colloidal solution with dispersed titania nanoparticles followed by coagulation through wet phase inversion. Titania in fiber shell was photo-activated by light radially refracted from the fiber core. Photocatalytic performance was optimized by controlling the pore-size, titania concentration and the thickness of the coated shell. Pore-sizes ranging from 50 nm up to 5 µm were achieved by varying the porogen concentration and selecting different solvent and non-solvent combinations. The core-shell interfacial interactions were also characterized using static mechanical tests and dynamic mechanical analysis. Finally, the photocatalytic performance of the fibers was characterized by monitoring the decomposition of methylene blue using UV-vis spectrophotometry. This research provided an understanding of the processing-structure-property relationships in the complex, multiphase core-shell structured fibers.

Band-Gap Engineering in Perovskite Heterostructure for Efficient Visible Light Induced Photocatalysis—A Detailed Photophysical Study
Smruti Purohit, Soumitra Satapathi and K.L. Yadav; Indian Institute of Technology Roorkee, India

Recently, photocatalysis has emerged as a potential solution for growing energy crisis and environment pollution issues. However, higher charge recombination, slow electron transfer rate and large band-gap of photocatalytic materials remain key challenges in photocatalysis.

Here, we report a systemic study of the photocatalytic performance of K₀.5Na₀.5NbO₃ (KNN)-BaBiO₃ (BBO) perovskite heterostructure. KNN and BBO are synthesized by solid state reaction method and the composite is prepared by ball-milling technique with appropriate stoichiometric ratio of KNN and BBO. The materials are characterized using XRD, SEM, XPS, and RAMAN spectroscopy techniques. Photocatalytic degradation of Rhodamine 6G is monitored through UV-Vis absorption spectroscopy. We observed higher photocatalytic efficiency with KNN-BBO heterostructure than single junction KNN. This was attributed to the reduced band gap (approx1.92 eV) and fast electron transfer rate in heterostructure under visible light irradiation. Moreover, the improved performance of the composite (KNN-BO) material may be attributed to heterojunction band alignment and higher ferroelectric polarization of the composite material. [3] We have also examined the effect of calcination temperature on the photocatalytic dye degradation activity of KNN-BO heterostructure. Transient absorption spectroscopy confirms the energetics and electron transfer kinetics in the composite system. Our study opens up the possibility of designing novel perovskite based materials for efficient photocatalysis.

References:

Hierarchically Structured, Oxygen Deficient, Tungsten Oxide Morphologies for Enhanced Photoelectrochemical Charge Transfer and Stability
Peng Chen, Matthew Baldwin and Prab Bandaru; University of California, San Diego, United States

The role of non-stoichiometry in a hierarchically structured WO₃₋ₓ electrode, constituted from nanoscale fuzziness as well as microscale wire morphology, on the photoelectrochemical response is investigated. Through X-ray photoelectron
spectroscopy (XPS) studies, the relative amounts of the various oxidation states of the constituent W are probed with respect to the observed response. It is concluded that an intermediate/optimal number of vacancies, yielding a \( W^{6+}/(W^{5+} + W^{4+}) \) ratio of around 2, would be beneficial for increasing the photocurrent. It is posited that defect engineering combined with optimized band structure modulation could be used for enhanced photocurrent density as well as electrode stability. The work would help considerably elucidate the role of defects as well as charge carriers for oxygen evolution reaction (OER) efficiency increase.

SESSION S.EN06.02: Photoelectrochemical Materials
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN06

5:00 AM S.EN06.02.01
Ultrafast Relaxation Dynamics in Bimetallic Plasmonic Catalysts Sangwan Sim¹, Alyssa Beierle², Philip Mantos², Steven McCrory², Rohit Prasankumar Prativadi³ and Sanchari Chowdhury²; ¹Hanyang University ERICA campus, Korea (the Republic of); ²New Mexico Tech, United States; ³Los Alamos National Laboratory, United States

Combining a plasmonic metal, such as gold, with other popular catalysts, such as Ni or Pt, can extend its benefit to many energy-extensive reactions catalyzed by those metals. The efficiency of a plasmon-enhanced the catalytic reaction is mainly determined by the light absorption cross-section and the photoexcited charge carrier relaxation dynamics of the nanoparticles. We have investigated the charge carrier relaxation dynamics of gold/nickel (Au/Ni) and gold/platinum (Au/Pt) bimetallic nanoparticles. We found that electron-phonon and phonon-phonon coupling rates in Au/Ag, Au/Ni, and Au/Pt nanoparticles are significantly different than that of pure Au nanoparticles. This is due to the large differences in their band structures and the electron-phonon coupling rate. Our findings thus provide important insights towards the rational design of bimetallic plasmonic catalysts.

5:10 AM S.EN06.02.05
Enhancing Solar Water Evaporation with Activated Carbon Sai Kiran Hota and Gerardo Diaz; University of California, United States

Thermal based desalination systems involve heating water and collecting the condensate. The use of solar energy to drive the desalination phenomena, utilizing the heat for enhancing water evaporation (steam generation) is attracting wide-spread attention. The process involves absorbing the spectral intensity of solar light and converting it to heat. This photo-thermal conversion can be enhanced by using a strong solar absorber diluted in water, which is a poor absorber of sun light. Among the solar absorbers, carbon materials have proven to enhance water desalination rate while being economical as compared to their plasmonic counterparts. Activated carbon is a carbon-rich source which has many applications such as toxic gas adsorption and industrial effluent treatment. Considering its optical quality, it has the potential to be a strong solar absorber for enhancing water evaporation rate. A series of characterization tests were performed on activated carbon. It showed 94.17% (granular) carbon composition with trace presence of hydrogen and oxygen through ultimate analysis. FT-IR analysis performed showed mostly C=C and aromatic C-H rings. Geometric (envelope) density of the sample was almost 710 kg/m³ with theoretical porosity of 0.663. The skeleton (true) density measured was 2106.9 kg/m³. The density measurements showed that activated carbon can be used as a solid dispersion in water. The granular particles sink to the bottom of the container and behave like a black bottom in enhancing water evaporation. The apparent zeta potential for nanoparticles was measured to be -47.9 mV, showing a good dispersion stability. Optical measurements showed that the absorbance of the activated carbon was 96.35%. The strength of absorbance increases with increasing concentration and can be attributed to increased extinction coefficient of the solar spectral intensity. This increases the fraction of solar absorption in the fluid dispersion system, leading to enhanced heat localization at higher concentrations. Outdoor experiments were performed to measure the mass loss of water utilizing activated carbon nanoparticle and granular activated carbon particles dispersed in DI water. The strong absorbance of the activated carbon led to increased water evaporation rate. Activated carbon particles are inexpensive compared to expensive plasmons such as copper or gold, and hence offer an economically viable solution for augmenting desalination of water.

5:20 AM S.EN06.02.06
Towards High-Performance and Low-Cost Plasmonic-Enhanced Wood-Based Solar Steam Generation Yang Li; Hong Kong University of Science and Technology, Hong Kong

Plasmonic nanoparticles that effectively convert light into nanoscale localized heat with low radiative losses are promising photothermal materials. A lot of plasmonic-enhanced interfacial solar steam generation devices have been developed based on a broad variety of floating substrates, showing improved evaporation rates and high solar-thermal efficiency. In particular, plasmonic wood-based devices are considered as one of the ideal platforms for steam generation due to the attractive cost-effectiveness. However, up to now, the efficiency of the plasmonic wood-based device is still below 80% (evaporation rate ~1.0 kg m-2h-1) due to the considerable heat losses. In this study, by taking the full advantage of plasmonic nanoparticles in heat localization, we created nanoscale hot spots with huge light absorption and negligible heat losses in a TiN nanoparticles/wood device. Specifically, we constructed an ultrathin uniform plasmonic nanoparticle film on the micro-channels of wood using solution-processed technique. For the first time, water boiling is observed on the surface of the device under the illumination of only one sun. As a result, the 1-sun evaporation rate of such a system reaches the theoretic limit of wood-based steam generation devices (~1.5 kg m-2h-1), indicating an extremely high solar-thermal efficiency.

5:30 AM *S.EN06.02.07
Inverse Opal Electrodes towards (Photo)Electrochemical Fuel Synthesis Julien Warnan1 and Erwin Reisner2; 1Technische Universität München, Germany; 2University of Cambridge, United Kingdom

Today, much research on water-splitting and fuel synthesis is directed at improving the efficiency of catalysts and their immobilisation on (photo)electrodes in order to be electroactive under aqueous conditions in photoelectrochemical (PEC) devices. In such hybrid configurations, metal oxide (MO) semiconductor materials hold the key to high efficiencies, as their facile preparation, stability in water and modular high surface-area architecture render them promising platforms. By greatly expanding in this area of research, our recent studies show that achieving a synergistic size parity between macromolecules and the substrate is a promising strategy to improve the electrocatalytic performance.

In this invited talk, I will present our rational development of macro-meso-porous inverse opal (IO) titanium dioxide and indium tin oxide electrodes[1], designed to host macromolecules – enzymes and polymeric catalysts – towards water-splitting and CO2 reduction. Our recent efforts allowed the development of semi-artificial photosynthetic systems that demonstrate how, using a dye-sensitised approach, natural archetypes – photosystem II, hydrogenase and formate dehydrogenase – can be interfaced with a synthetic organic dye to achieve unassisted solar-driven water-splitting into H2 and O2, and CO2-to-formate splitting.[2,3] We took further advantage of the wide pore architecture to develop catalytic copolymeric architectures capable of electrocatalysing the reduction of CO2-to-CO.[4] Capitalising on the multifunctional capabilities intrinsically delivered by copolymer scaffolds, this work also provided a seminal example of enhanced product selectivity achieved only by tuning the environmental surroundings of the molecular catalyst. The ability of IO electrodes to host and drive large, electrocatalytically active polymers was further demonstrated on silicon-based photoelectrodes, where selective, precious metal-free, solar-driven CO2 reduction was achieved in hydro-organic media.


5:45 AM *S.EN06.02.08
Photocatalytic and Photoelectrochemical Water Splitting by a Visible-Light-Absorbing Oxyfluoride Kazuhiko Maeda; Tokyo Institute of Technology, Japan

Mixed-anion compounds that consist of more than two anionic species in a single-phase have attracted attention as visible-light-absorbing semiconductors, since as compared to oxygen 2p orbital, p orbitals of less electronegative anion can form a valence band that possesses more negative potential. In this regard, oxyfluorides (oxide-fluoride) are obviously unsuitable as visible-light-responsive photocatalysts because of the highest electronegativity of fluorine. However, we found that an oxyfluoride Pb2Ti2O5.4F1.2 possessed an unprecedented small band gap of ca. 2.4 eV (corresponding to ca. 510 nm absorption edge), and functioned as a stable photocatalyst for visible-light water reduction/oxidation when modified with suitable promoters. Photoelectrochemical water oxidation to O2 was also achieved with a modified Pb2Ti2O5.4F1.2 electrode under simulated sunlight. Density functional theory calculations showed that the
unprecedented visible-light-response of Pb$_2$Ti$_2$O$_5$.4F$_{1.2}$ arises from strong interaction between Pb-6s and O-2p orbitals, which is caused by a short Pb–O bond in the pyrochlore lattice due to the fluorine substitution.

6:00 AM S.EN06.02.10
Visible Photocatalytic Activity of Nitrogen/Fluorine Codoped Rutile TiO$_2$: Akinobu Miyoshi$^{1}$, Junie J. Vequizo$^{2}$, Shunta Nishioka$^{1}$, Shunsuke Yamashita$^{3}$, Akira Yamakata$^{2}$, Koji Kimoto$^{3}$ and Kazuhiko Maeda$^{1}$; $^{1}$Tokyo Institute of Technology, Japan; $^{2}$Toyota Technological Institute, Japan; $^{3}$National Institute for Materials Science, Japan

Significant efforts have been made to develop a photocatalyst that functions under visible light from the viewpoint of solar energy utilization. Nitrogen/fluorine codoping into anatase TiO$_2$ allowed introduction of more nitrogen compared to only nitrogen-doped analogue, resulting in enhanced absorption and photocatalytic activity under visible light irradiation [K. Nukumizu et al. Chem. Lett. 2003, 32, 196; K. Maeda et al. J. Phys. Chem. C 2007, 111, 18264]. On the other hand, rutile TiO$_2$ (R-TiO$_2$), another representative polymorph of TiO$_2$, is known to possess high activity for O$_2$ evolution via water oxidation and used in Z-scheme water splitting in combination with a suitable H$_2$ evolution photocatalyst [A. Miyoshi et al. Chem. Eur. J. 2018, 24, 18204]. In this work, we succeeded in introducing visible light response into R-TiO$_2$ by N/F codoping and evaluated its photocatalytic O$_2$ evolution activity.

N/F codoped R-TiO$_2$ (R-TiO$_2$;N,F) was synthesized by nitriding a mixture of R-TiO$_2$ and (NH$_4$)$_2$TiF$_6$. R-TiO$_2$ and (NH$_4$)$_2$TiF$_6$ were mixed using an agate mortar and a pestle with various molar ratios. The mixture was heated at 773 K for 1 h under NH$_3$ flow. For convenience, the nominal concentration of (NH$_4$)$_2$TiF$_6$ in the mixture is denoted as value

Diffuse reflectance spectra showed more pronounced absorption in visible light region for materials synthesized using (NH$_4$)$_2$TiF$_6$ ($C \geq 10$) compared to the sample synthesized without (NH$_4$)$_2$TiF$_6$ ($C = 0$). Furthermore, the visible light absorption became more pronounced with increasing $C$ value. The enhanced visible light absorption in the R-TiO$_2$;N,F is attributed to increased nitrogen content, which was confirmed by combustion elemental analysis. Shift of diffraction peaks in XRD and increase in the pre-edge peak intensity in XAFS measurements compared to pristine rutile TiO$_2$ was observed, suggesting the incorporation of nitrogen and fluorine anions into R-TiO$_2$ causing lattice distortion.

Photocatalytic activity of R-TiO$_2$;N,F for water oxidation was tested using AgNO$_3$ as a sacrificial electron acceptor. The $C = 15$ sample marked the highest activity among the synthesized R-TiO$_2$;N,F. The increase in activity up to $C = 15$ can be explained by increase in the visible light absorption. On the other hand the decrease in the activity for $C > 15$ was suspected to be caused by defect formation. To make this point clear, transient absorption spectroscopy was employed. The result revealed difference of carrier dynamics among the different $C$ value samples. The $C = 50$ sample showed signals corresponding to deeply trapped electrons (~5000 cm$^{-1}$) and no free electrons (< 2000 cm$^{-1}$). On the other hand, the $C = 15$ sample had less deeply trapped electrons, but more free electrons. Since free electrons generally show higher reactivity compared to the trapped electrons [A. Yamakata et al. J. Photochem. Photobiol. A 2015, 313, 168], the decrease in the activity for $C \geq 20$ is most likely attributed to the smaller population of free electrons available for reaction and/or the presence of higher concentration of trap states. This suggests enhancing visible light absorption and suppressing the defect formation with appropriate nitrogen/fluorine codoping is important for achieving high photocatalytic activity.

Finally, the $C = 15$ sample was loaded with RuO$_2$ and applied in Z-scheme water splitting system in combination with Ru loaded Rh doped SrTiO$_3$ ($H_2$ evolution photocatalyst) and [Co(bpy)$_3$]$_{3/2+}$ (redox mediator). Stoichiometric water splitting was achieved upon visible light and simulated sunlight irradiation.

6:20 AM S.EN06.02.12
In Situ/Operando Study of Photocatalytic Materials Using Optical Liquid Cell Transmission Electron Microscopy
Khim Karki$^{1}$, Pawan Kumar$^{2,3}$, Antoine Verret$^{2}$, Noah Glachman$^{2}$, Rui Filipé Serra Maia$^{2}$, Deep M. Jariwala$^{2}$, Daan Hein Alsem$^{1}$ and Eric A. Stach$^{2}$; $^{1}$Hummingbird Scientific, United States; $^{2}$University of Pennsylvania, United States

The clean production of hydrogen from non-fossil energy sources is highly desirable for future energy needs and realization of hydrogen fuel cell vehicles. One way of producing green hydrogen is via photoelectrochemical splitting water into hydrogen by utilizing solar energy and/or highly active catalytic materials, both subjects of much research interests. In particular, the atomic scale mechanisms of the photocatalysts that facilitate the water splitting for efficient hydrogen generation are currently poorly understood. Further understanding of the role of various photocatalysts and the physics governing the active hydrogen evolution sites will allow for better and efficient design of photoelectrochemical devices.

We have developed a unique in situ/operando liquid cell transmission electron microscope (TEM) holder with photo-capable light source which can be used to study photocatalytic reactions in real time at nanometer length scales. Using some of the
model materials such as Au nanoprisms and MoS2 flakes, we will present the correlation of I-V characteristics with water splitting and simultaneous structural changes at the catalytically active sites. The following photocatalysts used were chosen because the proposed mechanism for each exhibits a spatial dependence: plasmonically enhanced catalysis for Au nanoprisms and catalytically active edge sites for MoS2 flakes. For accurate quantitative information and reliability of materials interface in liquid, we will also present strategies for site-specific deposition/loading of sample materials in the desired electrodes of liquid cell chips for electroanalytical characterization and TEM imaging. The availability and utilization of photo stimuli in liquid cell TEM can provide important fundamental insights into the understanding of several other photoelectrochemical systems.

References:
1 Nowotny, J.; Sorrell, C. C.; Sheppard, L. R.; Bak, T. Int. J. Hydrogen Energy 2005, 30, 521
4 Funding for the development of the sample holder was provided by the Department of Energy, Office of Basic Energy Sciences, through SBIR Grant # DE-SC0015213

6:30 AM S.EN06.02.14
Tailoring Layered Oxide Nanofiber Heterojunctions for Enhanced Photocatalytic Water Splitting Performance Roland Marschall; University of Bayreuth, Germany

For many semiconductors the large mismatch between their small charge carrier diffusion length and their much larger light penetration depth is one of the most critical parameters for their photocatalytic and photoelectrochemical performance. Preparation of nanofibers by electrospinning is one way to overcome this mismatch. We use this technique to prepare fibers of the (111)-layered perovskite Ba5Ta4O15.[1] The nanofiber diameter can be tailored by adjustment of the electrospinning parameters. We could show that the photocatalytic activity depends on the fiber diameter.[2] The fiber diameter for the optimum photocatalytic activity is ~160 nm. We could prepare composite nanofibers of Ba5Ta4O15−Ba3Ta5O15 and showed that this composite gives rise to strongly enhanced photocatalytic hydrogen production and water splitting performance compared to pure Ba5Ta4O15 fibers with comparable diameter due to an improved charge carrier separation. The photocurrent doubling effect with methanol as sacrificial agent with this composite could be confirmed.[3]

References

6:40 AM S.EN06.02.16
Generation of Hierarchically Porous Metal-Organic Frameworks through Photolysis Kunyu Wang and Hongcai Zhou; Texas A&M University, United States

Metal-organic frameworks (MOFs) are porous materials with various applications such as gas seperation and photocatalysis. Currently, most MOFs have micro-pores, which hamper diffusion within the framework and limit the potential applications. The pore size of MOFs can be enlarged through linker elimination, in which labile linkers in MOFs can be removed to generate hierarchically porous frameworks with enhanced mass transfer. Here we report a facile method to remove photosensitive linkers selectively through photolysis. The formation of mesopores is confirmed by N2 sorption test and the photolytic mechanism is studied through 1H NMR, thermogravimetry (TGA) and Raman spectroscopy. The photolytic approach can engineer MOF particles in a small domain and fabricate complicated patterns on MOFs, paving a way for programmable design of MOF-based devices.
The field of catalysis has been traditionally divided into subdisciplines of homogeneous and heterogeneous catalysis, where the former primarily studies catalytic processes by molecular structures and the latter chiefly deals with surface catalysis processes. Each subdiscipline enjoys a wealth of knowledge that underpins its own respective applications. For instance, researches on homogeneous catalysis have generated a wealth of knowledge on how to tailor the reaction selectivity and specificity at the atomic level for the production of high-value chemicals such as targeted drugs. The ease of separation and processing renders heterogeneous catalysts ideal for commodity chemical synthesis. However, how to take advantage of the two orthogonal fields and apply knowledge learned in one field to accelerate the advancements of both has remained a critical challenge. It is within this context that recent years have witnessed a surge of research activities on atomically dispersed catalysts. A prominent example is the single atom catalysts (SACs). On the one hand, such catalysts can maximize the atomic efficiency of heterogeneous catalyst materials by minimizing the amount of materials, especially precious metals such as Pt or Pd, used; on the other hand, such catalysts are reminiscent of homogeneous catalysts in that their structures tend to be better defined than conventional heterogeneous catalysts. It, therefore, opens up an opportunity to bridge the gap between the two traditional subfields. Within this context, we have focused on developing and understanding heterogeneous catalysts with dinuclear metal centers. They are similar to SACs in that the catalytically active centers are well-defined; they present a critical difference by featuring two metal atoms at the active site. This key feature enables the studies of chemical reactions that may benefit from the presence of the second metal centers. Examples of such reactions include H₂O oxidation, CH₄ activation, and preferential CO oxidation. In all cases, we have observed a clear benefit of having a second metal center at the active site. For instance, in water oxidation, we observed that the presence of the second Ir atom facilitates the proton-coupled electron transfer process so as to lower the activation energies during the rate-determining step of O-O bond formation. Similarly, for CH₄ activation, we found that the presence of the second Ir center promotes C-C bond formation for the synthesis of C₂ products. The same effect was observed for PROX, as well, where the presence of the 2nd Ir metal center was found to enable both CO adsorption and O₂ activation. Our work opens a new door to the study of atomically dispersed catalysts for the chemical transformations of significant industrial relevance. We envision that similar studies will be readily expanded to other chemical processes or other catalysts systems or both.

5:15 AM *S.EN06.03.02
Rationally Designed Hierarchical Nano-Bio Assemblies for Artificial Photosynthesis Elena A. Rozhkova; Argonne National Laboratory, United States

The biological use of solar energy for the synthesis of fuels from water and carbon dioxide inspires researchers and engineers in their efforts to replace existing exhaustible energy sources with renewable energy technologies. Environmentally friendly schemes of photocatalytic visible-light hydrogen production known as artificial photosynthesis along with inorganic semiconductor material also utilize biological structures, such as enzymes, machineries of whole microorganism, capable of light-harvesting, water splitting, carbon dioxide and proton reduction. A natural membrane complex of retinal-containing proton pump bacteriorhodopsin (also known as purple membranes, PM) from the extremophile microbe has been attracting an attention of researchers owing to its minimalistic structure, exceptional robustness, excellent photophysical properties, and functional sophistication. This biological material can be assembled with inorganic nanomaterials, such as semiconductor or photonic particles, into artificial hierarchical structures and demonstrate functionality that spans far beyond its natural property. This talk will provide examples of catalytic systems based on natural proton pump for light-driven H₂ production, ATP synthesis and CO₂ reduction.

5:30 AM S.EN06.03.03
Study on Preparation and Properties of Boron-Gallium Co-Doped Multicrystalline Ingots Hongzhi Luo¹,², Liang He¹,², Qi Lei¹,², Yunfei Xu¹,², Cheng Zhou¹,², Wei Mao¹,², Zhibin Fu¹,², Jianmin Li¹,², Xiaojuan Cheng¹,² and Guifu Zou²; ¹Jiangxi Saiwei LDK Solar High-Tech Co., Ltd, China; ²National Photovoltaics Engineering Research Center, China

In this paper, we present the preparation of multicrystalline silicon ingots with different boron-gallium doping ratio, resistivity distribution, minority carrier lifetime, photovoltaic conversion efficiency and light-induced degradation ratio were analyzed and contrasted. The result shows that within the increase of gallium doping ratio, resistivity and minority carrier lifetime of ingot, as well as conversion efficiency of silicon wafer were both in a decreasing trend, the light-induced degradation ratio also tended to decrease as a whole, but fluctuated locally. By comparing elements tested data, it was preliminarily concluded that the fluctuation may be caused by copper, iron and other impurities. Based on the performance of resistivity, conversion efficiency and light-induced degradation ratios of gallium-doped ingots, the optimal gallium-doped
ratio of multicrystalline ingots was determined to be about 25%.

5:40 AM *S.EN06.03.05
Rational Design of Photoelectrocatalytic Materials for Artificial Photosynthesis Guiji Liu and Francesca Maria Toma; Lawrence Berkeley National Laboratory, United States

Due to the rapid depletion of fossil fuels and related environmental issues, developing technologies for producing renewable, clean fuels for our future is of great importance. Artificial photosynthesis via water splitting or CO₂ reduction offers an attractive and cost-effective route to achieve this goal. However, existing photoelectrocatalytic materials generally suffer from low activity or instability, thus greatly impeding the feasibility of artificial photosynthesis technologies. Herein, we present design strategies for the synthesis and integration of photoelectrocatalytic materials.

References

5:55 AM S.EN06.03.06
Photoelectrochemical Selective Glycerol Reforming Using Fe Doped ZnS/ZnO Photoanode Seungkyu Kim, Sehun Seo and Sanghan Lee; Gwangju Institute of Science and Technology, Korea (the Republic of)

Photoelectrochemical (PEC) oxidation of glycerol is an attractive biomass feedstock for the production of renewable energy such as hydrogen and biofuel, such as glyceric acid, dihydroxyacetone, and formic acid. Recently, ZnS has been considered as a promising material for the production of biofuel because of its inexpensive cost and suitable potential for the oxidation of organic compounds. However, ZnS absorbs only ultraviolet region owing to a wide bandgap (~3.6 eV) and suffer from fast recombination of electron-hole pair.

In this study, we have synthesized Fe doped ZnS / ZnO photoanodes (FZZ) using all solution process for the efficient photo-oxidation of glycerol. By optimizing Fe doping concentration, FZZ samples have enhancement of light-harvesting at the visible region and high conversion efficiency of glycerol. In addition, the charge separation is enhanced by the formation of the heterostructure, providing a direct pathway for the electrons. As a result, the efficiency of photo-reforming of the FZZ is greatly improved over the pristine photoanode. Also, we can confirm the selectively oxidized product according to the various applied potential in PEC cells.

6:05 AM S.EN06.03.07
Adsorption and Photocatalytic Oxidation of Ibuprofen Using Nanocomposites of TiO₂ Nanofibers Combined with BN Nanosheets—Degradation Products and Mechanisms Huiyao Wang, Lu Lin, Wenbin Jiang, Pei Xu, Tanner Schaub and Rashi Sapkota; New Mexico State University, United States

This study investigated the adsorption and photocatalytic activity of TiO₂-boron nitride (BN) nanocomposites for the removal of contaminants of emerging concern in water using ibuprofen as a model compound. TiO₂ nanofibers wrapped by BN nanosheets were synthesized by electrospinning method. Characterization of the nanocomposite photocatalysts indicated the BN nanosheets improved the light absorbance and reduced the recombination of the photoexcited charge carriers (e⁻ and h⁺). The photocatalytic oxidation products and mechanisms of ibuprofen by the TiO₂-BN catalysts were elucidated using a multiple analysis approach by high performance liquid chromatography, ultraviolet absorbance, dissolved organic carbon, fluorescence excitation-emission matrices, and electrospray ionization–liquid chromatography–tandem mass spectrometry. The experimental results revealed that the photocatalytic oxidation by the TiO₂-BN nanocomposites is a multi-step process and the reactions between ibuprofen molecules and the TiO₂-BN nanocomposites govern the adsorption process. The increasing BN nanosheet content in the TiO₂ nanofibers facilitated the breakdown of ibuprofen degradation intermediates (hydroxyibuprofen, carboxyibuprofen, and oxypropyl ibuprofen). Kinetic modeling indicated both adsorption and photocatalytic oxidation of ibuprofen by the TiO₂-BN nanocomposites followed the first-order kinetic model. The photocatalytic oxidation rate increased with the increasing BN content in the nanocomposite catalysts, which was attributed to the enhanced light absorption capacity and the separation efficiency of the photoexcited electron (e⁻)-hole (h⁺) pairs. Multiple photocatalytic cycles were conducted to investigate the reusability and regeneration of the nanofibers for ibuprofen...
Copper-based transition metal chalcogenide (S, Se, Te) nanocrystals provide one of the most attractive platforms for both nanophotonic and photovoltaic applications as a vast range of material properties can be realized through compositional control of these nanocrystals consisting of earth-abundant elements. In transition metal Cu-chalcogenides, the strong p-d hybridization and the small variations in size and electronegativity between the transition metal cations and the chalcogens facilitate an extraordinary range of spectral and electroluminescence properties. Additionally, the defect concentrations and the possibility of non-stoichiometric and antisite defects in the Cu-chalcogenides can be used as key parameters to further tailor optoelectronic properties of these compounds. From the perspective of photovoltaic applications, the quest for a sustainable and affordable energy material still remains. A broad spectrum of electronic band gap can be realized through compositional control in the mixed metal Cu-chalcogenides. To this end, multinary Cu-chalcogenides offer further flexibility in band gap engineering and spectral properties through compositional variation of the different elements within the compound. However, it is synthetically challenging to realize the more complex multinary compositions of the Cu-chalcogenides. To date, several binary compositions of transition metal Cu-chalcogenides have been stabilized, but few reports of ternary, quaternary, and penternary complexes are available. What if we can synthetically realize a new gamut of higher order transition metal Cu-chalcogenides for a wide range of novel optoelectronic properties?

In this study, we report a new library of penternary Cu2ZnASxSe4-x (0 < x < 4, A = Al, In, Ga) nanocrystals and thin films. The nanocrystals are synthesized via a hot injection solution process to facilitate compositional control in these complex structures. These nanocrystals with multiple chalcogens and different cross-row elements within the structure are unique from the perspective of structural and material properties. The morphology and chemical composition of the new penternary nanocrystals are investigated via scanning and transmission electron microscopy equipped with energy dispersive x-ray spectroscopy. These materials exhibit a wide range of band gap, largely influenced by the Se content and cation composition, as determined through the experimental Tauc plots. In addition, a wide range of composition-controlled photoluminescence is obtained with this group of penternary Cu-chalcogenides. Thin films of these novel chalcogenide nanocrystals were deposited on Si wafer substrates using a spin coating technique. Transport properties (resistivity and Hall effect) of the complex structures to fabricate n-type or p-type semiconductors for photoanode and photocathode respectively. However, high light reflection, low photovoltage output due to its narrow bandgap, and severe photocorrosion in the electrolyte remain as serious limitations to manufacture efficient Si-based photoelectrodes.

In this talk, I will discuss the fabrication of Si-based photoelectrodes coupled with earth-abundant transition metal-based catalysts for efficient water splitting. We introduced two-dimensional (2D) transition metal dichalcogenides catalysts on p-type Si-photocathode for highly efficient PEC hydrogen production. 2D transition metal dichalcogenides such as MoS2 and WS2 are a promising materials to replace noble metal catalysts due to their high density of catalytically active edge sites and large surface-to-volume ratio. Wafer-scale transferable transition metal dichalcogenides thin-film catalysts can provide a low onset potential and high photocurrent density. I will also talk about n-type Si photoanodes with high catalytic activity in transition metal-based catalysts synthesized via facile electrodeposition method for efficient water oxidation. Si photoanodes covered with water oxidation catalysts such as layered-double hydroxides, metal nanoparticles, and thin films exhibited high photoelectrochemical property and long-term stability.
Heterogeneous catalysts are used to reduce energy barrier for chemical reactions by promoting gas adsorption. Such energy barrier is commonly overcome by heating a reactor filled with gaseous reactants. On plasmonic nanostructures, optically-excited localized surface plasmon (LSP) resonances were found to induce H₂ or O₂ dissociation at a reduced temperature, mimicking photocatalysis. Energy harnessed by plasmonic nanostructures and transferred to adsorbed reactants during the dephasing of LSP resonances is theorized to initiate such reactions by compensating for the thermal energy required otherwise. Therefore, resolving sub-nanoparticle information of surface plasmon induced reactions, including (1) reactant adsorption, (2) LSP resonance energy that overcomes reaction barrier, and (3) product desorption, could elucidate design rules of plasmonic catalysts. However, such information has not been obtained under reactive environments by variants of optical spectroscopy, since their spatial resolution is diffraction-limited at best and the excitation of LSP modes by light is polarization-sensitive. Herein, we demonstrate that sub-nanoparticle information gained from electron energy-loss spectroscopy (EELS) and cathodoluminescence (CL) can be used to measure these reaction details and drive selected reactions.

Electron-beam-excited LSP resonances on shape- and size-controlled nanoparticles are exploited to drive chemical reactions in an environmental scanning transmission electron microscope equipped with a monochromated electron gun operated at 80 kV with an energy resolution of 0.08 eV. Low-loss EELS hyperspectral imaging and CL maps, combined with theoretical predictions based on electromagnetic boundary element method, reveal the spatial distribution of coupling efficiency of the convergent electron beam to the LSP modes. Coupling efficiency maps, derived by applying the non-negative matrix factorization (NMF) to an EELS hyperspectral image, shows specific LSP mode can be preferentially excited by positioning the electron beam with a nanometer-level precision. In situ core-loss EELS data is employed to measure local chemical compositions and oxidation states of the nanostructure in vacuum and the gas environments. For the first time, gas adsorption maps, were obtained using in situ EELS spectrum imaging. For shape-controlled Au nanoparticles on TiO₂ support in a CO environment, the adsorption maps indicate that CO is adsorbed on selective nanoparticle edges but not on the entire surfaces. Under the same CO environment, the LSP dipole mode of an Au nanoparticle is preferentially exited using electron beam to drive CO disproportionation: 2CO(g) → CO₂(g) + C(s), at room temperature (commonly initiated above 400 °C). One of the reaction products – amorphous carbon – is deposited only at the cantilevered corner of Au nanoparticles, indicating that the active sites for the reaction are located where preferable gas adsorption sites and locations of maximum plasmonic field amplitude superimpose. Energy transferred to the adsorbed reactants is further identified based on the spectral difference between EELS and CL, acquired during the reaction. For size-controlled Al nanoparticles, elemental analysis using EELS shows a core-shell structure of Al-Al₂O₃, where a crystalline Al core is enclosed in an oxide shell. The oxide thickness modulates the LSP resonance energy and can be used to match the energy barrier for selected reactions. In one of the examples, the oxtupole mode on core-shell Al nanoparticles are utilized to initiate carbon etching in a CO₂ environment through the reverse Boudouard reaction (CO₂(g) + C(s) → 2CO(g)) without any additional heat in an endothermic reaction. Our methodology provides unprecedented information on LSP-induced chemical reactions at the nanometer scale, shedding light on the design principles for new hybrid plasmonic catalysts that will enable low-temperature, industry-relevant chemical processes.

6:50 AM S.EN06.03.17
Quasi-High Entropy Oxide with Ultra-Long Lifetime and Ferroelectric Catalyst- Ca(ZrYCeCrAg)O, Performing Piezo-Photo Catalytic Activity with Localized Surface Plasmonic Resonance Hsuanyu Chen¹ and Jyh-Ming Wu¹,²; ¹National Tsing Hua University, Taiwan; ²University of California, Los Angeles, United States

This work, Ca(ZrYCeCrAg)O, modified from pristine CaZrO₃, owning inner heterostructure, which was sonicated with visible light has been confirmed it can enhance piezo-photo catalytic activity for organic dye degradation. CaZrO₃(CZO) demonstrate remarkable optical information storage application due to possessing numerous intrinsic traps and ferroelectricity, which imply long recombination lifetime. However, the large band gap (3.3eV) restrict its photo-catalytic efficiency for dye degradation. Herein introduction of several transition metal elements into CZO nanoparticles has been synthesized by a sol-gel process and forms heterojunction nanostructure(fluorite-(Zr,Y,Ce)O₂ & perovskite-CaZrO₃) The time-resolved photoluminescence (TRPL) reveals that recombination lifetime have already improved up to 620% compared to pristine CZO. CZO, which belong to Pnma group of perovskite structure, displays unique ferroelectricity which has spontaneous polarization for prolonging lifetime and enhance piezo-photo activity. Besides, modified-CZO surrounded by silver nanoparticles, demonstrating localized surface plasmon resonance (LSPR) effect as observed by surface enhanced raman spectrum(SERS). Through ultraviolet-visible (UV-Vis) spectrophotometer measurement, modified-CZO is achieving almost 200% degradation performance compared to pristine CZO. The vast enhancement arises from piezo-photo activity, which was combined through ferroelectricity, charge transfer mechanism for prolonging recombination lifetime, and induced local electric field for generating numerous electron-hole pair. The COMSOL software was employed to simulate the charge...
distribution. The mechanism on LSPR enhanced piezo-photo catalytic dye degradation will be investigated.
Keywords: CaZrO3, Ag, Ferroelectricity, Lifetime, Surface Plasmon Resonance, Dye Degradation

SESSION S.EN06.04: Poster Session: Rational Designed Hierarchical Nanostructures for Photocatalytic System
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday
Morning, November 21, 2020
5:00 AM - 8:00 AM
S-EN06

S.EN06.04.02
Zinc Oxide Nanostructures Synthesized by a Simple Hot Water Treatment Method for Photocatalytic Degradation of Organic Pollutants in Water
Ranjitha Hariharalakshmanan, Busra Ergul, Nawzat S. Saadi, Khalidah Al-Mayalee and Tansel Karabacak; University of Arkansas at Little Rock, United States

The use of zinc oxide (ZnO) nanostructures as a photocatalyst for the degradation of organic pollutants in water has received significant attention over the recent years. However, synthesis methods for producing ZnO nanostructures are generally costly, complicated, and hazardous to the environment. In this work, we demonstrate the synthesis of zinc oxide nanostructures by a simple hot water treatment (HWT) method and the photocatalytic activity of the hence produced nanostructures. HWT is a one-step, low-cost, eco-friendly, and scalable nanostructure growth method. By HWT, various metal oxide nanostructures can be produced simply by the interaction of metals with hot water without the need for any chemical additives in the solution. Growth of metal oxide nanostructures by HWT involves the formation of metal oxides and their release from the surface of the metal into water, the migration of the metal oxides in water and their re-deposition at a different part of the metallic surface, which initiates the growth of nanostructures. In this study, we used zinc powder and plates for producing the ZnO nanostructures by HWT in DI water at 75 °C. Scanning electron microscopy images and X-ray diffraction were utilized to verify the formation of ZnO nanostructures. Zinc plates produced a suspension of ZnO nanostructures in water, while on the other hand Zn powder resulted in a predominantly core-shell geometry of Zn particle-core and ZnO nanostructures-shell also mixed in water. We used these nanostructures + water suspensions for our photocatalytic degradation studies. Methylene blue was used as a model organic pollutant. We mixed the ZnO nanostructure suspension with methylene blue and exposed it to UV light. The degradation of methylene blue was observed by measuring its absorbance values using a UV-Visible spectrophotometer over a period of four hours. We observed a 20% decrease in the concentration of methylene blue in four hours when nanostructured Zn/ZnO core-shell powder suspension was used, and a 30% decrease was achieved when ZnO nanostructure-only suspension was used. Methylene blue alone was also exposed to UV light for the same period as a control experiment and we did not observe any significant decrease in its concentration. These preliminary results indicate that hot water treatment method presents a very simple, cost-effective, scalable, and eco-friendly alternative for the synthesis of zinc oxide nanostructures for photocatalytic water treatment applications.

S.EN06.04.03
Carbon Dioxide Conversion to Methanol over Rh Intercalated Graphene/SiC—A First-Principles Study
Ashwin Kishore Munusamy Rajendran and Karin Larsson; Uppsala University, Sweden

Mitigating atmospheric CO2 concentration is a great challenge for the twenty-first century. It can be done only by capturing and converting CO2 into useful fuels with the help of catalysts. Knowledge of the reaction mechanism in CO2 hydrogenation reactions is key to the rational design of highly efficient catalysts. Here, we investigate the CO2 conversion into methanol on Rh intercalated Graphene/SiC using density functional theory calculations and kinetic Monte Carlo simulations. The adsorption energy, bonding configuration, bond lengths, and vibrational frequencies of all the surface intermediates involved in the reaction mechanisms are studied. Present results on methanol production suggest that the hydrogenation of CO2 to CO occurs via the reverse-water-gas shift (CO2 + H2 → CO + H2O) reaction rather than formate (HCOO-) or direct C−O bond cleavage pathways. The produced CO can either desorb or further react with hydrogen to produce CH4 or CH3OH since the adsorption energy of CO is low. The intermediates of the CO2 pathway for methanol production includes *OCOH, CO, *CHO, *CHOH, and *H2COH. The reaction barrier energy for each elementary steps involved in CO2 hydrogenation will be discussed, and that can provide further insights into the reaction mechanism. Finally, we will also discuss how the energetics affects the kinetics of the reaction, such as the overall rates for CO2 conversion and the production of CO, CH3OH, and CH4 under reaction condition.
Plasmonic Photonic Crystal Photocatalysts Consisting of TiO2 Nanotube Arrays Decorated/Embedded with Noble Metal Nanoparticles

Sheng Zeng¹, Ryan Kisslinger¹, Alexander Kobryn², Sergey Gusarov², Kazi Alam¹,² and Karthik Shankar¹; ¹University of Alberta, Canada; ²National Research Council Canada, Canada

Plasmonic photocatalysis offers the promise of using light as the energy source to drive a variety of thermal energy-intensive phonon-driven chemical reactions close to room temperature [1]. Industrially relevant heterogeneous catalytic reactions targeted by plasmonic photocatalysis include CO₂ reduction, water-splitting to generate H₂, hydrocarbon reforming, Fischer-Tropsch reactions, synthesis of azo dyes, nitrogen fixation, hydrogenation reactions, and the oxidative degradation of organic compounds. Plasmonic catalysis also offers unique chemical bond activation mechanisms that differentiate hot carrier-driven chemical reactions from routine carrier-driven catalysis [2].

Plasmonic photocatalysis utilizes nanophotonics in the service of catalysis. Another nanophotonic architecture, namely photonic crystals (PhCs) which allow the propagation of photons of selected frequency bands, has been explored much less for catalysis. The primary reason is the impracticality of using top-down fabrication techniques such as electron beam lithography to mass-produce PhC catalysts. Bottom-up fabrication techniques for PhCs are rare, and suffer from a lack of adequate control over the optical properties of the resulting PhCs.

Herein, we present the bottom-up synthesis of large area PhCs consisting of arrays of self-organized vertically oriented TiO₂ nanotubes (TNTAs) with periodically modulated diameters, grown by a charge controlled pulsed electrochemical anodization (CCPEA) technique. The CCPEA technique enables superior control over the optical resonances exhibited by TNTA PhCs, compared with galvanostatic & potentiostatic pulsed anodization processes. When TNTA PhCs with well-defined photonic stop-bands are decorated or embedded with nanoparticles (NPs) of Au, Ag, CuPt, TiN, etc, plasmonic photonic crystals result.

TNTAs partially embedded with Au NPs are shown to be excellent photoanodes for visible light-driven photoelectrochemical water-splitting in alkaline electrolytes. Embedding Au NPs in the nanotube walls as opposed to decorating them results in high extinction coefficient, high Q-factor, red-shifted plasmon resonances [3] that facilitate the injection of hot electrons formed by plasmon dephasing, into the conduction band of TiO₂ while residual hot holes oxidize water to O₂. The observation of photoelectrochemical quantum yields approaching 30 % for visible wavelengths indicates surprisingly efficient hot carrier harvesting. Likewise, TNTA PhCs decorated with Au NPs are also excellent photocatalysts for the vapor phase reduction of CO₂ into light hydrocarbons. TNTAs conformally coated with titanium nitride exhibit near-infrared resonances and appreciable photocatalytic activity [4]. The TNTA structure provides a high density of active surface sites for reactant adsorption, and its own optical properties (PhC and Mie scattering effects) [5] interact with the plasmons to influence the photocatalytic behavior.

REFERENCES


Solar Fuel Production—Opportunities for Nanostructures

Zhigang Zou; Nanjing University, China

The photocatalytic and photoelectrochemical reduction of water or CO₂ is an intriguing approach to producing sustainable solar fuels, and has attracted growing and intense interest. Nanostructuring of photocatalysts and photoelectrodes has been proven to be a strong strategy to dramatically improve overall solar-to-fuel conversion efficiencies. Another technological barrier for the practical implementation of solar fuel production is long-term material durability, which has recently been well addressed by using conformal coatings of protective layers onto the narrow band-gap semiconductors that are suitable for
efficient solar-to-fuel conversions but photoelectrochemically unstable. These significant progresses may lead us to the practical implementation of solar fuel production. We focused on the exciting progresses achieved by using nanostructuring strategies, specifically regarding how the nanostructure influences the charge transport and separation. Special attention was paid to investigate how a nanoscale coating (overlayer) passivates the surface states, thereby reducing the surface electron hole recombination, and how a nanoscale coating (protective layer) prevents the photocorrosion or photopassivation of the semiconductors with optimal band gaps. We hope that the design strategies using these nanostructures will offer new and greater opportunities for efficient solar fuel production to existing photocatalytic and photoelectrochemical systems.

S.EN06.04.11
Low Temperature and Green Synthesis of Diethylenediamine Functionalized Reduced-GO Grafted on SiC for Photodegradation and Conversion of Organic Pollutants to Useful Fuels
Olusegun Abass; Nanyang Technological University, Singapore

Conventional photocatalysts based on metals and semiconductors are sometimes rigid and possess stability issues when applied in the treatment of industrial wastewater. Thus, novel photocatalysts based on polymer/nanomaterial composites are attracting more interest. Although much effort has been devoted to acquire catalysts with high efficiency and long-term durability, this work proposes a simple and green three-steps procedure for synthesis of diethylenediamine-modified reduced graphene oxide (DD-rGO) grafted on a magnesio-thermically produced silicon carbide (SiC) to achieve one-vessel conversion of organic pollutants into useful fuels such as methanol and ethanol under simulated solar irradiation. The mechanism behind the distinct reactivity and stability of the as-prepared photocatalyst was proposed. We expect that these entirely new nanocomposite structures will not only pave way for the development of highly efficient and stable photocatalyst systems but also have a wider impact in applications (such as water treatment) where catalysts stability is essential.

S.EN06.04.13
Sodium Niobate (NaNbO3) Nanorods Coupled with RGO Nanocomposite for Enhanced Photoelectrochemical Water Splitting
Dheeraj Kumar and Neeraj Khare; Indian Institute of Technology Delhi, India

The utilization of fossil fuel subsidiaries, for example, coal, heavy oil, natural gas and petrol have transformed into global issue of environment concern. The use of energy is rapidly expanding with rising population in view of which there is a need of utilizing efficient green sustainable energy sources to fulfill the requirements of energy supply [1]. The solar light based energy can be converted and stored in the form of fuels, for instance, generation of hydrogen (H2) by photoelectrochemical (PEC) water splitting appears to be a potential alternative to the fossil fuels [2]. PEC water splitting is one of the most attractive technology for H2 generation using a semiconductor nanocomposite materials [3, 4]. In the present work, hydrothermally grown sodium niobate nanorods (NaNbO3-NRs) has been successfully coupled with reduced graphene oxide (RGO) nanosheets by using reflux method. Furthermore, the potentiality of the synthesized nanostructures has been investigated for photoelectrochemical (PEC) water splitting. A ~4 fold enhancement in the photocurrent density is demonstrated by fabricated RGO/NaNbO3-NRs nanocomposite photoanode than that of NaNbO3-NRs photoanode under UV-visible light illumination. The enhancement in the PEC activity of RGO/NaNbO3-NRs nanocomposite is attributed to the more absorption of visible light of the solar spectra and increase the mobility of photogenerated charge carriers which improves the separation efficiency and reduces the recombination of charges. The possible mechanism responsible for the PEC water splitting have been proposed.

References

S.EN06.04.14
Non-Noble Metal Plasmonic Nanoparticles as Highly Efficient Light Absorber for Solar Steam Generation
Fan Yang and Yadong Yin; University of California, Riverside, United States

Plasmonic nanoparticles have attracted great interest in harvesting solar energy due to their excellent capability in photothermal conversion. However, noble-metal-based plasmonic nanoparticles typically exhibit a narrow absorption peak, which limits their ability to fully utilize solar energy. Compared with conventional noble metal nanoparticles, transition metal nanoparticles show relatively broad resonance band, allowing absorption of a larger fraction of solar radiation. However, the application of these nanoparticles is limited due to their poor stability, especially in the presence of oxygen and water. In this
presentation, we report the synthesis of Ni@C@SiO₂ core-shell nanoparticles that can be used as light absorbers. The stability of Ni nanoparticles is greatly enhanced by a layer of densified SiO₂. Moreover, by adding a carbon layer between Ni and SiO₂, the absorption peak of Ni can be expanded and red-shifted to maximize the overlapping between the absorption spectra of core-shell nanoparticles and the solar radiation spectra. The colloidal nature of the nanoparticles allows their easy processing into a thin film that can be attached to a floating melamine foam, producing an integrated solar steam generator. The three-layered core-shell nanoparticles exhibit an excellent photothermal property and high steam generation efficiency under solar illumination.

S.EN06.04.19
**Photoelectrochemistry of Cobaloxime-Modified Gallium Phosphide and Gallium Arsenide Surfaces**
Nghi Nguyen, Brian L. Wadsworth, Edgar Reyes Cruz, Daiki Nishiori and Gary F. Moore; Arizona State University, United States

Photoelectrochemistry provides a strategy for creating fuels from sunlight. In this poster presentation, I will describe the chemistry of immobilizing polypyridyl coatings containing cobaloxime-type catalysts onto either GaP or GaAs surfaces. When wired in a three-electrode configuration with appropriate counter and reference electrodes, the hybrid constructs use light to power the production of hydrogen gas with near unity faradaic efficiency from aqueous solutions in the absence of sacrificial chemical reductants and with no electrochemical forward biasing. When operating at the equilibrium potential of the hydrogen evolution reaction under simulated 1-sun illumination, the modified- GaP and GaAs assemblies produce current densities of 1 and 10 mA cm⁻², respectively. Analyses of the wavelength-resolved external and internal quantum efficiencies show the modified-GaP assemblies are active over wavelengths ranging from 300 to 550 nm, and the modified-GaAs assemblies are active over wavelengths ranging from 300 to 870 nm. The cobaloxime-modified GaAs thus gives a higher rate of photoelectrochemical fuel production due to the improved spectral overlap of the semiconductor's absorption properties with the solar flux spectrum.


S.EN06.04.20
**Photoelectrochemistry of Metalloporphyrin-Modified Gallium Phosphide Surfaces**
Daiki Nishiori, Brian L. Wadsworth, Edgar Reyes Cruz, Nghie Nguyen and Gary F. Moore; Arizona State University, United States

Human-engineered materials capable of generating fuels from sustainable energy sources provide an approach to satiating modern societies' energy demands, with minimal environmental impact. In this poster presentation, I will describe hybrid photoelectrosynthetic assemblies composed of gallium phosphide (GaP) functionalized with metalloporphyrin complexes of five different transition metal ions: Fe(III), Co(II), Ni(II), Cu(II), and Zn(II). Surface attachment of these metalloporphyrin complexes was achieved using a previously reported UV-induced photochemical grafting method. The photoelectrochemical properties of these heterogeneous-homogeneous materials will be contrasted with electrochemical properties of the isolated, homogeneous metalloporphyrins and other previously reported heterogeneous-homogeneous constructs.


**SYMPOSIUM S.EN08**

**Multivalent-Based Electrochemical Energy Storage**

**November 21 - December 1, 2020**

**Symposium Organizers**

Tianbiao Liu, Utah State University  
M. Rosa Palacin, ICMAB-CSIC  
Jennifer Schaefer, University of Notre Dame  
Zhirong Zhao-Karger, Karlsruhe Institute of Technology

* Invited Paper

SESSION S.EN08.07: Live Keynote I: Multivalent-Based Electrochemical Energy Storage

Session Chairs: Tianbiao Liu and Jennifer Schaefer  
Monday Afternoon, November 30, 2020  
S.EN08

**7:30 PM S.EN08.01.05**

**Pairing Two-Electron Zinc Architectured Electrodes with Multivalent Cathodes for Enhanced Energy Storage** Debra R. Rolison1,2, Brandon J. Hopkins1,2, Samuel W. Kimmel3,4,1, Christopher N. Chervin1, Joseph F. Parker1, Jeffrey W. Long2 and Christopher Rhodes2; 1U.S. Naval Research Laboratory, United States; 2National Research Council Postdoctoral Associate, United States; 3Texas State University, United States; 4Naval Research Enterprise Internship Program (NREIP), United States

We previously demonstrated that reformulating zinc into a monolithic spongy form factor moved aqueous zinc-based batteries onto a new performance curve—one in which the zinc electrode can be rechargeably cycled at high rate, to deep utilization of the metal, all without generating separator-piercing dendrites. This breakthrough enables development of a broad class of rechargeable zinc-based aqueous batteries. Ideally a next-generation of batteries in which the accompanying cathode can match the two-electron redox of zinc. We will describe the improvement of system metrics when pairing the two-electron zinc sponge versus the two-electron silver oxide cathode, even without optimizing the silver electrode, including
Development of Magnesium Electrolytes—From Chloride Mixtures to Weakly Dissociated Anions

Chen Liao1,2; 1Argonne National Laboratory, United States; 2Joint Center of Energy Storage Research, United States

The fossil fuel energy crisis causes significant geopolitical stress, and renewable energy such as wind, tide, and solar is a green solution to this problem. Energy storage is required for any renewable energy utilization as they are of intermittent nature with usually high production during off-peak hours and low production in peak hours. Lithium ion battery is the main workhorse for portable electronics and portable tools and start adopting the market of electric vehicles, as well as electrochemical energy storage. However, they are reaching their maximum performance and a new breakthrough in electrochemical energy storage is necessary for a wide adaption of renewable energy. Multivalent ion batteries, particularly Mg and Ca, are of high interest because of their very electropositive electrochemical potentials: Mg has a reduction potential of -2.4 V vs NHE, while Ca has a reduction potential of -2.9 V vs NHE. Other favorable properties include high volumetric energy density and high crustal abundance.

The development of Mg has been mostly impeded by both the cathode and electrolyte developments, unlike its counterpart Li ion, Mg is notoriously famous for formation of a strong bond with oxygen and does not move easily in the lattice of MgO. A premise for a working Mg ion battery is that the surface of the Mg metal cannot be passivated in order to facilitate reversible Mg dissolution/deposition. A classical way of conditioning or preparing the Mg metal surface is either to provide a Cl- in a Mg solution.(1,2) The limited anodic stability of the Cl- would be problematic for Mg ion batteries because of corrosion issue with current collector. Using high-purity Mg salts with weakly associated anion (WCA) such as trifluorosulfonimidide (TFSI) (3) and carborane (4) has been a standard practice in the field since 2015. In 2019, our group introduced a new WCA group for the MV salts, the t-buty/perfluoroaluminate ([TPFA]− = [Al{OC(CF3)3}4]−) anion for Mg salts,(5) and demonstrated the highly reversibility of deposition/dissolution, unprecedented anodic stability, and lack of passivation layer formation during the high potentiostatic hold. The favorable properties of the salt make it a friendly anion for the quest of cathode development, especially the transition metal oxide spinels for Mg ion batteries.

We will cover the brief history of the development of Cl- containing electrolyte in our group since 2014 and will present the detailed electrochemical performance, and collaborated work on the decomposition mechanism understanding, solvation behavior in O-donor solvents, and expansion of these research

11:30 AM *S.EN08.01.03

Potential of Magnesium Batteries Robert Dominko1,2,3, Jan Bitenc1, Alen Vizintin1, Rekha Narayan1 and Anna Randon-Vitanova4; 1National Institute of Chemistry, Slovenia; 2FKKT, University of Ljubljana, Slovenia; 3Alistore ERI, France; 4Honda R&D Germany, Germany

Magnesium is a promising element for future batteries due to high gravimetric (2206 mAh/g) and volumetric capacity (3834 mAh/cm3) of Mg anode. It is considered as geopolitically neutral, sustainable and abundant metal, which can be used in batteries due to non-dendritic deposition during battery operation. Besides discussed benefits, there are several challenges connected with the use of Mg metal, mainly incompatibility of the Mg metal with the electrolytes and difficult insertion of magnesium into oxide based solid state host matrix. Alternative solutions can be use of redox active polymers with different active redox groups.

In this presentation, overview of recent achievements in our group on the field of magnesium batteries will be discussed with a focus on proper selection of battery components in order to achieve electrochemical properties attractive for the commercialization.

Acknowledgement: This work is supported HONDA R&D Europe and by the Slovenian Research Agency (research core funding No. P2-0393 and research project J2-8167).

References:

12:00 PM *S.EN08.02.04

Electrolytes for Rechargeable Aluminum Batteries—The Complexity of Chloroaluminate Ionic Liquids Juchen Guo; University of California, Riverside, United States

Reversible electrochemical reactions of aluminum (Al) that can be potentially used for energy storage technologies is an intriguing topic from both scientific and technological perspectives. The centerpiece of reversible Al electrochemistry is the electrolyte. To date, the overwhelming majority of Al battery research activities utilize Lewis acidic chloroaluminate ionic liquids as the electrolytes. However, the complex nature of these electrolytes, such as corrosiveness, proneness to oxidation, and rich coordination, can lead to unintended ambiguity. In this presentation, we demonstrate that cautions must be used to interpret results of Al electrochemical reactions along chloroaluminate ionic liquid electrolytes. We use aluminum chloride/1-ethyl-3-methylimidazolium chloride (AlCl3-[EMIm]Cl) ionic liquid as the example. We find Lewis acidic AlCl3-[EMIm]Cl is corrosive to many commonly used metal current collectors, and the resulting corrosion current could be mistaken as the current from the electrochemical reactions of Al. The proneness of electrochemical oxidation of AlCl4− anion (ultimately leading to chlorine evolution) causes complicated process in the previously reported reversible AlCl4− intercalation in graphite. As the results, fast self-discharge and large irreversible capacity is observed when graphite (either natural or synthetic) is used as the cathode materials. We further investigated the chemical compatibility of AlCl3-[EMIm]Cl with V2O5, which is a common cathode material reported in the literature of Al battery. Our study indicates V2O5 chemically reacts to both Lewis neutral and Lewis acidic AlCl3-[EMIm]Cl. By elucidating the reaction mechanisms, we conclude V2O5 is not a
feasible Al storage material in the chloroaluminate ionic liquid electrolytes. These findings could provide guideline for design more reliable electrolytes for rechargeable Al batteries.

SESSION S.EN08.10: Live Panel Discussion II: Multivalent-Based Electrochemical Energy Storage
Session Chairs: Tianbiao Liu and Jennifer Schaefer
Tuesday Afternoon, December 1, 2020
S.EN08

12:30 PM PANEL DISCUSSION: ROBERT DOMINKO, JUCHEN GUO, RANA MOHTADI AND ROBERT MESSINGER,

SESSION S.EN08.01: Progress in Multivalent Battery Design
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN08

5:00 AM *S.EN08.01.01
Developing Advanced Electrolytes for Multivalent Mg and Ca Batteries Jian Luo and Tianbiao L. Liu; Utah State University, United States

Mg is an earth abundant and low-cost metal (ca. 24 times cheaper than Li), and as an anode material, Mg is safe to use (vs. Li, Li-ion, or Na-ion batteries). Its high gravimetric capacity (2,333 Ah/kg) and high reduction potential (-2.37 V vs SHE) allow the assembly of high-energy density batteries. However, despite rapid research progress, the lack of high performance Mg2+ conductive electrolytes still presents a primary technical hurdle for developing practical Mg batteries. The presentation will cover our research efforts in developing high performance Mg electrolytes for Mg rechargeable batteries. Specifically, we will present the synthesis and electrochemical performance of ternary Mg/MgCl2/AlCl3 (MMAC) electrolytes and a novel Cl-free perfluorinated pinacolatoborate Mg electrolyte (Mg-FPB). These MMAC and Mg-FPB electrolytes exhibited up to 100% Coulombic efficiency, and 164 mV overpotential for Mg deposition, and 4.5 V vs Mg anodic stability. Solution and interfacial chemistry of the presented Mg electrolytes will be discussed in detail.

5:15 AM *S.EN08.01.02
Progress in Mg and Ca Batteries Maximilian Fichtner1,2, Zhenyou Li1 and Zhirong Zhao-Karger1; 1Helmholtz-Institute Ulm (HIU), Germany; 2Karlsruhe Institute of Technology, Germany

The stagnation in the development of Li ion batteries based on liquid electrolytes and resource issues associated with the current battery configuration have fueled activities which try to solve or circumvent these issues. The aim is to both increase the energy content of battery cells and to make them ready for future application. This requires a set of materials which do not only have exceptional standalone properties but can mutually interact in a harmonic manner. Multivalent batteries promise to have superior properties in terms of volumetric and gravimetric capacities, however suffer from major roadblocks such as low ionic conductivity in the solid, reversible and efficient transport in the liquid and reversibility of insertion/conversion reactions.

One concept to tap the potential of multivalent systems is using conversion electrodes, e.g. with sulfur/carbon composites as cathode. The contribution will comment on the actual state of development of sulfur-compatible electrolytes with high efficiencies, high ionic conductivities, wide electrochemical stability window, easy synthesis and excellent compatibility with electrode materials and other cell components. Recent results in the development of Mg- and Ca-sulfur batteries will be presented and the remaining challenges will be discussed. Furthermore, a new cathode material with a high capacity for Mg and a mixed storage mechanism will be presented.

5:30 AM *S.EN08.01.03
Potential of Magnesium Batteries Robert Dominko1,2,3, Jan Bitenc1, Alen Vizintin1, Rekha Narayan1 and Anna Randon-Vitanova4; 1National Institute of Chemistry, Slovenia; 2FKKT, University of Ljubljana, Slovenia; 3Alistore ERI,
Magnesium is a promising element for future batteries due to high gravimetric (2206 mAh/g) and volumetric capacity (3834 mAh/cm³) of Mg anode. It is considered as geopolitically neutral, sustainable and abundant metal, which can be used in batteries due to non-dendritic deposition during battery operation. Besides discussed benefits, there are several challenges connected with the use of Mg metal, mainly incompatibility of the Mg metal with the electrolytes and difficult insertion of magnesium into oxide based solid state host matrix. Alternative solutions can be use of redox active polymers with different active redox groups.

In this presentation, overview of recent achievements in our group on the field of magnesium batteries will be discussed with a focus on proper selection of battery components in order to achieve electrochemical properties attractive for the commercialization.

Acknowledgement: This work is supported HONDA R&D Europe and by the Slovenian Research Agency (research core funding No. P2-0393 and research project J2-8167).

References:
batteries onto a new performance curve—one in which the zinc electrode can be rechargeably cycled at high rate, to deep utilization of the metal, all without generating separator-piercing dendrites. This breakthrough enables development of a broad class of rechargeable zinc-based aqueous batteries. Ideally a next-generation of batteries in which the accompanying cathode can match the two-electron redox of zinc. We will describe the improvement of system metrics when pairing the two-electron zinc sponge versus the two-electron silver oxide cathode, even without optimizing the silver electrode, including electrochemical capacitor-worthy power. We then will describe the nanostructuring of α-Ni(OH)₂ in an attempt to stabilize the 1.67 electron redox characteristic of this precursor to the NiOOH cathode over the one-electron redox limit characteristic of β-Ni(OH)₂.

SESSION S.EN08.02: Ion Speciation and Complexity in Multivalent Electrolytes
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN08

5:00 AM *S.EN08.02.01 Development of Magnesium Electrolytes—From Chloride Mixtures to Weakly Dissociated Anions Chen Liao1,2; 1Argonne National Laboratory, United States; 2Joint Center of Energy Storage Research, United States

The fossil fuel energy crisis causes significant geopolitical stress, and renewable energy such and wind, tide and solar is a green solution to this problem. Energy storage is required for any renewable energy utilization as they are of intermittent nature with usually high production during off-peak hours and low production in peak hours. Lithium ion battery is the main workhorse for portable electronics and portable tools and start adopting the market of electric vehicles, as well as electrochemical energy storage. However, they are reaching their maximum performance and a new breakthrough in electrochemical energy storage is necessary for a wide adaption of renewable energy. Multivalent ion batteries, particularly Mg and Ca, are of high interest because of their very electropositive electrochemical potentials: Mg has a reduction potential of -2.4 V vs NHE, while Ca has a reduction potential of -2.9 V vs NHE. Other favorable properties include high volumetric energy density and high crustal abundance. The development of Mg has been mostly impeded by both the cathode and electrolyte developments, unlike its counterpart Li ion. Mg is notoriously famous for formation of a strong bond with oxygen and does not move easily in the lattice of MgO. A premise for a working Mg ion battery is that the surface of the Mg metal cannot be passivated in order to facilitate reversible Mg dissolution/deposition. A classical way of conditioning or preparing the Mg metal surface is either to provide a Cl- in a Mg solution(1,2) The limited anodic stability of the Cl- would be problematic for Mg ion batteries because of corrosion issue with current collector. Using high-purity Mg salts with weakly associated anion (WCA) such as trifluorosulfonylimide (TFSI) (3) and carborane (4) has been a standard practice in the field since 2015. In 2019, our group introduced a new WCA group for the MV salts, the t-butyl/perfluoroaluminate ([TPFA]⁻ = [Al{OC(CF₃)₃}₄]⁻) anion for Mg salts,(5) and demonstrated the highly reversibility of deposition/dissolution, unprecedented anodic stability, and lack of passivation layer formation during the high potentiostatic hold. The favorable properties of the salt make it a friendly anion for the quest of cathode development, especially the transition metal oxide spinels for Mg ion batteries. We will cover the brief history of the development of Cl- containing electrolyte in our group since 2014 and will present the detailed electrochemical performance, and collaborated work on the decomposition mechanism understanding, solvation behavior in O-donor solvents, and expansion of these research


2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
5:15 AM *S.EN08.02.02
Design of Charge Carriers for Multivalent Battery Electrolytes Patrik Johansson1,2; 1Chalmers Univ of Technology, Sweden; 2UPJV, France

As compared to Li-ion and Na-ion battery electrolytes the electrolytes for Mg, Ca and Al metal batteries are quite different. This is also reflected in the nature of the charge carriers e.g. the size and number of ligands coordinating to the central multivalent atom.
Furthermore the charge carriers are also affected by the salt concentration in a different way than the electrolytes based on monovalent central atoms.
We have studied several multivalent electrolyte designs and elucidated the preferable local structures both by modelling (MD + DFT calculations) and by experimental methods (IR, Raman and NMR spectroscopy) in terms of stability of the first solvation shell, while also addressing other properties such as the electrochemical stabilities and the coordination of active sites at the electrode. These results can be used for a more general understanding of the central atom - ligand relationship for these basic electrolytes.

References

5:30 AM S.EN08.02.03
From the Bulk to the Interface—“Ion Solvation Spectra” of Multivalent Ions in Aprotic Solvents Artem Baskin1,2 and David Prendergast1,2; 1Lawrence Livermore National Laboratory, United States; 2Joint Center for Energy Storage Research, United States

In the journey of the ions from the bulk to the interface the changes in their solvation structures and in their relative populations determine the essential characteristics of all the most important electrochemical processes. The ion solvation energy and the stiffness of its solvation sphere determine both thermodynamics and kinetics of the charge transfer at the interfaces. However, the atomistic details and thermodynamic characteristics of ion (de-)solvation process in the confined environment (e.g., near an electrode) remain largely unknown. For example, we still lack clarity on the locus and particular ion-solvent configurations at which the charge transfer occurs. On the other hand, the current paradigm of the solvation science provides well developed concepts and tools to study the ion solvation in the bulk liquid electrolytes (molecular dynamics and quantum chemistry hybrid protocols). These rely on the fundamental assumption of the uniqueness of the ion solvation structure. However, we have recently shown [1] that some even monoatomic cations in aprotic solvents exhibit multiple minima in the free energy landscapes with respect to ion-solvent coordination. As we will demonstrate, it has profound implications for the methodology to evaluate thermodynamic characteristics of electrolytes. Here we extend our approach of using advanced molecular dynamics free energy sampling techniques – both classical and ab initio – and explore the dynamics of the solvation structures of mono- and multivalent (Li+, Mg2+, Ca2+, and Zn2+) ions as they approach electrodes from the bulk in a range of aprotic solvents.


5:40 AM *S.EN08.02.04
Electrolytes for Rechargeable Aluminum Batteries—The Complexity of Chloroaluminate Ionic Liquids Juchen Guo; University of California, Riverside, United States

Reversible electrochemical reactions of aluminum (Al) that can be potentially used for energy storage technologies is an intriguing topic from both scientific and technological perspectives. The centerpiece of reversible Al electrochemistry is the electrolyte. To date, the overwhelming majority of Al battery research activities utilize Lewis acidic chloroaluminate ionic liquids as the electrolytes. However, the complex nature of these electrolytes, such as corrosiveness, proneness to oxidation, and rich coordination, can lead to unintended ambiguity. In this presentation, we demonstrate that cautions must be used to interpret results of Al electrochemical reactions using chloroaluminate ionic liquid electrolytes. We use aluminum chloride/1-ethyl-3-methylimidazolium chloride (AlCl3-[EMIm]Cl) ionic liquid as the example. We find Lewis acidic AlCl3-[EMIm]Cl is
corrosive to many commonly used metal current collectors, and the resulting corrosion current could be mistaken as the current from the electrochemical reactions of Al. The proneness of electrochemical oxidation of AlCl₄⁻ anion (ultimately leading to chlorine evolution) causes complicated process in the previously reported reversible AlCl₄⁻ intercalation in graphite. As the results, fast self-discharge and large irreversible capacity is observed when graphite (either natural or synthetic) is used as the cathode material. We further investigated the chemical compatibility of AlCl₃-[EMIm]Cl with V₂O₅, which is a common cathode material reported in the literature of Al battery. Our study indicates V₂O₅ chemically reacts to both Lewis neutral and Lewis acidic AlCl₃-[EMIm]Cl. By elucidating the reaction mechanisms, we conclude V₂O₅ is not a feasible Al storage material in the chloroaluminate ionic liquid electrolytes. These findings could provide guideline for design more reliable electrolytes for rechargeable Al batteries.

5:55 AM S.EN08.02.05
From Magnesium to Calcium—Translating Insights across Divalent Battery Electrolytes Nathan Hahn¹, Kevin R. Zavadil¹, Trevor Seguin², Kristin A. Persson², Darren Driscoll³ and Mahalingam Balasubramanian³; ¹Sandia National Labs, United States; ²Lawrence Berkeley National Laboratory, United States; ³Argonne National Laboratory, United States

Multivalent cation-based electrochemical energy storage concepts provide significant promise and challenges as beyond Li-ion technologies. In particular, chemistries based on Mg²⁺ or Ca²⁺ cations and their associated reactive metal anodes stretch the current limits of understanding regarding solvation and resultant electrochemistry in organic electrolytes. Furthermore, the recent discovery of semi-reversible calcium metal plating at room temperature in a very limited number of organic electrolytes provides a new and exciting opportunity to study the key aspects of solvation interactions that apply to transport and electrochemical stability across this set of alkaline earth metals. To this end, we present comparative studies of solvation phenomena and related electrochemical behavior using analogous sets of Mg²⁺ and Ca²⁺ salts in ethereal solvents. Differences in dication size and attendant solvation shell structures drive unique ion pairing tendencies and coordinating solvent structures, as determined through combined experimental and computational investigation. These coordination differences are further linked to both ion transport and electrochemical stability as they pertain to reversible metal plating. Based on these results, we will discuss strategies for designing electrolytes capable of maintaining efficient delivery of alkaline earth cations to and from their respective metal anodes or cathode hosts within a battery architecture.

SESSION S.EN08.03: Electrolytes and Interfaces in Multivalent Batteries
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN08

5:00 AM S.EN08.03.05
Probing Multivalent Cation Electrolytes at Dynamic Interfaces through X-Ray Spectroscopy and Modelling Ana Sanz-Matias¹, Jinghua Guo¹, Kevin R. Zavadil¹ and David Prendergast¹; ¹Lawrence Berkeley National Laboratory, United States; ²Sandia National Laboratories, United States

The increasing demand of large-scale energy storage with improved performance, safety and sustainability for renewable variable energy sources and automotive applications drives the search for post-Li-ion batteries based on multivalent cation chemistries (e.g., Mg, Zn and Ca). However, poor electrolyte stability against metal anodes and high voltage cathodes has been so far one of many barriers to the development of multivalent cation rechargeable batteries. Understanding and controlling (electro)chemistry at the electrolyte-electrode interface is critical on improving battery performance. Multivalent cations are prone to complex formation with solvent molecules and anions, leading to different interfacial species with characteristic (electro)chemical properties. Although multivalent cation solvation/complexation structures have been investigated in the bulk, fundamental understanding of speciation at the interface is lacking.

Recently, these buried solid-liquid interfaces have been accessed experimentally via total electron yield (TEY) soft X-ray absorption spectroscopy (XAS), sensitive to just a few nanometers above the solid electrode surface, and total fluorescence yield (TFY), more sensitive to the liquid bulk electrolyte. Interfacial species identification has been realized only in a handful of systems, formed by chemically stable electrodes (Au, Pt) and water or sulfuric acid solutions, although efforts toward exploring more complex systems are ongoing.

This work explores the structure, dynamics and spectroscopic signatures of a matrix of multivalent cations (Zn²⁺, Mg²⁺,
Ca\textsuperscript{2+}), nonaqueous electrolytes, and the bis(trifluoromethylsulfonyl)imide anion (TFSI\textsuperscript{−}) through TEY/TFY soft X-ray absorption spectroscopy and atomistic simulations. While the metal K-edge may provide insight into cation coordination, the previously unexplored F K-edge contains unique information about the complexation in bulk and at the interface. The limited studies in the literature show the rich behavior of the F K-edge in materials. However, the origin of the high sensitivity of the F K-edge XAS spectral profile to the chemical environment still lacks theoretical interpretation.

TEY/TFY experiments carried out at the ALS reveal unique interfacial speciation as a function of the cation and the coordinative strength of the solvent (2-methyltetrahydrofuran, 2MeTHF; 1,2-dimethoxyethane, G1; 1,2-dimethoxyethane, G2). A recently developed many-body formalism based on Density Functional Theory (MBXAS) was used to calculate the F K-edge X-ray absorption spectroscopic signature of the counterion TFSI\textsuperscript{−} in different coordination environments (contact and solvent-separated ion pairs) and in proximity to the electrode. Furthermore, the energy lanscapes of the different interfacial species were probed using classical and first-principles Molecular Dynamics simulations so as to understand subsequent temperature effects on the spectra.

With this work, we intend to highlight the promise of F K-edge X-ray absorption spectroscopy in combination with computational modelling as a unique channel to detect interfacial populations of anions (and associated solvent and cations).

5:10 AM *S.EN08.03.06
Functional Electrolytes and Interface Design for Multivalent-Metal Batteries Guanglei Cui and Jingwen Zhao; Chinese Academy of Sciences, China

Although lead-acid batteries managed to dominate market share of the low-cost power source, their high toxicity and negative environmental impact urge the development of low-cost batteries.[1] The divalent cation (e.g. Zn\textsuperscript{2+} and Mg\textsuperscript{2+} etc.) chemistries are principally advantageous for their adequate resources and improved safety. However, rechargeable divalent metal-based batteries is currently limited by the unavailability of electrolytes which must simultaneously satisfy wide enough electrochemical stability window, good compatibility with electrodes and current collector corrosion resistance.[2] Based on the precise design of electrolytes with reasonable composition and structures, we developed a series of boron-centered-anion-based Mg-ion electrolytes characterized by high ionic conductivity, non-nucleophilicity, and wide electrochemical window (Adv. Energy Mater. 2017, 1602055; Electrochem. Commun. 2017, 83, 72). Based on an in situ crosslinking reaction of magnesium borohydride and hydroxyl-terminated polytetrahydrofuran, a gel polymer electrolyte exhibits reversible Mg plating/stripping performance, high Mg-ion conductivity, and remarkable Mg-ion transfer number (Adv. Mater. 2019, 1805930; Energy Environ. Sci. 2017, 10, 2616; Small 2017, 1702277). Meanwhile, we demonstrated the solid-electrolyte interface formation on Zn anodes based on eutectic electrolytes that can optimize the stripping/deposition processes (Nano Energy 2019, 57, 625; Nat. Commun. 2019, accepted; Electrochem. Commun. 2016, 69, 6.). We further creatively proposed a thermoreversible polymer-based electrolyte with the ability of cooling-recovery to repair the interfacial failure during cycling (Angew. Chem. Int. Ed. 2017, 56, 7871) and a brightener-inspired interface for suppressing Zn dendrite and side reactions (Energy Environ. Sci. 2019, 12, 1938; NPG. Asia Mater. 2019, accepted). These prospective researches on the rechargeable Zn and Mg batteries are highly in compliance with the lead-free trend in the EVs and corresponding low-cost applications.

5:25 AM *S.EN08.03.07
Electrolyte, Solvation Shell and Interphase for Ca Metal Anode Based Batteries Alexandre Ponrouch; ICMAB-CSIC, Spain

Various metals have been used as battery anodes in electrochemical cells ever since the birth of the batteries with Volta’s pile and in the first commercialized primary (Zn/MnO\textsubscript{2}, Leclanché 1866) and secondary (Pb/acid, Planté 1859) batteries. Li-MoS\textsubscript{2} cells, employing Li metal anodes, with specific energies two to three times higher than both Ni/Cd and Pb/acid cells, were withdrawn from the market due to safety issues related to dendrites growth. Instead, Ca is currently being considered as safer metal anode alternative.[1] Pioneering work by Aurbach et al. in the early 1990’s showed a surface-film controlled electrochemical behavior of Ca metal anodes in electrolytes with conventional organic solvents.[2,3] The lack of metal plating was attributed to the poor divalent cation migration through the passivation layer.

Nevertheless, recent demonstration of Ca plating and stripping in the presence of a passivation layer[4,5] has paved the way for assessment of new electrolyte formulations with high resilience towards oxidation. However, several challenges remain to be tackled for the development of Ca based batteries.[1,6] Among these, the need for reliable electrochemical test protocols, mass transport limitations and high desolvation energies (due to strong cation-solvent and cation–anion interactions) are implied.[8] Here, the reliability of electrochemical set-ups involving multivalent chemistries is discussed,[9] and a systematic
investigation of the electrolyte formulation impact on the cation solvation structure and transport is presented.[10] Finally, a systematic characterization of the SEI formed on the Ca metal anode in various electrolyte formulations using complementary techniques allowed for the identification of the most suitable SEI components in terms of divalent cation mobility.

References
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Mapping Interphasial Phenomena in Electrodeposited and Cycled Calcium Metal Anodes Scott A. McClary, Nathan Hahn, Damion Cummings, Timothy Ruggles, Mark Rodriguez, Joseph Michael and Kevin R. Zavadil; Sandia National Laboratories, United States

Secondary batteries based on divalent calcium ions are attractive due to the high theoretical capacities of calcium metal anodes, low reduction potential nearing that of lithium, and earth abundance of calcium. In a significant milestone towards calcium-based batteries, the feasibility of reversibly plating and stripping calcium at room temperature from ether-based electrolytes was recently demonstrated. However, secondary phases such as calcium hydride [1] and calcium fluoride [2] form concurrently with deposited Ca metal and accumulate over time, contributing to coulombic efficiencies far below the threshold required for a practical rechargeable battery. Determining the formation mechanisms and distribution of these secondary phases is a critical first step in understanding and harnessing potential benefits of their presence to improve reversible battery operation. In this talk, we present the results of experiments utilizing a suite of electron microscopy techniques to map the distribution of calcium metal and secondary phases throughout electrochemically deposited and cycled calcium anodes. Calcium borohydride [Ca(BH₄)₂] in tetrahydrofuran (THF) was used as the primary model electrolyte for this study. Focused ion beam-generated cross sections were extracted from deposited and cycled anodes and characterized using Scanning Transmission Electron Microscopy (STEM) and Transmission Kikuchi Diffraction (TKD), revealing the preferred locations for calcium nucleation and growth, as well as the evolving morphology and accumulation of secondary phases over time. The deposits were also characterized using XRD in an inert environment, allowing for quantification of secondary phases and revealing crystallographic texturing of the calcium metal. We also present preliminary studies of cycled calcium anodes using STEM-EELS to chemically map calcium hydride. The work presented here provides critical insights regarding the morphology of deposited calcium metal and the extent and distribution of secondary phase formation and is an important step towards increasing the coulombic efficiency of calcium plating and stripping for next-generation rechargeable batteries.

References:

Computational Modeling of the Anode-Electrolyte Interface of Calcium-Ion Batteries Joshua Young¹², Stuart Shepard¹ and Manuel Smeu¹; ¹Binghampton University, United States; ²New Jersey Institute of Technology, United States

Rechargeable batteries are critical components of portable electronics, electric vehicles and grid storage. Li-ion is the dominant technology because of its low weight, large voltage and high capacity, but the demand for raw materials is putting

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strain on the supply chain, and there are several safety, ethical and environmental concerns. Therefore, developing adequate alternatives to Li-ion batteries is an active research area around the world. Multivalent ion batteries (MVIBs), utilizing Mg, Ca, Zn and Al, are promising due to being based on earth-abundant materials, and their higher weight can be compensated by their multivalent nature, which allows their ions to carry multiple charges. We are particularly interested in Ca ion batteries, which have received relatively little attention compared to Mg and Al, yet they are predicted to provide the largest voltage for a multivalent ion. However, their development has been limited by challenges in identifying adequate electrolytes to reversibly plate and strip metal Ca anodes. While there have been some encouraging recent developments, a systematic understanding of the interactions between electrolytes and Ca is needed. For example, it is not clear how the electrolyte (e.g., ethylene carbonate) decomposes at a Ca metal surface, nor are the structure and composition known of the solid-electrolyte interphase (SEI) that forms between the metal anode and the electrolyte. Furthermore, the diffusion of Ca^{2+} ions through the SEI is not well understood.

We aim to address some of these points with computational modeling that combines density functional theory (DFT) with ab initio molecular dynamics (AIMD). We investigate the electrolyte decomposition of ethylene carbonate, with and without salt, at the Ca metal interface. We then compare this process to those occurring at Li and Al metal surfaces. The DFT calculations reveal the mechanism and energy barriers associated with the possible electrolyte decomposition pathways, while the AIMD trajectories reveal how quickly molecules decompose and their location. Next, we investigate the electron conductivity of the anode-electrolyte interface region at various stages of SEI layer formation. We accomplish this with the non-equilibrium Green’s function technique combined with DFT (NEGF-DFT), which not only tells us the conductivity but also the electron pathway through the interface. Finally, we investigate the possibility of protecting the electrolyte from reacting with the anode by separating them with an artificial SEI that still allows Ca^{2+} ions to diffuse through it. We propose that this strategy can aid in the development of rechargeable Ca-ion batteries by bypassing the formation of an ionically insulating SEI due to electrolyte decomposition.

6:00 AM S.EN08.03.10
Calcium Plating and Stripping in an Alkyl Carbonate Electrolyte at Room Temperature Shreyas Pathreeker, Saeid Biria, Hansheng Li and Ian D. Hosein; Syracuse University, United States

Calcium is the 5th most abundant element in the Earth’s crust and a candidate material for next-generation non-Lithium rechargeable batteries. Its standard electrode potential of -2.87 V is close to that of Lithium and double the energy density compared to that of Lithium-ion batteries would be possible due to Calcium’s bivalent nature. Additionally, dendrite formation is alleviated with Calcium due to its high density and high thermal stability. In comparison to other multivalent ions such as Magnesium, Calcium possesses a smaller charge density and higher standard electrode potential, affording faster ion diffusion through cathode materials. However, to practically realize these advantages, Calcium metal anodes are necessary, which makes reversible plating and stripping Calcium on metallic substrates an important area of research. Recent work has successfully demonstrated electrochemical deposition of Calcium in EC/PC at elevated temperatures1, THF2, and DME3, whereas here, we report reversible plating and stripping of Calcium in an EC/PC based electrolyte at room temperature. Stable redox reactions were observed with cyclic voltammetry, and reversible plating and stripping was achieved galvanostatically at room temperature. Crystalline deposits in the form of thin films were successfully confirmed using XRD and FTIR measurements to be consisting of Calcium metal with traces of side products. Deposition on other substrates in other non-aqueous electrolytes is currently being investigated. This work provides an avenue for reliably developing Ca-metal electrodes for next-generation batteries.

References
Elucidating the Relationships between Performance, Transport Phenomena and Materials Properties for Functional Components of Multivalent-Ion Batteries

**Hunter Ford, Peng He and Jennifer L. Schaefer; University of Notre Dame, United States**

The development of new rechargeable battery systems employing novel chemistries is imperative to meet the increasing energy storage demands of emerging technologies such as electric vehicles and grid load leveling. Of particular interest is the development of battery systems employing multivalent metal anodes. Using a multivalent metal anode increases the energy density of the cell by providing an electrode consisting of entirely active material. Furthermore, many such elements such as magnesium are far more naturally abundant than lithium, ensuring they are economically viable and sustainable. Due to these benefits, multivalent-ion battery systems have recently received significant research attention. One of the outstanding challenges is dealing with the multivalency of the active cation, in regards to how the high charge density of the ion generally exacerbates traditional transport problems. For instance, conduction of multivalent cations Mg$^{2+}$ and Ca$^{2+}$ within single-ion conducting polymers is 1-3 orders of magnitude slower than their monovalent cation equivalents. This general problem of charge density presents itself in all components of the battery, from promoting decomposition on the anode to limiting the selection of electrolyte salts to the few that can adequately dissociate in solution. In regards to magnesium-sulfur batteries, poor cation diffusivity in solid discharge products makes oxidation to higher order polysulfides and sulfur difficult, a problem made worse by the low solubility of magnesium polysulfides and consequent lack of intrinsic redox mediators. Herein, we explore recent attempts within our group to provide solutions to these challenges, focusing primarily on electrolyte and conversion cathode development. We aim to link material properties to observed transport behavior, specifically in how to enhance divalent cation transport and minimize anion transport under an applied potential while maintaining electrochemical activity.

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Disulfide Redox Chemistry Boosts Energy Density and Divalent Ion Kinetics

**Zhenyou Li$^1$, Zhirong Zhao-Karger$^1$ and Maximilian Fichtner$^{1,2}$; 1Helmholtz Institute Ulm, Germany; 2Karlsruhe Institute of Technology, Germany**

Multivalent batteries are promising candidates for next generation battery technologies in terms of capacity and resource abundance. However, the theoretically high capacity of multivalent metals attributes to the multiple charge of the cations, which usually leads to a high charge density, thus causing sluggish insertion and diffusion kinetics at the corresponding cathode side. Taking rechargeable Mg batteries (RMBs) as an example, there is no report about insertion-type oxide cathode, which could provide reversible Mg storage with fair capacity at an acceptable current rate. The kinetic issue can be alleviated to some extent by using layered transition metal sulfide, due to the lower charge density of S than O. However, both diffusion kinetics and achievable capacity are not satisfying even if cointercalation of a second species is employed, which is supposed to screen the high charge density of Mg$^{2+}$. [1] In this regard, further “softening” the host structure is essential to realize fast Mg$^{2+}$ mobility. On the other hand, the realization of the high energy density requires enabling a reversible multi-electron redox reaction, which is seldom reported in insertion-type cathode for multivalent batteries. In fact, classical cationic redox with stepwise single electron reactions have not been able to fulfil the requirement for multi-electron redox reactions so far. Here, anionic redox chemistry with multi-electron transfer may be a possible solution. [2]

In this talk, we will present a new insertion-type cathode for multivalent batteries, which not only offers much more structural flexibility but also exhibits high energy density than the layered materials. Mg$^{2+}$ storage mechanism and possible diffusion pathways will be discussed in detail.

References


5:15 AM S.EN08.05.03
Effects of Nanoparticle Size and Solvent Molecule on Mg$^{2+}$ Insertion into the Cathode Materials Wenxiang Chen¹, Xun Zhan¹, Cheng Zhang¹, Ryan Stephens², Hong Yang¹, Jian-Min Zuo¹ and Qian Chen¹; ¹University of Illinois at Urbana-Champaign, United States; ²Shell International Exploration and Production Inc., United States

We study the electrochemical and structural responses of nanoparticles of different sizes as cathode materials in magnesium ion batteries. By systematically varying the electrolytes, we observe a consistent solid-solution phase transition in small nanoparticles during discharge, in contrast to the mixed-phase evolution or surface reactions in big nanoparticles. Further examination by scanning electron nanobeam diffraction (SEND) in scanning transmission electron microscope (STEM) revealed the strain and phase distribution in the small nanoparticles at nanometer resolution. We observe a non-uniform, scattered phase distribution in small nanoparticles in the non-aqueous electrolyte, in contrast to the uniform one in the aqueous electrolyte. The varied phase behaviors are associated with the co-intercalation of solvent molecules in the discharge processes. Our work shows that nanoparticle size and solvent molecules have a direct influence on Mg ion insertion processes, which rationally guide the design of Mg ion batteries with high capacity and high stability.

5:25 AM *S.EN08.05.04
Calcium Intercalation in Inorganic Materials—Pondering on Application in Rechargeable Batteries Arturo Torres, Miguel Recio-Poo and M.E. Arroyo de Dompablo; Universidad Complutense de Madrid, Spain

Li-ion batteries are currently approaching its fundamental limits in terms of energy density, which in addition to the reduced supply of Li instigate the race for the development of alternative technologies exhibiting advantages in terms of energy density, safety and cost. Although rechargeable batteries based on a Ca-metal anode are attractive, the development of such batteries is intricate due -among other factors- to the lack of competitive cathode materials. To the date, restricted reversible electrochemical Ca intercalation has been reported for a handful of compounds (see [1] and references therein), all of them showing poor cycling capability, if any. Parallel experimental-computational investigations establish a link between the lack of reversible electrochemical activity (experimentally observed) and a hampered Ca diffusion (computationally estimated). Hence Ca diffusion is a key parameter, for which the migration energy barriers provide an approximate indication. In this communication we analyse the calculated DFT-energy barriers for Ca migration found for a large set of Ca-transition metal compounds including oxides, sulphides, phosphates, nitrides, carbonates and phosphates. The possible application of Ca intercalation materials as cathode in rechargeable batteries is further discussed considering other basic electrode characteristics.

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5:40 AM S.EN08.05.06
Insertion Type Cathodes for Calcium-Ion Batteries Shrevas Pathreker, Sophia Figueroa, Madison E. Leiman, Seth Reed, Katharine V. Statson and Ian D. Hosein; Syracuse University, United States

Developing batteries beyond those based on Lithium is critical to the advancement of next-generation energy storage technology with lower cost and higher energy density. To this end, Calcium has been identified as a candidate material due to its Earth-abundancy, reduction potential similar to that of Lithium, and divalency, which can enable the development of high-voltage and high-energy density batteries. While various Calcium based compounds have been suggested as potential cathode materials for Ca-ion batteries using DFT calculations¹, very few have been synthesized and evaluated experimentally. Here, we report the facile synthesis and evaluation of some Calcium containing transition metal oxides as potential cathode materials for Ca-based batteries. X-ray diffractograms of the as-synthesized powders are in agreement with powder patterns obtained theoretically. Electrochemical de-insertion/insertion from and into the structure of the host materials was conducted in 0.5 M Ca(BF₄)₂ in Acetonitrile electrolyte and evaluated using X-ray diffraction. Further electrochemical evaluation of these cathode materials by galvanostatic charge/discharge measurements is currently being investigated. This work provides opportunities to identify, synthesize and evaluate low-cost cathodes for next-generation Calcium batteries.
Rechargeable Aluminum Batteries Based on 2D Transition Metal Carbide (MXene) Cathodes

Armin VahidMohammadi1,2, SIna Shahbazmohamadi2 and Majid Beidaghi1, 1Auburn University, United States; 2University of Connecticut, United States

The market of electric vehicles (EVs) is growing fast and is expected to take over the gas-powered vehicles in the upcoming years. However, the bottleneck for the development of EVs remains to be the battery technology, where batteries with higher energy and power densities are required. Also, battery chemistries with higher safety and lower cost must be developed to enable EVs to compete with gasoline-powered cars in the price range of under $30K. Despite the significant developments made in lithium-ion (Li-ion) batteries, their flammability and high cost, as well as concerns about the availability of economically viable lithium resources have considerably increased the need for alternative battery chemistries. Rechargeable aluminum batteries with aluminum metal anode are considered as one of the most promising alternative energy storage systems to current Li-ion batteries. Aluminum is the most abundant metal in Earth’s crust, and it can potentially offer three-electron redox reactions resulting in the highest theoretical volumetric capacity of 8040 mAh cm⁻³ among all metals and a reasonably high theoretical gravimetric capacity of 2980 mAh g⁻¹. Recently, we reported on the performance of two-dimensional (2D) V₂CTₓ MXene as an intercalation-type cathode for rechargeable aluminum batteries delivering exceptional capacities and rate-capabilities. MXenes are a family of 2D transition metal carbides and nitrides that are produced by selective etching of the A layer atoms (i.e., Al) from MAX phases (i.e., V₂AlC), a large group of layered ternary carbides and nitrides. Despite the promising performances in our early work, the V₂CTₓ MXene cathode showed severe capacity decay in over hundreds of cycles. In this presentation, through a combination of various structural characterizations techniques (XRD, SEM, HRTEM, and XPS) and electroanalytical analyses such as Galvanostatic Intermittent Titration Technique (GITT) and Electrochemical Impedance Spectroscopy (EIS) we provide valuable insights about the underlying reasons for the capacity loss and further shed light on the thermodynamics and kinetics of Al³⁺ intercalation into V₂CTₓ MXene cathode. We further demonstrate that by designing new electrode architectures and modifying electrolyte composition, different 2D MXenes can deliver stable cyclic performance in the aluminum battery system. The 2D MXene cathodes can also be fabricated as freestanding and binder-free electrodes with exceptional volumetric capacities and long cycle life. Considering that the family of the MXenes now includes ~30 different compositions, our research guides the preparation of an entire group of cathode materials for rechargeable aluminum batteries based on these 2D materials.

References

2:45 PM *S.EN09.01.11

High Performance Solar Flow Batteries

Song Jin, Wenjie Li and Hui-Chun Fu; University of Wisconsin-Madison, United States

Due to the intermittent nature of sunlight, practical solar energy utilization systems demand both efficient solar energy conversion and inexpensive large scale energy storage. We report novel hybrid solar-charged storage devices that integrate redox flow batteries (RFBs) and regenerative semiconductor solar cells that share the same pair of redox couples. In these integrated solar flow batteries (SFBs), photoexcited carriers are collected at the semiconductor-liquid electrolyte interface and used to convert the redox couples in the RFB to charge up the battery without external electric bias; which can be discharged to generate the electricity when electricity is needed. Carefully matching high performance III-V solar cells with various high voltage organic couples and optimizing several generations of SFB device designs enabled integrated SFB device with an overall direct solar-to-output electricity efficiency (SOEE) of 14%. We have further improved the cycling performance of the SFBs by integrating robust organic redox couples and photodetectors. I will also describe our recent effort in achieving a record 20% SOEE SFB with at least hundreds of hours of lifetime using novel tandem devices designed with the quantitative voltage matching model. Such highly efficient and robust SFBs that can be fabricated at low cost would enable practical distributed and standalone solar energy conversion and storage systems in remote locations.

3:15 PM *S.EN09.02.07

Electrode Chemistry for Flow Systems—Elucidating the Degradation of Redoxmer Electrolytes at the Carbon-Electrolyte Interface Using Spatially-Resolved Electrochemistry

Counihan J. Michael1, Dipobrato Sarbapalli1, Tylan Watkins2, Danis Andrew1, Kevin R. Zavadil2 and Joaquin Rodriguez-Lopez; 1University of Illinois at Urbana Champaign, United States; 2Sandia National Laboratories, United States

Non-aqueous redox flow batteries (NRFBs) are attractive technologies that offer the promise of providing higher cell voltages than their aqueous counterparts. In NRFBs, redoxmers are charged and discharged through electrodes such as carbon. Interactions between the electrode structure and concentrated redoxmer solutions cause adsorption of these species, which may lead to subsequent degradation reactions and state-of-charge dependent phenomena. Likewise, the interaction of the redoxmers with highly polarized electrodes may lead to a modified chemical reactivity at the electrochemical interface. In this work, we will describe our experiments probing the chemical and electrochemical reversibility of catholyte redoxmers such as alkoxybenzene derivatives on model carbon electrodes. Using scanning electrochemical microscopy (SECM), we probe the real-time evolution of the reactivity of the redoxmer-carbon interface by measuring the local redox kinetics, film formation processes, and the generation of reactive intermediates. Chemical interactions at the interface were further probed via *in-situ* Raman electrochemical measurements, and the newly developed Raman-SECM approach. We will describe the reactivity of different carbon features, as well as the interactions with model redoxmers. SECM revealed a wealth of reversible and irreversible changes in the kinetics of electron transfer, including the observation of transient enhancements in electrochemical rates and slow passivation processes. Simultaneous operation of SECM and Raman also created new opportunities to probe the impact of reactive radical cations on the chemistry of the carbon host and on film-formation processes through electropolymerization. These studies help direct the design of redoxmers with increased stability at the...
Flow and Redox-Based Electrochemical Water Desalination Yanbo Pan, Abdulaziz Bentalib and Zhenmeng Peng; University of Akron, United States

Desalination of seawater has emerged as an area of critical need, but remains challenging, to solve the fresh water supply problem caused by the steady growth of human population and industry. Although the previous research efforts led to development of a number of desalination methods, for instance distillation, reverse osmosis, electrolysis and capacitive deionization, their applications were largely restricted by the inherent energy efficiency and effectiveness issues. Thus, there is a demand of new methods that allow efficient and effective separation of salt ions from water.

In this talk we review recent progress of water desalination research based on battery mechanism, and report our efforts in developing flow and redox-based electrochemical systems for water desalination application. Specifically, we have prepared FePO4-based electrode material for sodium ion removal and copper-based electrode material for chloride ion removal. An electrochemical cell composed of the two electrode materials has been demonstrated with promising desalination capacity and efficiency.

Recent Progress in Organic-Based Aqueous Flow Batteries Michael J. Aziz; Harvard University, United States

The ability to store large amounts of electrical energy is of increasing importance with the growing fraction of electricity generation from intermittent renewable sources such as wind and solar. Wide-scale utilization of flow batteries is limited by the cost of redox-active metals such as vanadium or precious metal electrocatalysts. We have developed high performance flow batteries based on the aqueous redox behavior of small organic and organometallic molecules, e.g. [1-7]. These redox active materials can be very inexpensive and exhibit rapid redox kinetics and high solubilities, potentially enabling massive electrical energy storage at greatly reduced cost. We have developed new protocols for measuring capacity fade rates, which are particularly important for establishing very low capacity fade rates, and have discovered that the capacity fade rate is determined by the molecular calendar life, which can depend on state of charge, but is independent of the number of charge-discharge cycles imposed [6]. We will report the performance of the very few chemistries with long enough calendar life for practical application in stationary storage, and on the prospects for reversing capacity fade by recomposing decomposed molecules [7].

http://dx.doi.org/10.1038/nature12909


http://dx.doi.org/10.1038/nenergy.2016.102

http://dx.doi.org/10.1021/acsenergylett.7b00019

Aqueous Organic Redox Flow Batteries for Energy Storage
Bo Hu, Jian Luo and Tianbiao L. Liu; Utah State University, United States

Electrification of modern society including portable devices, electrical vehicles, and grid-scale storage has driven intensive research development of inexpensive, safe, long-cycling life, high performance energy storage technologies. The presentation will primarily discuss our recent research efforts in developing viologen and quinone anolyte materials for both anion and cation exchange Aqueous Organic Redox Flow Batteries (AORFBs) with a variety of catholyte materials including ferrocene, TEMPO, ferrocyanide and halides. Particularly, the presentation emphasizes that fundamental understandings of redox active electrolytes at molecular level are crucial to develop new generations of redox flow and Mg batteries for sustainable energy storage.

Unexpected Electrochemical Behavior of 2,1,3-Benzothiadiazole Anolyte Redoxmer for Nonaqueous Redox Flow Batteries—Solvation Enabled Low Redox Potential and High Stability
Lu Zhang1,2, Yuyue Zhao1,2, Yu Zhou1,2, Lily Robertson1,2, Tao Li1,2, Rajeev S. Assary1,2, Sambasiva R. Bhemireddy1,2, Zhengcheng (John) Zhang1,2, Kristin A. Persson2,3, Ilya Shkrob1,2 and Lei Cheng1,2; 1Argonne National Laboratory, United States; 2Joint Center of Energy Storage Research, United States; 3Lawrence Berkeley National Laboratory, United States

Redoxmer is a term coined for redox active materials with tunable architectures. In nonaqueous redox flow batteries, the properties of redoxmers often dominate the cycling performance, including energy density, power, and cycle life. However, the choice of supporting electrolytes can also dramatically impact the properties of redoxmer via tuning solvating environment; therefore it is of crucial importance to build understanding of such phenomenon. In this talk, a systemically approach was adapted to probe solvating impact of 2,1,3-benzothiadiazole (BzNSN) in various supporting electrolytes. BzNSN is an energy dense anolyte molecule with a low redox potential. When cycled in flow cells, the choice of salts significantly impact the measured redox potentials and cycling life. As shown in Figure 1, when measured in electrolytes containing Li salts, BzNSN delivers increased redox potentials, implying Li+ involved interactions. Moreover, by changing cations of different sizes, such as Na+, K+, and NEt4+, the redox potential of BzNSN shift nearly 200 mV from -1.65 V for Li+ to -1.85 V for NEt4+. For an anolyte material, the lower redox potential usually leads to worse stability as it becomes thermal dynamically unstable. Surprisingly, this is not the case for BzNSN in electrolytes with different cations. Despite the lower redox potential, BzNSN radical cation delivers a much longer life time (t1/2 = 90 h) in 0.5 M KTFSI acetonitrile electrolyte than in LiTFSI acetonitrile electrolyte (t1/2 = 42 h). This is the first time that we observe an anolyte redoxmer can deliver a longer life time at a lower potential, which might be a practical approach for designing high energy density flow cells. Molecular dynamic simulation was used to explain the observed results.

Organic Redox Active Solutes in Deep Eutectic Solvents for Flow Batteries
Burcu Gurkan; Case Western Reserve University, United States

The discovery of electrolytes that have low vapor pressures, wide electrochemical window and high solubility towards redox active species with an ability to undergo multiple electron transfer reactions is a challenge to realize large-scale energy storage. Deep eutectic solvents (DESs), which are eutectic mixtures of hydrogen bond donors and acceptors, are attractive electrolytes as they have good solvent strength that is also tunable along with other physical, thermal, electrochemical and transport properties. We have examined the electrochemical behavior of various organic redox active solutes, specifically methyl viologen (MV), quinones and nitroxy radicals, in a common DES known as ethaline; a 1 to 2 molar mixture of choline chloride and ethylene glycol. While the reactivity of most quinones investigated are found to fall outside of the
electrochemical window of ethaline, nitroxy radicals and MV provide reversible redox couples that are practical. In particular, TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) demonstrates two single electron transfer reactions separated by 1.3 V in ethaline. However, the solubility of TEMPO in ethaline is found to be limited to 0.17 M at room temperature. The hydrogen bonding achieved by –OH substitution on TEMPO and electrostatic interactions achieved by the functionalization of halide salts with TEMPO are shown to improve solubility in ethaline close to 2 M. This study illustrates that chemical modification of redox active organic molecules impacts both their solubility in a DES electrolyte, as well as their redox performance and physical properties of the solutions.

SESSION S.EN09.01: Aqueous Redox Flow Batteries
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN09

5:00 AM *S.EN09.01.01
Electrolyte Flow in Vanadium Redox Flow Battery Electrodes—A Synchrotron Imaging Study Roswitha Zeis; Karlsruhe Institute of Technology, Germany

Two major limitations of Vanadium Redox Flow Batteries (VRFBs) are (1) the transport losses of getting the electrolyte into the electrode and to the reaction sites with minimum resistance, and (2) Lack of access to all reaction sites due to relatively low saturation levels of the electrolyte [1,2]. Although the porous carbon electrodes have a high porosity, a large pressure may be required to pump the electrolyte through the electrode during operation. The flow-through porous carbon electrode can be further hampered due to the presence of hydrogen bubbles, which are formed as a parasitic side product of the V^{3+} reduction reaction at the anode in VRFBs [3]. This affects the efficiency and stability of the VRFB cells. Besides mixed potentials, the Hydrogen bubbles could also damage the pore structure of the electrode and create inaccessible surface area where otherwise the reaction would occur. To investigate the formation of gas bubbles inside the small pores of the carbon electrode, we carried out an experiment based on a novel beamline half-cell measurement setup. During the experiment the electrolyte was injected into the cell using a peristaltic pump. Radiography was conducted during the injection process to track the flow of the electrolyte through the electrode. Simultaneously, pressure drop was measured to characterize the transport process and identify the breakthrough of the electrolyte on the opposite side of the electrode. The setup also allows us to evaluate various types of carbon electrodes such as felts, woven or paper style materials. Flow-by and flow-through geometries and manifolds can be exchanged to study their impact on the flow dynamics. These measurements help us develop theoretical models for a better understanding of the multiphase and interfacial flow phenomena within the porous electrode. These experiments are essential for the evaluation and optimization of electrode materials and manifolds currently being used in VRFBs.

References

5:15 AM *S.EN09.01.04
PBI Based Membranes for Redox Flow Batteries Dirk Henkensmeier1,2,3; 1Korea Institute of Science and Technology, Korea (the Republic of); 2University of Science and Technology, Korea (the Republic of); 3Korea University, Korea (the Republic of)

Membranes need to balance a low resistance and a low crossover of redox-active species, and they have to be chemically stable in the electrolyte. For vanadium redox flow batteries, this implies stability against sulphuric acid and stability against VO_2^+ ions. For many years, the latter criteria strongly limited the choice of membrane materials, and perfluorinated Nafion membranes became the state of the art.[1]

A very recent development is the use of polybenzimidazole membranes, which do not conduct ions in the pure form, but become proton conductive in contact with the sulfuric acid containing electrolyte. The positive charge on the protonated polymer backbone and the narrow size of the electrolyte filled voids between the polymer chains successfully repels
vanadium ions in ex-situ permeability measurements. Most interestingly, we observed that both voltage efficiency and coulomb efficiency increase when the membrane thickness decreases. This probably is related to the average charging potential, which increases with the membrane thickness and thus a) increases migration in the electric field, providing some vanadium ions with the energy to pass the energy barrier which hinders them from entering the membrane, and b) possibly enhances side reactions. This result suggests that cells with thin PBI films would be very efficient in terms of both voltage and coulomb efficiency; the thinner, the better [2].

Building up on this finding, we prepared porous Nafion membranes coated with a thin PBI layer [3] and porous PVDF membranes coated with a thin PBI layer [4].

Another way to improve the voltage efficiency of PBI membranes is to blend them with anion exchange ionomers [5, 6].

The very low permeability for metal ions of PBI membranes also enables the operation of iron-vanadium flow batteries (Fe-VRFB), reducing the costs of the electrolyte and increasing the upper temperature limit [7].

By alkylating PBI membranes, a permanent charge can be fixed on the PBI backbone, turning the membranes into anion exchange membranes with a high IEC [8]. While the alkyl groups may be a starting point for degradation by VO₂⁺, this type of anion exchange membranes can be used well in aqueous organic flow batteries [9].

References

5:30 AM S.EN09.01.05
Hetero-Atom Functionalised Quinoidal Electrolytes for Redox Flow Batteries Rajesh B. Jethwa1, Evan Wenbo Zhao1, Rachel Kerber1, Erlendur Jónsson1,2, Dominic Wright1 and Clare Grey1; 1University of Cambridge, United Kingdom; 2Chalmers University of Technology, Sweden

Redox flow batteries are quickly developing as a potential solution for current grid-level electrochemical energy storage concerns where high cycle number durability, long calendar life, high efficiency, low cost and fast response times are required.1,2 However, currently low energy density3–5 and high capital costs3,4 limit the industrial implementation of such systems.

It should come as no surprise therefore that electrolytes are a topic of active research, with a view to increasing the energy density while reducing the cost. Increasing energy density can be achieved in various ways: expanding the voltage window or by minimising the mass and/or volume per electron transferred.6 These strategies correspondingly open up various avenues through which novel electrolytes can be explored.

Previous examples of electrolytes for flow batteries have included a variety of metal-based systems and a range of organic molecules.7,8 Of these, quinones are a common electroactive class of organic molecules that have been investigated due to their fast kinetics, high tunability and low cost.8 In the current work, benzoquinone derivatives were synthesised and investigated as potential anolytes for redox flow batteries. Benzoquinone has a higher aqueous solubility and a lower molecular weight than anthraquinone, but it is more prone to electrochemical degradation.8

The derivatised quinones explored in this work are anticipated to benefit, in comparison to previous anthraquinones, from a higher energy density through greater solubility, and a lower cost. Electrochemical screening was carried out using cyclic voltammetry as an initial test of redox properties and stability. Selected molecules that exhibited favourable behaviour were then run in a lab-scale full cell and through the aid of in situ NMR and EPR spectroscopy, the behaviour of the species under cycling conditions was investigated. Density functional theory modelling was used to complement the analysis. The current investigation has shown promising results towards the possibility for new routes towards functionalisation and stabilisation of such organic systems.


5:40 AM S.EN09.01.06
In Situ NMR Metrology Reveals Reaction Mechanisms and Electron Transfer Rates in a Flow Battery Evan Wenbo Zhao1, Tao Liu2, Erlendur Jónsson1,3, Jeongjae Lee4, Israel Temprano1, Anqi Wang5, Holly Smith1, Javier Carretero González6, Qilei Song5 and Clare Grey1; 1University of Cambridge, United Kingdom; 2Tongji University, China; 3Chalmers University of Technology, Sweden; 4Seoul National University, Korea (the Republic of); 5Imperial College London, United Kingdom; 6ICTP-CSIC, Spain

We report two in situ NMR methods to study flow batteries. While flow batteries are low-cost and environmentally benign large-scale energy storage devices, an increased understanding of the battery chemistry is required to improve their energy densities, lifetimes and to reduce cost. Demonstrating the approach on two separate anthraquinones, 2,6-dihydroxyanthraquinone, DHAQ and 4,4’-(9,10-anthraquinone-2,6-diyl) dioxy) dibutyrate, DBEAQ as redox-active electrolytes, we confirm that the reduction reactions occur via a two-step, one-electron redox process coupled with a comproportionation reaction. Using the bulk magnetisation changes, observed via the 1H NMR shift of the water resonance, we determine the potential differences of the two one-electron couples. Electron transfer between radical and the diamagnetic anions is observed and is quantified via the linebroadening of the resonances of the diamagnetic anions. This linebroadening and shifting of the resonance – coupled with EPR measurements - provide direct evidence for the degree of electron delocalization of unpaired spin over the radical anions. Electrolyte decomposition and battery self-discharge is explored in real time, the results indicating that DHAQ decomposition is an electrochemical reaction which can be minimized by limiting the voltage used on charging. Applications of the new NMR metrologies to understand a wide range of redox processes in flow and other battery systems is readily foreseen.

5:50 AM S.EN09.01.07
Micellization-Enabled Ultrastability and Crossover Suppression in Aqueous RFB Jianbing J. Jiang, Jingchao Chai, Xiao Wang and Caroline Williams; University of Cincinnati, United States

Redox flow batteries (RFBs) are a highly promising large-scale energy storage technology for mitigating the problematic intermittency of renewable energy sources such as solar and wind. Organic redox species in aqueous RFBs have attracted substantial attention due to their facile synthesis, structural diversity, and low cost. Here, our group present the design and implementation of a micellization strategy in a pH-neutral, nontoxic, metal-free, aqueous RFB. The PEGylated micelle is constructed in an aqueous KCl solution as the anolyte. The micellization strategy (1) improves stability by protecting the redox-active molecules with the hydrophilic PEG tail to suppress parasitic reactions; and (2) increases the overall size to a mean hydrodynamic radius of 500 nm to mitigate the crossover issue via the physical blocking mechanism. Paired with a well-established potassium ferrocyanide catholyte, the micelle-based RFB in a pH-neutral aqueous electrolyte solution displayed an excellent capacity retention of 90.7% after 3600 charge/discharge cycles (28.3 days), corresponding to a capacity retention of 99.67% per day and 99.998% per cycle. Mechanistic studies of redox-active materials are also conducted during and after the cycling by proton nuclear resonance spectroscopy and cyclic voltammetry and indicate the absence of side reactions that are commonly observed in other RFBs. This work represents the longest consecutive running time and the highest charge/discharge cycles among the reported organic material-based aqueous RFBs. The outstanding performance of our RFB demonstrates the effectiveness of the micellization strategy for enhancing the performance of organic material-based aqueous RFBs.

6:00 AM *S.EN09.01.08
Recent Progress in Organic-Based Aqueous Flow Batteries Michael J. Aziz; Harvard University, United States

The ability to store large amounts of electrical energy is of increasing importance with the growing fraction of electricity...
generation from intermittent renewable sources such as wind and solar. Wide-scale utilization of flow batteries is limited by the cost of redox-active metals such as vanadium or precious metal electrocatalysts. We have developed high performance flow batteries based on the aqueous redox behavior of small organic and organometallic molecules, e.g. [1-7]. These redox active materials can be very inexpensive and exhibit rapid redox kinetics and high solubilities, potentially enabling massive electrical energy storage at greatly reduced cost. We have developed new protocols for measuring capacity fade rates, which are particularly important for establishing very low capacity fade rates, and have discovered that the capacity fade rate is determined by the molecular calendar life, which can depend on state of charge, but is independent of the number of charge-discharge cycles imposed [6]. We will report the performance of the very few chemistries with long enough calendar life for practical application in stationary storage, and on the prospects for reversing capacity fade by recomposing decomposed molecules [7].


6:15 AM *S.EN09.01.10
Aqueous Organic Redox Flow Batteries for Energy Storage Bo Hu, Jian Luo and Tianbiao L. Liu; Utah State University, United States

Electrification of modern society including portable devices, electrical vehicles, and grid-scale storage has driven intensive research development of inexpensive, safe, long-cycling life, high performance energy storage technologies. The presentation will primarily discuss our recent research efforts in developing viologen and quinone anolyte materials for both anion and cation exchange Aqueous Organic Redox Flow Batteries (AORFBs) with a variety of catholyte materials including ferrocene, TEMPO, ferrocyanide and halides. Particularly, the presentation emphasizes that fundamental understandings of redox active electrolytes at molecular level are crucial to develop new generations of redox flow and Mg batteries for sustainable energy storage.

6:30 AM *S.EN09.01.11
High Performance Solar Flow Batteries Song Jin, Wenjie Li and Hui-Chun Fu; University of Wisconsin-Madison, United States

Due to the intermittent nature of sunlight, practical solar energy utilization systems demand both efficient solar energy conversion and inexpensive large scale energy storage. We report novel hybrid solar-charged storage devices that integrate redox flow batteries (RFBs) and regenerative semiconductor solar cells that share the same pair of redox couples. In these integrated solar flow batteries (SFBs), photoexcited carriers are collected at the semiconductor-liquid electrolyte interface and
used to convert the redox couples in the RFB to charge up the battery without external electric bias; which can be discharged to generate the electricity when electricity is needed. Carefully matching high performance III-V solar cells with various high voltage organic couples and optimizing several generations of SFB device designs enabled integrated SFB device with an overall direct solar-to-output electricity efficiency (SOEE) of 14%. We have further improved the cycling performance of the SFBs by integrating robust organic redox couples and photoelectrodes. I will also describe our recent effort in achieving a record 20% SOEE SFB with at least hundreds of hours of lifetime using novel tandem devices designed with the quantitative voltage matching model. Such highly efficient and robust SFBs that can be fabricated at low cost would enable practical distributed and standalone solar energy conversion and storage systems in remote locations.

SESSION S.EN09.02: Nonaqueous Redox Flow Batteries
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN09

5:00 AM *S.EN09.02.01
Redoxmer Design, Engineering and Use Shelley Minteer; University of Utah, United States

This paper will detail the use of quantitative structure-property relationships for the design of next-generation redoxmers. This will include redoxmers design for fuel cells and redox flow batteries. The first half of the talk will discuss predictive modeling of nitroxy1 radical-based redoxmers for the anode of fuel cells. The second half of the talk will discuss predictive modeling of electrolytes for non-aqueous redox flow batteries. This will discuss parameterization for improving stability and cyclability. The talk will finish with a discussion of future needs in redoxmer design and engineering.

5:15 AM *S.EN09.02.02
Unexpected Electrochemical Behavior of 2,1,3-Benzothiadiazole Anolyte Redoxmer for Nonaqueous Redox Flow Batteries—Solvation Enabled Low Redox Potential and High Stability Lu Zhang1,2, Yuyue Zhao1,2, Yu Zhou1,2, Lily Robertson1,2, Tao Li1,2, Rajeev S. Assary1,2, Sambasiva R. Bheemireddy1,2, Zhengcheng (John) Zhang1,2, Kristin A. Persson2,3, Ilya Shkrob1,2 and Lei Cheng1,2; 1Argonne National Laboratory, United States; 2Joint Center of Energy Storage Research, United States; 3Lawrence Berkeley National Laboratory, United States

Redoxmer is a term coined for redox active materials with tunable architectures. In nonaqueous redox flow batteries, the properties of redoxmers often dominate the cycling performance, including energy density, power, and cycle life. However, the choice of supporting electrolytes can also dramatically impact the properties of redoxmer via tuning solvating environment; therefore it is of crucial importance to build understanding of such phenomenon. In this talk, a systemically approach was adapted to probe solvating impact of 2,1,3-benzothiadiazole (BzNSN) in various supporting electrolytes. BzNSN is an energy dense anolyte molecule with a low redox potential. When cycled in flow cells, the choice of salts significantly impact the measured redox potentials and cycling life. As shown in Figure 1, when measured in electrolytes containing Li salts, BzNSN delivers increased redox potentials, implying Li+ involved interactions. Moreover, by changing cations of different sizes, such as Na+, K+, and NEt4+, the redox potential of BzNSN shift nearly 200 mV from -1.65 V for Li+ to -1.85 V for NEt4+. For an anolyte material, the lower redox potential usually leads to worse stability as it becomes thermal dynamically unstable. Surprisingly, this is not the case for BzNSN in electrolytes with different cations. Despites the lower redox potential, BzNSN radical cation delivers a much longer life time (t1/2 = 90 h) in 0.5 M KTFSI acetonitrile electrolyte than in LiTFSI acetonitrile electrolyte (t1/2 = 42 h). This is the first time that we observe an anolyte redoxmer can deliver a longer life time at a lower potential, which might be a practical approach for designing high energy density flow cells. Molecular dynamic simulation was used to explain the observed results.

5:30 AM *S.EN09.02.04
Redox-Mediated Electrochemical Energy Conversion and Storage Qing Wang; National University of Singapore, Singapore

Redox reaction involving charge transfer at the electrode-electrolyte interface represents an essential process for various electrochemical energy conversion and storage applications, such as fuel cell, electrolyzer and battery, etc. As a result, the
operation (i.e. cell voltage, current density, number of charges, etc.) of the above devices is inherently dictated and
constrained by the redox reactions. The redox-mediated process, a chemical reaction between an electrolyte-borne redox
species electrochemically generated on electrode and a material (generally insoluble in electrolyte) off the electrode, provides
additional flexibility in circumventing the constraints intrinsically confronted by the conventional electrochemical devices.
One example is the redox targeting of energy storage materials for flow batteries. The redox-mediated reactions of high
capacity solid material stored in the tank with redox electrolyte flowing through it considerably boost the energy density of
redox flow battery without compromising its operation flexibility. Another example is redox-mediated oxygen evolution
reaction (OER) for water electrolysis. The concurrent electrochemical-chemical cycle enables continuous reaction between
an electrolyte-borne redox mediator and an OER catalyst loaded in a fixed-bed reactor spatially separated from the cell,
which is believed to be advantageous to enhanced safety.

In this talk, I will report our latest advancement in the above area. In addition, I will briefly introduce some other studies on
redox-mediated reactions, such as low-grade waste heat harnessing based on a thermal-electrochemical cycle and battery
material recycling based on a one-way redox targeting reaction.

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Y. Chen, M. Zhou, Y. Xia, X. Wang, Y. Liu, Y. Yao, H. Zhang, Y. Li, S. Lu, W. Qin, X. Wu, and Q. Wang, A Stable and

5:45 AM S.EN09.02.06
Low-Cost and High-Energy Redox Flow Batteries Achieved by Metal-Based Deep Eutectic Solvents Leyuan Zhang and
Guihua Yu; The University of Texas at Austin, United States

Given the advantages of low cost, high concentration and potential biodegradability, the concept of deep eutectic solvents
(DESs) is beneficial to developing cost-effective and sustainable batteries with high-energy density. In this talk, we will
present our recent study on the Al- and Fe-based DESs as potential anolytes and catholytes, respectively, for hybrid redox
flow batteries. Benefitted from special interactions between metal chlorides and urea, both Al and Fe DESs have high
concentrations of active species, showing great potential to boost the energy density. Moreover, through investigating the
redox chemistry and coordination chemistry of metal centers with possible additives, the stable deposition and stripping of Al
and long cycling of Fe DES with high utilization are achieved. An all-DES-based hybrid flow battery taking advantages of
the Al DES and Fe DES has been demonstrated with high performance. As the chemical and physical properties of DESs can
be tuned by appropriate additives, it provides a new platform for developing promising redox flow batteries based on new
chemistry.

5:55 AM *S.EN09.02.07
Electrode Chemistry for Flow Systems—Elucidating the Degradation of Redoxmer Electrolytes at the Carbon-
Electrolyte Interface Using Spatially-Resolved Electrochemistry Counihan J. Michael¹, Dipobrato Sarbapalli¹, Tylan
Watkins², Danis Andrew¹, Kevin R. Zavadil² and Joaquin Rodriguez-Lopez¹; ¹University of Illinois at Urbana Champaign,
United States; ²Sandia National Laboratories, United States

Non-aqueous redox flow batteries (NRFBs) are attractive technologies that offer the promise of providing higher cell
voltages than their aqueous counterparts. In NRFBs, redoxmers are charged and discharged through electrodes such as
carbon. Interactions between the electrode structure and concentrated redoxmer solutions cause adsorption of these species,
which may lead to subsequent degradation reactions and state-of-charge dependent phenomena. Likewise, the interaction of
the redoxmers with highly polarized electrodes may lead to a modified chemical reactivity at the electrochemical interface.
In this work, we will describe our experiments probing the chemical and electrochemical reversibility of catholyte redoxmers
such as alkoxybenzene derivatives on model carbon electrodes. Using scanning electrochemical microscopy (SECM), we
probe the real-time evolution of the reactivity of the redoxmer-carbon interface by measuring the local redox kinetics, film
formation processes, and the generation of reactive intermediates. Chemical interactions at the interface were further probed
via in-situ Raman electrochemical measurements, and the newly developed Raman-SECM approach. We will describe the
reactivity of different carbon features, as well as the interactions with model redoxmers. SECM revealed a wealth of
reversible and irreversible changes in the kinetics of electron transfer, including the observation of transient enhancements in electrochemical rates and slow passivation processes. Simultaneous operation of SECM and Raman also created new opportunities to probe the impact of reactive radical cations on the chemistry of the carbon host and on film-formation processes through electropolymerization. These studies help direct the design of redoxmers with increased stability at the electrode-electrolyte interface and reveal the complex interplay of redoxmer and electrode chemistries at NRFB structures.

6:10 AM *S.EN09.02.09
Organic Redox Active Solutes in Deep Eutectic Solvents for Flow Batteries Burcu Gurkan; Case Western Reserve University, United States

The discovery of electrolytes that have low vapor pressures, wide electrochemical window and high solubility towards redox active species with an ability to undergo multiple electron transfer reactions is a challenge to realize large-scale energy storage. Deep eutectic solvents (DESs), which are eutectic mixtures of hydrogen bond donors and acceptors, are attractive electrolytes as they have good solvent strength that is also tunable along with other physical, thermal, electrochemical and transport properties. We have examined the electrochemical behavior of various organic redox active solutes, specifically methyl viologen (MV), quinones and nitroxy radicals, in a common DES known as ethaline; a 1 to 2 molar mixture of choline chloride and ethylene glycol. While the reactivity of most quinones investigated are found to fall outside of the electrochemical window of ethaline, nitroxy radicals and MV provide reversible redox couples that are practical. In particular, TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) demonstrates two single electron transfer reactions separated by 1.3 V in ethaline. However, the solubility of TEMPO in ethaline is found to be limited to 0.17 M at room temperature. The hydrogen bonding achieved by –OH substitution on TEMPO and electrostatic interactions achieved by the functionalization of halide salts with TEMPO are shown to improve solubility in ethaline close to 2 M. This study illustrates that chemical modification of redox active organic molecules impacts both their solubility in a DES electrolyte, as well as their redox performance and physical properties of the solutions.

5:00 AM S.EN09.03.07
Enhanced Voltage Generation through Electrolyte Flow on Liquid-Filled Surfaces Prab Bandaru and Bei Fan; University of California, San Diego, United States

The generation of electrical voltage through the flow of an electrolyte over a charged surface may be used for energy transduction. Here, we show that enhanced electrical potential differences (i.e., streaming potential) may be obtained through the flow of salt water on liquid-filled surfaces that are infiltrated with a lower dielectric constant liquid, such as oil, to harness electrolyte slip and associated surface charge. A record-high figure of merit, in terms of the voltage generated per unit applied pressure, of 0.04 mV/Pa is obtained through the use of the liquid-filled surfaces. In comparison with air-filled surfaces (AFS), the figure of merit associated with the liquid-filled surface (LFS) increases by a factor of 1.4. These results lay the basis for innovative surface charge engineering methodology for the study of electrokinetic phenomena at the microscale, with possible application in new electrical power sources.

Our work has experimentally demonstrated the largest figure of merit thus far, to the best of our knowledge, with primary focus on methodologies related to enhance the streaming potential (Vs) per unit pressure difference (ΔP) through the use of LFS. The use of the LFS yields a figure of merit increase in comparison to that obtained using an AFS. It has been shown that larger voltages, through a measured streaming potential, may be achieved through careful engineering of the coupled electric field and fluid flow. The application of the related increase in the electrokinetic energy conversion efficiency would need further optimization of the fluidic and electrical impedances, in concert with the streaming conductance, as matched to an appropriate load. Concomitantly, unipolar transport (where for example, either Na+ or Cl− ions are transported) through EDL (electrical double layer) overlap in nanoscale channels may be coupled with LFS to yield much larger voltages, comparable to that of batteries.

5:10 AM S.EN09.03.08
Generation and Modulation of the Streaming Potential and Slip Characteristics in Electrolyte Flow over Liquid-Filled Surfaces

Prab Bandaru and Bei Fan; University of California, San Diego, United States

The generation of electrical voltage through the flow of an electrolyte over a charged surface may be used for energy transduction. A significant enhancement in the streaming potential ($V_s$) was obtained in experiments considering the flow of electrolyte over liquid-filled surfaces (LFSs), where the grooves in patterned substrates are filled with electrolyte immiscible oils. Such LFSs yield larger $V_s$ (by a factor of 1.5) compared to superhydrophobic surfaces, with air-filled grooves, and offer tunability of electrokinetic flow. It is shown that the density, viscosity, conductivity, as well as the dielectric constant of the filling oil, in the LFS, determine $V_s$. Relating a hydrodynamic slip length to the obtained $V_s$ offers insight into flow characteristics, as modulated by the liquid interfaces in the LFS.

5:20 AM S.EN09.03.10
Enhanced Solar Thermal Evaporation of Ethanol–Water Mixtures, through the Use of Porous Media

Prab Bandaru and Fatih Canbazoglu; University of California, San Diego, United States

A significant enhancement of solar irradiation induced evaporation of water, and ethanol–water mixtures, through the use of carbon foam based porous media, is demonstrated. A relationship between the consequent rate of mass loss, with respect to the equilibrium vapor pressure, dynamic viscosity, surface tension, and density, was developed to explain experimental observations. The evaporative heat loss was parametrized through two convective heat transfer coefficients—one related to the surface and another related to the vapor external to the surface. The work promotes a better understanding of thermal processes in binary liquid mixtures with applications ranging from phase separation to distillation and desalination.

5:00 AM *S.EN09.04.02
Flow and Redox-Based Electrochemical Water Desalination

Yanbo Pan, Abdulaziz Bentalib and Zhenmeng Peng; University of Akron, United States

Desalination of seawater has emerged as an area of critical need, but remains challenging, to solve the fresh water supply problem caused by the steady growth of human population and industry. Although the previous research efforts led to development of a number of desalination methods, for instance distillation, reverse osmosis, electrodialysis and capacitive deionization, their applications were largely restricted by the inherent energy efficiency and effectiveness issues. Thus, there is a demand of new methods that allow efficient and effective separation of salt ions from water. In this talk we review recent progress of water desalination research based on battery mechanism, and report our efforts in developing flow and redox-based electrochemical systems for water desalination application. Specifically, we have prepared FePO₄-based electrode material for sodium ion removal and copper-based electrode material for chloride ion removal. An electrochemical cell composing of the two electrode materials has been demonstrated with promising desalination capacity and efficiency.

5:15 AM S.EN09.04.05
Cascade CO₂ Electroreduction to Selective C-C Coupled Products in a Flow Cell

Junrui Li¹,², Linh Chung², Gurudayal Gurudayal¹,², David Larson¹, Wee-Jun Ong³,¹ and Joel W. Ager¹,²,¹; ¹Lawrence Berkeley National Laboratory, United States; ²University of California, Berkeley, United States; ³Xiamen University Malaysia, Malaysia

Electrochemical conversion of CO₂ into useful products with good efficiency and high selectivity presents challenges due to the distinctive bonding strengths of the various intermediates and products. Reducing CO₂ into C-C coupled products, such as ethylene, ethanol and other hydrocarbons or oxygenates with 2 or more carbon atoms, is particularly interesting technically and scientifically. However, because of the so-called “scaling relationship”, tuning the selectivity on a single catalyst surface is rather difficult as the intermediates leading to specific products have similar binding energies. Cascade catalysis breaks this scaling relationship by separating the catalysis processes into two or more steps on different catalyst surfaces with transport of the intermediates between them.
Here, we report a flow cell with a cascade configuration of two closely spaced working electrodes (Ag and Cu) for electrochemical reduction of CO2 into C-C coupled products. The Ag electrode is located upstream in the reactor to convert CO2 into CO, and CO is convectively transported to the downstream Cu electrode for further C-C coupling catalytic reactions. The porous Ag and Cu working electrodes are separately controlled by two different potentiostat channels allowing for precise control of the conversion rates in the cascade. The porosity of the metal electrodes was controlled by precision laser drilling. A COMSOL model was developed using preliminary experimental data to tune the cell design and operating conditions, such as the flow rate of electrolyte and optimal pore size of the working electrodes. When both Ag and Cu electrodes are activated, CO is generated at Ag and is transported to Cu, leading to a significant increase in generated C2-C3 oxygenates compared to control experiments with only the Cu activated. The flow cell configuration can also be extended to other working electrodes by using carbon cloth as a supporting substrate and depositing powder catalysts.

5:25 AM S.EN09.04.07
Towards TEM Observation of Ion-Current Induced Nanoprecipitation Kyle Sendgikoski1, Alokik Kanwal2, James A. Liddle2, Zuzanna Siwy3 and John Cumings1; 1University of Maryland, United States; 2National Institute of Standards and Technology, United States; 3University of California, Irvine, United States

Lime scaling, the precipitation of calcium salts, is a major hindrance encountered in desalination processes. Recently, nanopore precipitation has been shown to cause oscillation of ion-current through nanopore membranes, a similar model system. Unfortunately, due to the geometry of the pore, direct observation of the precipitates is not possible, so the exact structure is unknown. We report on progress towards direct observation measurements, with transmission electron microscopy (TEM), of the nanoprecipitation that causes ion current oscillations. We have engineered a novel, monolithic in-situ TEM liquid cell that overcomes common shortcomings of other two-piece TEM liquid cells such as liquid thickness and alignment. The customizable geometry and reproducibility of this TEM liquid cell enables investigation of various chemistries and confinement physics.


SESSION S.EN09.05: Poster Session: Flow-Based Open Electrochemical Systems
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
5:00 AM - 8:00 AM
S-EN09

S.EN09.05.01
Self-Assembling Effects of NiFe Hydroxide on 3D Nano-Morphology and Enhanced Oxygen Evolution Performance Li Ren, Jiaqi Wang, Fangfei Li, Yang Yang, Jingru Liu, Kuizhou Dou and Yongqiang Yu; Jilin University, China

Layered double hydroxide (LDH) has been proven to have excellent performance in water splitting reactions, especially toward the oxygen evolution reaction (OER). The morphology of NiFe LDH is one of the key factors in improving its electrochemical performance. However, the controlling factors and mechanisms of morphological evolution of the nanoflower-shaped NiFe LDH remain poorly understood. In this study, NiFe LDH nanoflowers were synthesized by hydrothermal method, and the morphology and structure of NiFe LDH crystals are carefully controlled during the synthetic stage. The results indicate that NiFe LDH primary nano flakes rapidly agglomerate to form a nucleus matrix at the initial stage. Subsequently, these nano flakes are laterally aggregated and connected orderly on the substrate to form nanoflowers, and the nano-petals are generated by a rotating and edge-to-edge orientation attachment (OA) mechanism. The morphological evolution occurred by staged three-dimensional OA process plays an essential role in the self-assembly of flower-like NiFe LDH crystals. The well-formed NiFe LHD nanoflowers, grown by 10 hours of hydrothermal treatment, exhibits excellent OER performance in alkaline electrolyte, which displays very low overpotential of 190 mV at the current density of 10 mA cm$^{-2}$ and small Tafel slope of 35 mV per decade (much better than RuO2 catalyst). Furthermore, the prepared NiFe LDH still showed high stability after 10,000 cycles of cyclic voltammetry tests. This work provides new insights into the relationship between catalyst morphology and OER performance, and provides new fundamental understanding of hydrothermal synthetic process of NiFe LDH.
First-Principles Modeling of Galvanic Corrosion Behavior of Metal Alloys  Yaowei Wang, Tian Xie, Zhe Luo, Hong Zhu and Xiaoqin Zeng; Shanghai Jiao Tong University, China

Some emerging alloys, such as Mg alloy, are susceptible to galvanic corrosion, consequently accelerating corrosion process and resulting in severe financial loss. The galvanic corrosion potential and current obtained by experimental polarization curves could differ a lot between different literature. Herein, we proposed a semi-empirical model based on the mixed potential theory and first principles calculation to analyze the galvanic corrosion of the metal alloys. Our model is further validated in the case of Mg-Ge alloys, which is composed of anode Mg matrix and cathode Mg$_2$Ge second phase. The combination of the large anode equilibrium potential difference between Mg and Mg$_2$Ge, and the Schottky barrier across the interface indicates that the Mg$_2$Ge second phase can prevent the Mg grain from serving as the cathode and impede the electron transfer between the Mg grains. First principles calculations on the kinetics of hydrogen evolution reaction upon Mg$_2$Ge reveal that the rate-determining step is the hydrogen adsorption, which is extremely energetically unfavorable but an inevitable intermediate state. The estimated exchange current of the hydrogen evolution upon Mg$_2$Ge is about 3 orders of magnitude smaller than that on pure Mg, depressing the hydrogen exchange current upon Mg$_2$Ge and hence the galvanic corrosion of the Mg-Ge alloys. Moreover, some other Mg alloys, such as Mg-Zn and Mg-Sc, were also investigated, which is in close agreement with the experimental observations. Our model is capable of predicting the galvanic corrosion behavior and provide a promising perspective for designing better corrosion-resistant metal alloys.
technologies offer versatile options. This presentation will provide an overview of the U.S. Department of Energy’s Hydrogen and Fuel Cell Technologies Office’s early-stage R&D activities in hydrogen production and storage and fuel cell technologies within the Office of Energy Efficiency and Renewable Energy. The presentation will focus on their relevance to the evolving energy storage needs of a modernized grid, and discuss R&D needs and challenges. Specific examples of advanced materials research relevant to address energy storage challenges will be provided. The presentation will also cover DOE’s H2@Scale initiative which will enable innovations to generate cost-competitive hydrogen as an energy carrier, coupling renewables, as well as nuclear, fossil fuels, and the grid, to enhance the economics of both baseload power plants and intermittent solar and wind, enhancing resiliency and avoiding curtailment.

5:28 PM *S.EN11.04.12
Multiscale Modeling of Materials Interfaces for Hydrogen Storage, Generation and Delivery Brandon Wood; Lawrence Livermore National Laboratory, United States

Developing viable solutions for the efficient production and storage of hydrogen requires understanding chemical process occurring at solid-gas, solid-liquid, and solid-solid interfaces in advanced materials. Probing behavior of these interfaces under operating conditions presents significant challenges; however, predictive modeling offers an opportunity for providing key insights into interface chemistry, particularly when operating in tandem with high-fidelity experimental characterization techniques. Within the DOE Hydrogen Materials—Advanced Research Consortium (HyMARC) and the HydroGEN Advanced Water Splitting Materials Consortium, we are using multiscale models to understand properties of reactive interfaces for the production, storage, and delivery of hydrogen. I will provide an overview of our materials modeling strategy within these consortia, ranging from first-principles calculations of interface chemistry to continuum methods for microstructure-level properties. I will then review some of our recent activities for simulating thermodynamic and kinetic properties of hydrogen-related materials. Specific examples will be given of how these computational models have helped to elucidate mechanisms of interface chemical reactions, the formation of new phases, and the impact of solid-state interfaces on key reaction pathways. I will also show how simulations have been combined with experimental probes to improve models and obtain new understanding of materials interfaces under operating conditions. Finally, I will discuss how this understanding is being used to guide new strategies for improving materials functionality for storage, generation, and delivery of hydrogen. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

5:51 PM *S.EN11.06.02
Techno-Economic Analysis of Hydrogen Transmission and Distribution Aikaterini Anastasopoulou and Hanna Breunig; Lawrence Berkeley National Laboratory, United States

As more nations make long-term commitments to clean infrastructure, it is critical that we better understand technologies that act at the interface of traditionally decoupled systems. Hydrogen (H2) will likely lie at the interface of energy storage, transportation, and industry. Here, we use ex-ante techno-economic analysis to characterize pathways for H2 delivery. We evaluate the impact of different process system parameters on the levelized H2 delivery cost ($/kg H2), and identify barriers and opportunities for achieving industrial competitiveness. Three carrier market applications are studied: transmission, which we define as long-distance delivery from a large H2 source to an end use; distribution, which we define as short-distance delivery from a city-gate to fueling stations within the city; and transmission-distribution, which we define as long distance delivery from a large H2 source all the way to fueling stations. For each of these market applications, we evaluate the energy intensity and other key system level performance metrics for high pressure (350 and 500 bar) truck transportation, cryogenic liquid H2 truck transportation, and carrier-based truck transportation. Ancillary equipment and operation conditions, including systems at the H2 source and refueling station which are unique to adsorption systems are included in the analysis.

For a base transmission application, where 50 Mg H2/day is delivered 100 km from a gas terminal to an end point application, the delivery cost is approximately $1.6/kg H2 and $1.8/kg H2 for 500 bar and 350 bar trucks, respectively. Liquid H2 transport is less competitive at this short distance, and costs $3.1/kg H2. A truck packed with metal organic framework (MOF) Ni2(m-dobdc) and modeled at 100 bar and 200K has a delivery cost of $7.7/kg H2. Transmission costs for the MOF-H2 system can reach as low as $1.8/kg H2 (on par with 350 bar trucks) in a scenario where driverless trucks are employed, a highly durable material is developed (15,000 cycles), material costs are $10/kg MOF, and where bed porosity and pellet porosity are substantially lower (or rather increasing H2 uptake without increasing upstream cooling requirements).

For the distribution application, the delivery cost is dominated by the CAPEX and OPEX of the refueling stations. For a base scenario where 50 Mg H2/day is delivered 1 km from a city-gate gas terminal to distributed fueling stations, the delivery cost
is between $3.4/kg H2 and $4.6/kg H2 for 500 bar and 350 bar trucks, respectively, and $5.3/kg H2 for liquid H2 transport. Liquid trucks for distribution perform better in larger markets (40% lower costs for a 120 Mg/day market). The MOF-H2 systems studied performs poorly in this market application (above $20/kg H2) as 10x more fueling stations and trucks are required to meet the same daily H2 demand as compared to the liquid or high pressure systems.

These results demonstrate capabilities of the hydrogen delivery models developed at the Lawrence Berkeley National Laboratory for the Department of Energy HyMARC program. Any path to substantial greenhouse gas emissions (GHG) reduction will include market transformations in the transportation sector, as it remains the single largest primary source of GHGs in the United States and the third largest primary source globally. Advances in carrier materials such as liquid organic hydrogen carriers (LOHC) and MOFs, which exhibit a wide range of tunability for hydrogen storage, could radically change the way hydrogen is stored and transported globally to meet fuel demand in zero direct emission vehicles. In this research work, we present a framework for characterizing and benchmarking the performance of emerging carrier systems.

6:14 PM S.EN11.07.17
Alkylphosphine as a Ligand for Shape-Controlled Synthesis of Metal Nanostructures Shutang Chen and Gugang Chen; Honda Research Institute USA Inc., United States

Metal nanoparticles with high index facets and controllable shape have demonstrated excellent catalytic performance because of their unique surface chemistry. Generally, the selection of proper ligand plays an important role for the shape-control of nanoparticles. Here, different kinds of alkylphosphines with high temperature solution reduction method are adopted to synthesize metal nanostructures. With increasing chain length of alkylphosphines, different morphologies of copper nanoparticles were synthesized in a hydrophobic system, such as nanocubes, tetrahedron nanoparticles, nanowires, and nanosheets. All these copper nanostructures demonstrated excellent catalytic performance and selectivity to carbon dioxide reduction reaction. Such simple strategy is also extended to the design of other metal nanoparticles for their potential applications in catalysis, sensor, and electronics.

SESSION S.EN11.09: Live Keynote II: Materials, Modeling and Technoeconomic Impacts for Large-Scale Hydrogen and Energy Applications
Session Chairs: Thomas Gennett, Bojana Ginovska and Alexander Headley
Monday Morning, November 30, 2020
S.EN11

11:30 AM INTRODUCTION AND ANNOUNCEMENTS

11:35 AM *S.EN11.02.03
Toyota's Hydrogen Future Jacquelyn Birdsell and Dallas Fox; Toyota Motor North America, United States

Hydrogen fuel cell technology is gaining momentum throughout the transportation industry for use in a variety of applications - from on road light duty to heavy duty. This presentation will highlight Toyota's image for hydrogen fuel cells in our electrification strategy and our need for a robust supply of renewable low or zero CO2 hydrogen.

11:58 AM *S.EN11.03.01
A Step Change in the Cost of PEM Water Electrolysers? Gareth Hinds, Hans Becker and Luis Castanheira; National Physical Laboratory, United Kingdom

Reduction in the cost of polymer electrolyte membrane water electrolyser (PEMWE) technology is urgently required for the realisation of commercially viable green hydrogen production. However, at present up to two thirds of the manufacturing cost of a PEMWE stack is associated with the current collector components, with platinum-coated titanium a common material of choice. This presentation will describe in situ measurements of the local potential at the current collectors during PEMWE cell operation, demonstrating for the first time that the corrosion potential of the anode current collector is completely decoupled from the potential of the anode electrode due to the low ionic conductivity of the deionised water phase. This new observation opens up the possibility of using cheaper materials such as carbon and carbon-coated stainless steel for anode current collector components, which could lead to a dramatic decrease in the cost of the technology.
Among various materials for hydrogen storage, alloys and intermetallics forming hydrides are one of the most important classes due to their high volume density, reversibility and safety. Within the class of conventional metals and alloys for hydrogen storage, the body centered cubic (bcc) alloys based on early 3d transition elements (Ti, V, Cr...) represent one of the most promising class due to their high hydrogen storage capacity up to 2 Hydrogen per metal atoms (H/M). These alloys show two plateaus at low and ambient pressure in the Pressure-Composition-Isotherms. But, for practical applications only the second plateau is available reducing the reversible quantity of hydrogen that could be stored. Consequently, new metallurgical concepts and materials are stringently required to develop more efficient multifunctional hydrides. Recently, a new paradigm of alloying strategy has emerged based on the original concept of multi-principal-element alloys (MPEAs), initially proposed to develop materials with enhanced mechanical properties. The principle is laid on the mixing of elements close to the equimolar proportion for systems up to five and more containing elements. This mixing may lead to the formation of single simple solid solutions (body centered cubic-bcc, face centered cubic-fcc and hexagonal close packed-hcp). The formation and the stability of such phases are still under consideration and seem to be based on several chemical and physical quantities such as, configurational entropy, mixing enthalpy, atomic misfit, valence electron concentration. Among MPEAs, alloys with at least five principal elements with atomic concentrations in the range 5 to 35% are called high entropy alloys (HEAs). Most of reports concerning these alloys describe their structure, microstructure and mechanical properties, whereas functional properties such as, hydrogen sorption, are only scarcely investigated. We present here the study of hydrogen absorption properties of MPEAs based on refractory metals. The TiVZrNbX (X = Mg, Al and Ta) alloys have been synthesized by classical metallurgical high temperature methods or mechano-synthesis by ball milling under protective atmosphere. To produce directly metal hydrides we have employed the reactive ball milling under hydrogen gas starting from the pure metal powders. The properties of TiVZrNbX (X = Mg, Al and Ta), TiZrNbHfTa and related hydrides have been studied by a large set of experimental techniques: laboratory X-ray diffraction, electron microscopy, in situ synchrotron X-Rays or neutron diffraction, pressure-composition-isotherm, thermal desorption spectroscopy and differential scanning calorimetry. All the TiVZrNbX alloys are single-phase bcc and undergo a one-step reaction with hydrogen at room temperature. The single-phase TiZrNbHfTa alloy also crystallizes in a bcc phase but undergoes a two-stage hydrogen absorption reaction to a fcc dihydride phase with an intermediate tetragonal monohydride at high temperature. We suggest that the lattice distortion, δ, as defined for MPEAs, might play an important role: larger δ would favors a single-step reaction with hydrogen (bcc → bct hydride with large hydrogen content), whereas small δ would favor a two-steps phase transition (bcc → bct → fcc), as also encountered for conventional bcc alloys. The most promising alloy is the TiVZrNb composition which, despite a fading of the capacity for the first cycles, shows a stable reversible capacity around 2 wt% for further cycling. In the light of scarce literature on the subject, hydrogen adsorption in MPEAs/HEAs is an original research topic that might open new routes for the design of promising materials for hydrogen storage.

Adsorption of molecules in functionalized and high surface area metal-organic frameworks (MOFs) is of emergent technological importance in a multitude of areas ranging from chemical separations to energy storage. We have been studying the properties of MOFs for storage and separations of industrially important small molecules such as hydrogen, oxygen, carbon dioxide, noble gases, and short chain organics. Besides the geometrical and porosity control available in MOF chemistry, the properties of the frameworks can be tweaked to elevate electrostatic interactions by exposing open metal cation sites or functionalizing ligands. Here, we discuss the information accessible from neutron scattering experiments on hydrogen adsorbed in a selection of nominally rigid MOFs with some surprising subtle flexibility that greatly enhances metal-hydrogen interactions.

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5:00 AM S.EN11.01.02
Colloidal Synthesis of Al/C-Based Composite Energetic Nanoparticles with Tunable Interfacial Activities via Laser Ablation Synthesis in Solution Dibyendu Mukherjee1,1, Seyyed A. Davari2, Jennifer L. Gottfried3 and Gerd Duscher1; 1University of Tennessee, United States; 2University of California Davis, United States; 3US Army Research Laboratory, United States

Energetic nanomaterials (ENMs) find applications in solid-state propellants and explosives. Yet, the large heat release in the Al nanoparticle (NP)-based first-generation ENMs were offset by hindered detonation rates due to the fuel-oxidizer diffusion lengths and rates being compromised by excessive oxide shell formations and NP aggregations.1-3 Efforts have been made to tune their energetic behaviors by tailoring their interfacial structures that can control the oxide shell formation while leading to excessive internal stresses within the metallic cores. Yet, there exists weak fundamental understanding and considerable challenges in the rational design and synthesis of such nanostructured architectures. To this end, carbon (C) coatings on Al NPs facilitate safe handing while promoting enhanced activities due to the added advantages of the coating itself oxidizing into gaseous products (CO2, CO etc.) without any residual ash formation, while allowing the C shell to retard NP aggregations. But, the challenge remains in the facile yet, chemically clean colloidal synthesis of these encapsulated NPs without contaminating and/or oxidizing the metal cores. Here, we address this challenge through rational design and structure-property characterizations of graphitic shell coated Al NPs (< 20 nm sizes) dispersed in pyrolyzed C matrices via laser ablation synthesis in solution (LASiS) to preserve high surface areas and interfacial properties of Al NPs.4 Such nanostructures allow tailored design of interfacial structures that can either lead to strain energy manifestation or, rate-controlled release of solid propellants under high pressure/temperature to prevent oxide shell-mediated surface passivation. Energetic activities of the C/Al composite NPs were tested via Laser-induced Air Shock from Energetic Materials (LASEM) technique at the US Army Research Laboratory, Aberdeen Proving Ground, MD. We demonstrate that synthesis parameters such as organic solvents, laser flux and ablation times can be tuned to provide superior control on NP sizes/aggregation, composition, crystallinity, metastable structures and, in turn, their energetic behavior with the aid of the C shell nanostructures and matrices. The study unveils synthesis-structure-property relations in LASiS-based manufacturing of composite ENMs capsuled in graphitic shells that are safe to handle and undergo kinetically controlled energy release under desired conditions. Such Al/C-based composite ENMs can be immediately employed for high energy density munitions in defense applications.

References:

5:10 AM S.EN11.01.03
Capillary-Driven Solar-Thermal Water Desalination Using a Porous Selective Absorber Xuanjie Wang and Shankar Narayanan; Rensselaer Polytechnic Institute, United States

Freshwater is critical to humankind’s survival, as well as to global health and economic development. Providing clean water in a safe, reliable and affordable manner is a considerable challenge as demand increases with a growing population. Although 71% of the Earth’s surface is covered by water, most of it is saltwater and therefore non-potable. Therefore, large-scale and efficient deployments of seawater desalination are greatly needed. Traditional desalination technologies such as reverse osmosis (RO) and multi-stage flash (MSF) are limited by efficiency and cost. Solar vapor generation, on the other hand, is an emerging and promising technology that takes advantage of clean and abundant energy from the sun by converting the solar energy to thermal energy. More recently, efforts have been made to reduce heat loss[1][2], enhance the broadband absorption of sunlight[3], and design efficient water supply channels. Meanwhile, various materials such as carbon-based materials[4], plasmonic nanoparticles[5], polymer-based materials and metal oxides have been explored in an attempt to further increase the efficiency of solar water evaporation.

However, there are only few studies regarding the radiation loss coming from the broadband solar absorbers, which emit thermal radiation to the environment like a blackbody in the infrared region. Compared with broadband absorbers, the selective solar absorbers with strong solar absorptance and low infrared emitance can efficiently absorb the solar spectrum
while largely suppressing the heat loss, resulting in the enhancement of solar evaporation efficiency. Nevertheless, many existing selective absorbers involve either expensive materials or complicated fabrication protocols, which limit the potential for scalable applications. Therefore, developing solar steam generation devices that takes into consideration light absorption, heat loss, and feasible scalability is challenging but also desirable.

In this study, we report on selective solar absorber with uniform self-assembled nanowires fabricated by an electrochemical deposition process. We demonstrate that the solar-thermal performance can be further enhanced by applying selective solar absorbers, compared with graphite broadband absorbers. Our results provide a feasible path for selective solar absorbers with cost-effective and scalable fabrication processes that may be beneficial for various solar-based applications.


5:20 AM S.EN11.01.04
Measuring the Dielectric Constant of Perovskite Nanoparticles Embedded in a Polymer Matrix
Jackson Baker1, Daniel Brito1, Josh Morgan1, Guadalupe Quirarte1, Eleanor Rackoff4, Albert Dato1 and Todd C. Monson2; 1Harvey Mudd College, United States; 2Sandia National Laboratories, United States

Barium titanate (BTO) is a perovskite material used in energy storage applications because of its high dielectric constant [1,2]. Wada et al. discovered that the size of BTO nanoparticles strongly affects their dielectric constant [2]. Particles with diameters above 300nm exhibited a dielectric constant of 4000, but a sharp increase in dielectric constant to over 15,000 was observed at a diameter of 70 nm [2]. These intriguing, yet highly contested results have motivated us to develop a process that further investigates the relationship between BTO nanoparticle size and their dielectric constant. With this goal in mind, we have developed novel methods of (1) functionalizing BTO nanoparticles using ball milling and (2) integrating functionalized BTO nanoparticles into a polymer matrix using injection molding. These processes enable us to create a solid colloid from which the dielectric constant of the nanoparticles can be extracted. Here we present our methods of nanoparticle functionalization and nanocomposite fabrication. We also introduce the results of our investigation, which focused on characterizing and measuring the dielectric constants of nanocomposites containing BTO nanoparticles with sizes ranging from 50 to 500 nm. We will also discuss our method of extracting the dielectric constant of the BTO nanoparticles in the polymer matrix and present the effect of nanoparticle volume loading on the dielectric constant of the nanocomposite.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.

Hydrogen could be an ideal energy carrier for a sustainable energy supply system because it combusts cleanly without producing CO₂ or any other pollutants, and this chemical energy is easier to store than electricity. However, the current industrial production of hydrogen (most commonly by steam reforming of natural gas) is energy-intensive and produces CO₂ and other pollutants, making the overall system far from being sustainable.

Alternative environment-friendly H₂ production methods include photoelectrolysis or electrolysis of water using a renewable energy source. Photovoltaic cell–electrochemical cell (PV–EC) is such an approach to solar energy-driven water splitting, which combines PV for power generation and EC for electrochemical H₂ production from water. To realize a practical PV–EC system, both PV and EC components should be highly efficient, durable, and cost-effective. The electrochemical cell has received renewed interest recently to improve its performance as well as cost. The electrocatalytic water splitting consists of two electrochemical reactions; hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in acidic or alkaline media. Regardless of the system types and media, sluggish OER kinetics limits the efficiency of overall water splitting reaction owing to its more complex reaction mechanism and higher overpotential (0.2 V) relative to HER (0.05 V). To maximize the efficiency of a PV–EC system, reducing the overpotential of OER by developing a highly efficient oxygen evolution catalyst (OEC) is indispensable. Although noble-metal based OECs including IrOₓ and RuO₂ exhibit great OER catalytic activity in acidic media, they are not only expensive but often susceptible to corrosion and deactivation in alkaline media without proper modification.

Alternatively, many first-row transition metal oxides, hydroxides, and present great OER activity and stability in alkaline conditions in addition to the advantages of being made of earth-abundant elements and the low price compared to precious metals. Many recent studies have demonstrated great OER performance of binary and ternary mixed oxyhydroxides of Ni, Fe, and Co, synthesized by various methods. However, in order to apply these catalysts to a practical industrial scale, it is required to develop an advanced synthesis method capable of producing multicomponent electrocatalysts with a simpler synthesis step under mild conditions at ambient pressure and temperature preferably with an all-solution-based process.

In the present work, we present an ingenious synthesis method of “precipitating metal nitrate deposition (PMND)” to prepare amorphous phases of unary or binary transition metal oxyhydroxide (TMOH) films containing Ni, Fe, and Co. This technique can easily control the composition of the metals in the catalyst and thus is suitable to study its effects on the catalytic activity of the electrocatalysts. By examining a series of unary and binary TMOH catalysts of 30 different ratios of elements on fluorine-doped tin oxide (FTO) substrate, it is shown that their OER activity is represented by a volcano plot as a function of a single experimental descriptor, i.e., the fraction of hydroxide in the surface oxygen species. We also demonstrate the versatility of the PMND method by preparing the catalysts on various substrates of FTO, nickel foam, nickel mesh, and carbon felt. The optimized NiFe (2:8) electrocatalyst on nickel foam exhibits great OER activity in an alkaline medium superior to conventional noble metal oxides and other reported electrocatalysts of similar composition. Finally, we fabricate a PV–EC device by connecting our optimized EC with a commercial crystalline c-Si PV module, which records a solar-to-hydrogen conversion efficiency (STH) of 9.84 %.

[Y. K. Kim et al. ACS Catalysis 2019, 9 (10), 9650-9662.]

5:10 AM *S.EN11.02.02

Today the technology around generating and storing efficient and sustainable energy is rapidly evolving and hydrogen technologies offer versatile options. This presentation will provide an overview of the U.S. Department of Energy’s Hydrogen and Fuel Cell Technologies Office’s early-stage R&D activities in hydrogen production and storage and fuel cell technologies within the Office of Energy Efficiency and Renewable Energy. The presentation will focus on their relevance to the evolving energy storage needs of a modernized grid, and discuss R&D needs and challenges. Specific examples of advanced materials research relevant to address energy storage challenges will be provided. The presentation will also cover DOE’s H₂@Scale initiative which will enable innovations to generate cost-competitive hydrogen as an energy carrier, coupling renewables, as well as nuclear, fossil fuels, and the grid, to enhance the economics of both baseload power plants and intermittent solar and wind, enhancing resiliency and avoiding curtailment.

5:25 AM *S.EN11.02.03
Toyota’s Hydrogen Future Jacquelyn Birdsal and Dallas Fox; Toyota Motor North America, United States

Hydrogen fuel cell technology is gaining momentum throughout the transportation industry for use in a variety of
applications - from on road light duty to heavy duty. This presentation will highlight Toyota's image for hydrogen fuel cells in our electrification strategy and our need for a robust supply of renewable low or zero CO2 hydrogen.

SESSION S.EN11.03: Electrolysis
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN11

5:00 AM *S.EN11.03.01
A Step Change in the Cost of PEM Water Electrolysers? Gareth Hinds, Hans Becker and Luis Castanheira; National Physical Laboratory, United Kingdom

Reduction in the cost of polymer electrolyte membrane water electrolyser (PEMWE) technology is urgently required for the realisation of commercially viable green hydrogen production. However, at present up to two thirds of the manufacturing cost of a PEMWE stack is associated with the current collector components, with platinum-coated titanium a common material of choice. This presentation will describe in situ measurements of the local potential at the current collectors during PEMWE cell operation, demonstrating for the first time that the corrosion potential of the anode current collector is completely decoupled from the potential of the anode electrode due to the low ionic conductivity of the deionised water phase. This new observation opens up the possibility of using cheaper materials such as carbon and carbon-coated stainless steel for anode current collector components, which could lead to a dramatic decrease in the cost of the technology.

5:15 AM S.EN11.03.02
Embedded Ions Activating Water Oxidation Yingfang Yao1,2; 1Nanjing University, China; 2Jiangsu Key Laboratory for Nano Technology, China

Clean hydrogen from water splitting driven by electrocatalysis provides an alternative to fossil fuels. However, the oxygen evolution reaction (OER) is the rate determining step of water splitting. Therefore, there is an urgent need to develop low-cost and highly efficient OER electrocatalysts. Low-cost carbon-based materials with a high surface area that expose more active centers are the ideal candidates for OER. Challenges to reduce OER overpotentials and to increase stability still limit the practical applications of carbon-based materials. However, substantial overpotentials above thermodynamic requirements limit their efficiency and stability in OER-related energy conversion and storage technologies. Here, we embedded CrN crystals into graphene and in situ electrochemically oxidized them to construct graphene materials with encapsulated Cr$^{6+}$ ions (Cr$^{6+}$@G). These Cr$^{6+}$@G materials exhibit the lowest OER overpotential of 197 mV at 10 mA cm$^{-2}$ and excellent stability over 200 h at a high current density of about 120 mA cm$^{-2}$ in an alkaline electrolyte. Spectroscopic and computational studies confirm a stable ion coordination environment significantly benefiting the downshift of the graphene Fermi level via hybridization of C p orbitals with d orbitals of Cr$^{6+}$ ions that enhances the OER activity and stability.

References

5:25 AM S.EN11.03.03
Device Properties of Polymer Electrolyte Electrochemical Cells (PEEC) Influenced by the Operating Conditions of Electric Energy Management System Katsushi Fujii, Kayo Koike, Kei Morishita, Katsushiko Tsuno and Satoshi Wada; RIKEN, RAP, Japan

Electric energy storage is an important part to establish natural energy-originate electric power like solar cells and wind power generations as a user-on-demand power supply system. Hydrogen storage is a suitable method for a long-term and a large amount of energy storage while the rechargeable battery is good for fast demand response. We proposed a new control concept of the user-on-demand electric supply system taking both advantages of hydrogen storage and rechargeable battery [1]. For the system, not only the rechargeable battery is used as a fast response device but also hydrogen storage is for a large amount of energy storage device, with DC bus voltage as the signal of the power flow balance. In such kind of system, hydrogen is stored by polymer electrolyte electrochemical cell (PEEC) and is consumed by polymer electrolyte fuel cell (PEFC). Thus, the system operating conditions influence the PEEC and PEFC properties. In this report, some of the possible
system conditions influencing the PEEC properties are mainly discussed. The evaluated PEEC was the conventional one, that is, the anodic catalyst is IrOx and the cathodic catalyst is Pt. Step-like electric power changes by the voltage and by the current for a PEEC were performed. The current by the step-like voltage change showed a large overshoot for voltage increase and undershoot for voltage decrease were observed. In contrast, the voltage by the step-like current change showed a relatively smooth increase and decrease without overshoot nor undershoot. This is explained by the EC as a capacitor, and the power change should be controlled by the current.

The performance of water electrolysis is improved with increasing temperature due to the overall electric resistance decreasing and the overvoltage of water splitting decreasing. The hydrogen leakage to the oxygen evolution reaction (OER) side is also well-known properties for PEEC. The leakage was also observed to be increased with cell temperature. This means that the cell temperature must be considered because IrOx water oxidized catalyst may be reduced. This leakage may also affect device reliability, but the details are still obscured.

From the impurity analysis of the supplied water for a PEEC after the current-voltage (I-V) relationship degraded (electric resistivity increased), the component metal ions of PEEC were detected. After replacing the water with pure one, the I-V characteristic was recovered. This probably shows that the dissolved metal ions decrease the ion transferability in the proton exchange membrane. The result shows that especially for the long-term water electrolysis operation requires water purification.


SESSION S.EN11.04: Hydrogen Storage Materials
On Demand Abstracts Available for Viewing Starting Saturday
Morning, November 21, 2020
S-EN11

5:00 AM *S.EN11.04.01
Hydrogen Storage in Metal-Organic Frameworks Probed through Neutron Scattering Craig Brown; National Institute of Standards and Technology, United States

Adsorption of molecules in functionalized and high surface area metal-organic frameworks (MOFs) is of emergent technological importance in a multitude of areas ranging from chemical separations to energy storage. We have been studying the properties of MOFs for storage and separations of industrially important small molecules such as hydrogen, oxygen, carbon dioxide, noble gases, and short chain organics. Besides the geometrical and porosity control available in MOF chemistry, the properties of the frameworks can be tweaked to elevate electrostatic interactions by exposing open metal cation sites or functionalizing ligands. Here, we discuss the information accessible from neutron scattering experiments on hydrogen absorbed in a selection of nominally rigid MOFs with some surprising subtle flexibility that greatly enhances metal-hydrogen interactions.

5:15 AM S.EN11.04.03
Synchrotron X-Ray Characterization of Candidate Hydrogen Storage Materials Nicholas A. Strange1,2, Sarah Shulda1, Thomas Gennett3,1 and Michael F. Toney2; 1National Renewable Energy Laboratory, United States; 2SLAC National Accelerator Laboratory, United States; 3Colorado School of Mines, United States

Hydrogen is an ideal renewable fuel source due to its superior energy density and absence of harmful emissions. A significant obstacle for a hydrogen-based energy economy is efficient storage post-production, during transportation and within the target technology (e.g. vehicles). Two primary methods are employed to achieve these goals: physical and chemical storage. Physical storage (e.g. high surface area frameworks) is limited by inadequate volumetric capacities near ambient temperatures and pressures. Chemical storage materials exhibit high decomposition temperatures with poor kinetics and cyclability. The synthesis of novel molecules/frameworks or improvement of existing technology is critical for advancing hydrogen storage toward meeting DOE’s technical targets. As such, high-resolution synchrotron x-ray characterization has become increasingly necessary for deriving complex structure-property relationships of developing storage materials. This presentation will highlight recently developed in situ x-ray scattering and spectroscopy measurements performed on leading candidate chemical (borohydrides) and physical (MOFs, COFs) hydrogen storage materials. Approaches for improving decomposition and cyclability of borohydrides include ALD coating, nanoconfinement, eutectic mixtures. Temperature-resolved phase transformations recorded with XRD and SAXS demonstrated structural mechanisms leading to hydrogen
Mono- and Bimetallic MOF-74 Frameworks as Non-Precious Metal Catalysts for Dehydrogenation of Alcohols for Energy Storage

Jonathan L. Snider\textsuperscript{1}, Ji Su\textsuperscript{2,3}, Pragya Verma\textsuperscript{2}, Alexander Baker\textsuperscript{3}, Yi-Sheng Liu\textsuperscript{2}, Jinghua Guo\textsuperscript{2}, David Prendergast\textsuperscript{2,4}, Vitalie Stavila\textsuperscript{1}, Gabor Somorjai\textsuperscript{2,4} and Mark D. Allendorf\textsuperscript{\textsuperscript{4}}; \textsuperscript{1}Sandia National Laboratories, United States; \textsuperscript{2}Lawrence Berkeley National Laboratory, United States; \textsuperscript{3}Lawrence Livermore National Laboratory, United States; \textsuperscript{4}University of California, Berkeley, United States

The transition to a sustainable hydrogen economy requires liquid organic hydrogen carriers (LOHCs) to enable efficient, high density storage and transportation of hydrogen-based energy. LOHCs, such as alcohols, require an effective and economical catalyst to promote the chemical reactions which store and release hydrogen from the molecule.\textsuperscript{1} In recent years, metal-organic frameworks (MOFs) have emerged as an exciting class of materials with applications in catalysis due to unsurpassed tailorability of pore size and local chemical environment and high thermal and chemical robustness required for industrial-scale processes. The MOF-74 framework (M(dobdc), where M is a divalent metal and dobdc = 2,5-dioxido-1,4-benzenedicarboxylate) is a particularly versatile structure which can incorporate many different open metal sites and has been shown to perform a variety of reactions, including hydrogenolysis of aryl ethers\textsuperscript{2}, dehydrogenation of ammonia borane\textsuperscript{3}, and methanol-catalyzed water dissociation\textsuperscript{4}. In this work, we investigate a series of mono- and bimetallic MOF-74 catalysts with activity towards the methanol dehydrogenation reaction. Reactions were carried out in a packed bed reactor with methanol vapor and nitrogen carrier gas. While Mg-MOF-74 was found to be inactive for this reaction, other M-MOF-74 (M= Zn, Co, Ni, bimetallic Ni-Mg) catalysts turnover the reaction at pressures of 1 bar with temperatures above 200 °C. At 300 °C, the Ni\textsubscript{0.2}Mg\textsubscript{0.8} composition achieved the greatest hydrogen productivity of the sample series at 20.3 mL H\textsubscript{2}/min. This catalyst demonstrated stability under the reaction conditions, maintaining the MOF-74 structure and high activity for 6 hours. In contrast, the Ni-MOF-74 catalyst had diminished hydrogen productivity and decomposed under the reaction conditions, suggesting a promotional effect was achieved by maintaining the MOF-74 framework. Ex situ X-ray absorption spectroscopy and density functional theory were used to probe the stability and properties of the open metal sites thought to play a role in the observed catalytic activity. These investigations into methanol demonstrate the catalytic activity of a variety of MOF-74 catalysts towards alcohol dehydrogenation and provide important mechanistic understanding of the factors that affect the catalytic activity and selectivity of MOFs for hydrogen generation from hydrocarbon carriers.

References

Refractory Multi-Principal-Element Alloys as Novel Solid-State Hydrogen Stores

Claudia Zlotea and Jorge Montero; ICMPE CNRS, France

Among various materials for hydrogen storage, alloys and intermetallics forming hydrides are one of the most important classes due to their high volume density, reversibility and safety. Within the class of conventional metals and alloys for hydrogen storage, the body centered cubic (bcc) alloys based on early 3d transition elements (Ti, V, Cr...) represent one of the most promising class due to their high hydrogen storage capacity up to 2 Hydrogen per metal atoms (H/M). These alloys show two plateaus at low and ambient pressure in the Pressure-Composition-Isotherms. But, for practical applications only the second plateau is available reducing the reversible quantity of hydrogen that could be stored. Consequently, new metallurgical concepts and materials are stringently required to develop more efficient multifunctional hydrides.

Recently, a new paradigm of alloying strategy has emerged based on the original concept of multi-principal-element alloys (MPEAs), initially proposed to develop materials with enhanced mechanical properties. The principle is laid on the mixing of elements close to the equimolar proportion for systems up to five and more containing elements. This mixing may lead to the formation of simple single-phased solid solutions (body centered cubic-\textit{bcc}, face centered cubic-\textit{fcc} and hexagonal close packed-\textit{hcp}). The formation and the stability of such phases are still under consideration and seem to be based on several chemical and physical quantities such as, configurational entropy, mixing enthalpy, atomic mismatch, valence electron concentration. Among MPEAs, alloys with at least five principal elements with atomic concentrations in the range 5 to 35 % are called high entropy alloys (HEAs). Most of reports concerning these alloys describe their structure, microstructure and mechanical properties, whereas functional properties such as, hydrogen sorption, are only scarcely investigated.

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We present here the study of hydrogen absorption properties of MPEAs based on refractory metals. The TiVZrNbX (X = Mg, Al and Ta) alloys have been synthesized by classical metallurgical high temperature methods or mechano-synthesis by ball milling under protective atmosphere. To produce directly metal hydrides we have employed the reactive ball milling under hydrogen gas starting from the pure metal powders. The properties of TiVZrNbX (X = Mg, Al and Ta), TiZrNbHfTa and related hydrides have been studied by a large set of experimental techniques: laboratory X-ray diffraction, electron microscopy, in situ synchrotron X-Rays or neutron diffraction, pressure-composition-thermometry, thermal desorption spectroscopy and differential scanning calorimetry. All the TiVZrNbX alloys are single-phase bcc and undergo a one-step reaction with hydrogen at room temperature. The single-phase TiZrNbHfTa alloy also crystallizes in a bcc phase but undergoes a two-stage hydrogen absorption reaction to a fcc dihydride phase with an intermediate tetragonal monohydride at high temperature. We suggest that the lattice distortion, δ, as defined for MPEAs, might play an important role: larger δ would favor a single-step reaction with hydrogen (bcc → bct hydride with large hydrogen content), whereas small δ would favor a two-steps phase transition (bcc → bct → fcc), as also encountered for conventional bcc alloys. The most promising alloy is the TiVZrNb composition which, despite a fading of the capacity for the first cycles, shows a stable reversible capacity around 2 wt% for further cycling.

In the light of scarce literature on the subject, hydrogen adsorption in MPEAs/HEAs is an original research topic that might open new routes for the design of promising materials for hydrogen storage.

5:50 AM S.EN11.04.07

Colloidal Covalent Organic Frameworks for Hydrogen Storage and Delivery

Wade Braunecker¹,², Rachel E. Mow¹,² and Thomas Gennett¹,²; ¹National Renewable Energy Laboratory, United States; ²Colorado School of Mines, United States

Several approaches for designing and synthesizing colloidal covalent organic frameworks (COFs) are discussed, along with their unique application as hydrogen storage and delivery media. Using novel catalysts and conditions, the particle size of 3D COFs can be tuned between 50 and 600 nm with surface areas > 500 m²/g. Several functionalization strategies are discussed that help promote long-term colloid stability. When purified and resuspended in a bulky ionic liquid that is size excluded from entering the COF pore, the material behaves as a ‘porous liquid’, dramatically improving gas uptake in the liquid. Using temperature programmed desorption, we investigate how the frozen liquid matrix can be used to trap gas in the COF pores and effectively tune gas desorption temperatures. Finally, a technique for growing a solid-state COF monolith from densely packed COF colloids is presented, along with its characterization.

6:00 AM S.EN11.04.09

Enhanced Water Oxidation Performance by Prompting Higher Active Sites Using Transition-Metal (Co, Ni, and Cu) Oxides and CeO2 Heterointerfaces

Zahra Albu, Fahad Alzaid, Salma Alqahtani, Nawal Al Abass, Feriah Alenazey and Bandar Alotaibi; King Abdulaziz City for Science and Technology, Saudi Arabia

Since the depletion of fossil fuel is inevitable, exploring an alternative green energy carrier is of an urgent demand. Hydrogen fuel produced from renewable resources such as photovoltaic cells coupled with electrolyzers for water splitting can offer a very attractive route to address the aforementioned issue. The major bottleneck for deploying such technology is to find a practical electrocatalyst that can efficiently oxidize water. Many research efforts have been made towards finding new electrocatalytic materials to enhance the oxygen evolution reaction (OER). However, precious metals, such as Ru and Ir, containing oxides are still the best-known electrocatalysts for OER. This entails finding a new technique to improve the electrocatalytic activity of cost-effective metal oxides. In this study, we attempt a different approach to promote more active sites for OER using transition metal oxides (i.e., CoO₂, NiO, and CuO) and tailoring their heterointerfaces with CeO₂. The metal-oxide/metal-oxide (MO/MO) heterointerfaced nanoparticles were prepared by co-synthesizing the two MOs using wet chemistry. X-ray diffraction spectra and scanning tunneling microscope images confirm the formation of heterointerfaces between CeO₂ and the other MOs under study. That is, low magnification TEM images show that the synthesized particles compose of nano-sized crystallites of CoO₂ embedded on CeO₂ matrix. Electrochemical performance CeO₂/MOs are significantly improved compared to pure CeO₂ or any other MOs alone. Among all the CeO₂/MO structures, CeO₂/CoO₂ shows the highest cathodic shift (~ 0.65 V) and also it shows the lowest Tafel slope (~ 59 mV/dec). Mott-Schottky analysis illustrates that the presence of MOs interface with CeO₂ has formed an n-p junction where CeO₂ has an n-type characteristic while the other MOs have a p-type characteristic. This property can be very beneficial for the separation of optically excited electron-hole pairs due to the internally induced electric field. Therefore, exploring the potential use of our MO/MO structures as photoelectrodes was conducted using chronoamperometry under a chopped light source at 1.5 V vs. RHE. These results showed that CeO₂/CoO₂ electrode has the highest photo-response as compared to the other CeO₂/MOs or any single MO under this study. Additional investigations using density functional theory (DFT) of pure CeO₂, pure CoO₂, and heterointerfaced CeO₂/CoO₂ were performed. It was confirmed using DFT calculations that CeO₂/CoO₂ heterointerface has the lowest Gibbs free energy and lowest adsorption energy for OH⁻ intermediate compared...
Borohydride compounds have been to have great potential for as hydrogen storage materials. Solid state density functional theory calculations were performed to identify key intermediates and gain insight into the reaction pathways involved in the release and uptake of hydrogen from the thermal decomposition of Mg(BH₄)₂. Even tough improved theoretical methods for calculating thermodynamic properties of complex BₓHᵧ borohydrides have been developed, we find that there are still limitations to understanding mechanistic details of these complex reactions, and approaches that focus on NMR and other spectroscopic characterisations are necesary to complement the thermodynamic data and provide mehcanistic insight into these pathways. We will report both on molecular and solid state DFT calculations, and the gains from empolyong both approaches in these studies.

Developing viable solutions for the efficient production and storage of hydrogen requires understanding chemical process occurring at solid-gas, solid-liquid, and solid-solid interfaces in advanced materials. Probing behavior of these interfaces under operating conditions presents significant challenges; however, predictive modeling offers an opportunity for providing key insights into interface chemistry, particularly when operating in tandem with high-fidelity experimental characterization techniques. Within the DOE Hydrogen Materials—Advanced Research Consortium (HyMARC) and the HydroGEN Advanced Water Splitting Materials Consortium, we are using multiscale models to understand properties of reactive interfaces for the production, storage, and delivery of hydrogen. I will provide an overview of our materials modeling strategy within these consortia, ranging from first-principles calculations of interface chemistry to continuum methods for microstructure-level properties. I will then review some of our recent activities for simulating thermodynamic and kinetic properties of hydrogen-related materials. Specific examples will be given of how these computational models have helped to elucidate mechanisms of interface chemical reactions, the formation of new phases, and the impact of solid-state interfaces on key reaction pathways. I will also show how simulations have been combined with experimental probes to improve models and obtain new understanding of materials interfaces under operating conditions. Finally, I will discuss how this understanding is being used to guide new strategies for improving materials functionality for storage, generation, and delivery of hydrogen. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Two-dimensional (2D) materials consisting of a single or a few layers of atoms have superior performance compared to conventional materials or their bulk counterparts in a variety of applications, because of their unique properties, including their flexibility, high specific surface area, and quasi-2D electron confinement. Recently, we have revealed that the hydrogen boride (HB or borophane) sheets with an empirical formula of H₁B₁ can be formed by exfoliation and complete ion-exchange between protons and magnesium cations in magnesium diboride (MgB₂) with an average yield of 42.3% at room temperature [1], as a new member of 2D sheets and boron-based nanomaterials [2]. The sheets feature an sp²-bonded boron planar structure without any long range order. A hexagonal boron network with bridge hydrogens is suggested as the possible local structure, where the absence of long range order was ascribed to the presence of three different anisotropic domains originating from the 2-fold symmetry of the hydrogen positions against the 6-fold symmetry of the boron networks. Our recent analysis with soft x-ray absorption and emission spectroscopy at the B K-shell also supports this view and show the semimetallicity of HB sheets [3]. We have then found several intriguing properties of HB sheets for the applications of hydrogen (H₂) release (as much as 8 wt%) by UV irradiation at room temperature under mild ambient conditions [4], and the solid-acid catalyst [5] that convert C₂H₅OH to C₂H₄ and water. In the presentation, synthesis, characterization, and application of HB sheets will be introduced.

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Iimura, Dr. A. Hirata, Dr. N. Umezawa, Prof. S. Okada, Prof. E. Nishibori, Mr. A. Fujino, Mr. R. Ishibiki, Mr. T. Goto, Dr. S. Ito, Dr. Tateishi, Prof. Niibe, Prof. J. N. Kondo, Dr. T. Fujitani, Prof. I. Matsuda, Prof. J. Nakamura, and Prof. H. Hosono.


6:45 AM S.EN11.04.14
Effect on Melting Temperature and Cyclability of Magnesium Borohydride and Non-Metallic Borohydride Additive Systems Robert T. Bell¹, Nicholas A. Strange¹, Noemi Leick¹, Michael F. Toney², Tom Autrey³ and Thomas Gennett¹,²; ¹National Renewable Energy Laboratory, United States; ²SLAC National Accelerator Laboratory, United States; ³Pacific Northwest National Laboratory, United States; ⁴Colorado School of Mines, United States

Despite the high theoretical ~15wt% hydrogen content of magnesium borohydride, reusable dehydrogenation/hydrogenation cycling of pure Mg(BH₄)₂ requires economically infeasible high temperatures and pressures in excess of 300°C and 350 bar. However, many properties of Mg(BH₄)₂, such as the melting point, are readily altered through the use of additive compounds, including metal borohydrides, metal hydrides, and organics (ethers/glymes). In the case of organic additives, both the melting point and the hydrogen evolution temperature have been shown to decrease. The zeroth order description of this behavior is that organic molecules (e.g. THF) act as ligands, attach to Mg and effectively change the cation size in the Mg(BH₄)₂ salt which disrupts the solid structure. In this work we investigated a previously unreported family of non-metallic borohydrides as Mg(BH₄)₂ additives. Of specific interest were tetramethylammonium and tetra-n-butylammonium borohydrides. These non-metallic borohydrides have low melting points (<300°C), and much larger cations than Mg²⁺, similar to the zeroth order picture of Mg²⁺:THF complexes. In-situ diffraction, temperature programmed desorption, mass loss, and heat flow were used to establish a full picture of the behavior of these additive systems. With regards to phase mapping, we will report the solid solubility of the additives in Mg(BH₄)₂, the presence of line compounds predicted in literature, and the initially nucleated phases during quench. We also report the phase behavior of quenched dehydrogenated samples as well as the reversibility of re-hydrogenated material. This work demonstrates a novel additive family with high cyclability and low melting points for lowering reaction and phase change temperatures of Mg(BH₄)₂.

6:55 AM S.EN11.04.15
Towards Viable Solid-State Hydrogen Storage via Bypassing Unwanted Intermediates in Complex Metal Hydrides ShinYoung Kang, Tae Wook Heo, Keith R. Ray and Brandon Wood; Lawrence Livermore National Laboratory, United States

Complex metal hydrides have attracted great attention in the hydrogen storage community due to its high gravimetric capacity (14.9 and 8.8 wt% H₂ for Mg(BH₄)₂ and LiNH₂) and relatively small reaction enthalpy (<50-100 kJ/mol H₂). However, sluggish kinetics and the formation of stable intermediate compounds result in poor reversibility, high hydrogenation pressure and dehydrogenation temperature, hampering its application for onboard hydrogen storage. In this presentation, we propose a new concept to destabilized and bypass the formation of unwanted intermediates. In Mg(BH₄)₂ system, using first-principles calculations we explored the interplay between intermediate morphology and reaction pathways. Our results verify that the effective reaction energy landscape strongly depends on the morphological features and associated chemical environment, offering a successfully explanation of the formation of intermediates, especially Mg(B₃H₈)₂, which was observed in nuclear magnetic resonance (NMR) measurements, but predicted too unstable to form in conventional bulk simulations. In addition, our joint experimental-theoretical work in the LiNH₂ system revealed that the high interface energy suppressed the formation of Li₃NH intermediate in nanoscale. Our understanding introduces the possibility of tuning solid-state hydrogen-storage materials by tailoring morphology and internal microstructure, representing a new paradigm for engineering materials that could meet established performance targets.
Hydrogen (H2) is one of the mostly used gases in industry. The term hydrogen economy dates back to the early 1970s in the context of energy storage and electrical energy 1. Since, photoelectrochemical cells (PEC) were studied in recurring episodes for solar H2 production 2. MRS Meetings are having PEC Symposia since 2009 3. Since 2015, H2 mobility with commercial available fuel cell cars has become a reality 4, which requires a wide network of H2 fuel infrastructure 5. Most H2 for industry use today is of fossil origin, but H2 can be produced sustainable by electrolysis. The Swedish consortium for Artificial Photosynthesis is working since 1994 6. In Switzerland, PEChouse started in 2007 as an umbrella activity for the development of PEC technology for solar H2. The Joint Center for Artificial Photosynthesis (JCAP) in California is a large scale research program with a substantial hydrogen economy component 7. More clusters, centers and consortia are spreading 8. Since about 7 years, there is in Europe a large consortium 9 preparing for a large scale R&D initiative, aiming at renewable, artificial fuels and chemicals, in which hydrogen production plays a central role (SUNRISE) 10.

SUNRISE aims at meeting the goals of the Paris Agreement by decarbonization of the atmosphere. By providing large scale production of green H2, and converting the CO2 with H2 to solar fuels and base chemicals, SUNRISE wants to reshape the European energy landscape towards a circular and decentralized energy system. Production, storage and conversion of hydrogen are thus key technologies, which need to be further developed and integrated in existing infrastructure and made compatible with the built environment and the natural landscape.

The SUNRISE Consortium encompasses a diverse assembly of disciplines including economy, Life Cycle Assessment, social sciences, engineering, and the basic sciences in physics, chemistry and biology. By a concerted effort, SUNRISE aims to bring disruptive technology from a low readiness level to commercial maturity within a 10-year period.


As more nations make long-term commitments to clean infrastructure, it is critical that we better understand technologies that act at the interface of traditionally decoupled systems. Hydrogen (H2) will likely lie at the interface of energy storage, transportation, and industry. Here, we use ex-ante techno-economic analysis to characterize pathways for H2 delivery. We evaluate the impact of different process system parameters on the levelized H2 delivery cost ($/kg H2), and identify barriers and opportunities for achieving industrial competitiveness. Three carrier market applications are studied: transmission, distribution, and storage.
which we define as long-distance delivery from a large H2 source to an end use; distribution, which we define as short-distance delivery from a city-gate to fueling stations within the city; and transmission-distribution, which we define as long distance delivery from a large H2 source all the way to fueling stations. For each of these market applications, we evaluate the energy intensity and other key system level performance metrics for high pressure (350 and 500 bar) truck transportation, cryogenic liquid H2 truck transportation, and carrier-based truck transportation. Ancillary equipment and operation conditions, including systems at the H2 source and refueling station which are unique to adsorption systems are included in the analysis.

For a base transmission application, where 50 Mg H2/day is delivered 100 km from a gas terminal to an end point application, the delivery cost is approximately $1.6/kg H2 and $1.8/kg H2 for 500 bar and 350 bar trucks, respectively. Liquid H2 transport is less competitive at this short distance, and costs $3.1/kg H2. A truck packed with metal organic framework (MOF) Ni2(m-dobdc) and modeled at 100 bar and 200K has a delivery cost of $7.7/kg H2. Transmission costs for the MOF-H2 system can reach as low as $1.8/kg H2 (on par with 350 bar trucks) in a scenario where driverless trucks are employed, a highly durable material is developed (15,000 cycles), material costs are $10/kg MOF, and where bed porosity and pellet porosity are substantially lower (or rather increasing H2 uptake without increasing upstream cooling requirements).

For the distribution application, the delivery cost is dominated by the CAPEX and OPEX of the refueling stations. For a base scenario where 50 Mg H2/day is delivered 1 km from a city-gate gas terminal to distributed fueling stations, the delivery cost is between $3.4/kg H2 and $4.6/kg H2 for 500 bar and 350 bar trucks, respectively, and $5.3/kg H2 for liquid H2 transport. Liquid trucks for distribution perform better in larger markets (40% lower costs for a 120 Mg/day market). The MOF-H2 systems studied performs poorly in this market application (above $20/kg H2) as 10x more fueling stations and trucks are required to meet the same daily H2 demand as compared to the liquid or high pressure systems.

These results demonstrate capabilities of the hydrogen delivery models developed at the Lawrence Berkeley National Laboratory for the Department of Energy HyMARC program. Any path to substantial greenhouse gas emissions (GHG) reduction will include market transformations in the transportation sector, as it remains the single largest primary source of GHGs in the United States and the third largest primary source globally. Advances in carrier materials such as liquid organic hydrogen carriers (LOHC) and MOFs, which exhibit a wide range of tunability for hydrogen storage, could radically change the way hydrogen is stored and transported globally to meet fuel demand in zero direct emission vehicles. In this research work, we present a framework for characterizing and benchmarking the performance of emerging carrier systems.

5:15 AM S.EN11.06.07
Formates and Formic Acid as Hydrogen Carriers Mark Bowden, Kat Grübel, Jotheswari Kothandaraman, Kriston P. Brooks and Tom Autrey; Pacific Northwest National Lab, United States

Formic acid (FA) is a potential material for transporting hydrogen with a higher volumetric density (53 g H2/L) than compressed hydrogen gas (ca. 40 g H2/L at 700 bar). Hydrogen can be released from FA in a catalytic process which is exergonic (ΔG = -33 kJ/mol) and can therefore be used to generate hydrogen pressure without a mechanical compressor. An equimolar quantity of carbon dioxide is also generated which needs to be separated from the hydrogen. Hydrogen can also be generated from formate salts (FS) in a reaction with water with close to zero free energy change. Gaseous separation is not required in this case since the product is a bicarbonate salt. In aqueous solution, faster kinetics are found for a mixture of FA and FS compared to either end member. We have studied reaction rates, the degree of conversion, and product distribution for FA, FS and their mixtures as a function of composition, pH, catalyst, and temperature. The results will provide valuable inputs technoeconomic modelling to assess the suitability of these compounds as hydrogen carriers.

5:25 AM S.EN11.06.08
Density Functional Theory Investigation of Ethanol Adsorption on Ag(111) Surface Defect Sites Dariia Yehorova, Daniel Schlosser, Ashleigh Baber and Kendra Letchworth-Weaver; James Madison University, United States

In spite of the rapid development of hydrogen fuel cell (HFC) technologies, the unstable nature of hydrogen fuel presents complications for the versatile application of this energy production method. Alternatively, direct ethanol fuel cells (DEFC) are a competitive method of clean energy production due to their non-toxic, abundant, and high energy density fuel. A common barrier for modern implementations of these technologies is their dependence on high-cost precious metal catalysts. Furthermore, the search for alternative catalyst materials is limited by a poor understanding of the relationship between reactivity and structural defects. The promising performance of silver as part of heterogeneous catalytic nanoparticles, where under-coordinated sites are prevalent, motivates on investigation of ethanol on Ag(111) defects. In this study we utilize temperature programmed desorption (TPD) experiments and plane-wave density-functional theory (DFT) to investigate
fundamental electronic properties and adsorption mechanisms of ethanol on realistic metal surfaces in search for alternative lower cost catalytic materials. TPD experiments determine an analyte adsorption energy by increasing the temperature of the substrate in a high vacuum environment, showing higher adsorption energy of ethanol to defect sites on Ag(111) compared to smooth surfaces. In order to understand the atomic-scale origin of the increased reactivity of under-coordinated surface atoms we used the JDFTx software to calculate theoretical ethanol adsorption. Adsorption on Ag(111) terrace sites as well as on structural defects such as kinks, vacancies, and step edges was modeled using theory with and without van der Waals interactions to investigate the bonding character at each site. The trends in theoretical adsorption energy, geometry of the adsorbate, and bonding character at different defect sites complements and deepens our understanding of the experimental TPD spectra. Therefore, fundamental insights obtained from this study provide a pathway for development of commercially viable, effective catalysts for ethanol oxidation reactions.

5:35 AM S.EN11.06.09
Electron Microscopy of Zeolite Structural Evolution During and After Growth Andrew C. Meng1, Ke-Bin Low2, Junmei Wei2, Nicholas Favate3, Thomas Gegan2, Ivan Petrovic2 and Eric A. Stach1; 1University of Pennsylvania, United States; 2BASF Corporation, United States

The fluid catalytic cracking process with zeolite catalysts is used to produce a large fraction of the world’s gasoline. Although the process has been known for many years, the field remains very active as interest in the mechanism and applications involving new chemical feedstocks such as shale gas pose new challenges. In-situ electron microscopy offers new insights into the structural evolution of zeolites during chemical processes such as growth or steaming, which is used to convert the material to the catalytically active phase. We report the synthesis and characterization of a model FCC material during the different stages of growth using ex-situ scanning and transmission electron microscopy. Based on different growth conditions, zeolite-Y, which is the precursor to the active catalytic phase, defective zeolite phases, which are catalytically inactive, or other phases can be favored. Finally, we report the behavior of the different zeolites under intermediate temperature steaming in situ in an environmental scanning electron microscope. The results are promising towards method development for in-situ observation of zeolite structure evolution in both scanning and transmission electron microscopy for fundamental understanding of how nucleation and growth occur in an isolated, model system and how the structure evolves under high temperatures and pressures.
LiMnO$_2$ (Mn$^{3+}$) or even into MnO (Mn$^{2+}$).

An interesting ~2% weight loss was observed at the beginning of all the isotherms (before weight gain started). In order to elucidate the process associated to this, several thermogravimetric and catalytic experiments were carried out. Their solid and gas products were identified by XRD and mass spectrometry, respectively. The catalytic experiments showed CO$_2$ production at the same temperature range where Li$_2$MnO$_3$ weight loss take place. Moreover, after this ~2% weight loss occurs and before weight gain process would perform, the material composition was analyzed by XRD and ATR-FTIR, where Li$_2$MnO$_3$ was the only crystalline phase identified in addition to carbonates.

Based on these results, it may be pointed out that an oxidation step is performed at the material surface to oxidize CO into CO$_2$, where some part of it is chemisorbed as Li$_2$CO$_3$, while the rest is released from the material’s surface. In addition, lithium diffusion from bulk to surface in Li$_2$MnO$_3$ may be triggered by oxygen vacancies formation (at surface) due to CO oxidation. This could explain wherefore chemisorption process was not performed in CO$_2$ atmosphere or in oxygen presence. To further analyze Li$_2$MnO$_3$, dynamical and isothermal experiments were performed varying the CO-CO$_2$ partial pressures. These results demonstrated that if CO$_2$ is involved into the gas flow composition, the CO oxidation-capture process is displaced to higher temperatures and the total weight gain decreases as consequence of less superficial oxygen vacancies formation. Moreover, kinetic constants were calculated using the Jander-Zhang diffusion model, which can be related to $\Delta$H$^\circ$ by the Eyring equation. Results showed that, in addition of CO$_2$, kinetics diffusion become slower than those obtained into a CO atmosphere, although the $\Delta$H$^\circ$ values decreased.

Finally, Li$_2$MnO$_3$ was dynamically tested on H$_2$ and H$_2$-CO atmospheres (Ar balanced). These experiments showed a preference oxidation of CO over H$_2$. Nevertheless, ~10% of hydrogen was oxidized into water while CO was chemisorbed.

**Evaluation of Boron Doped Reduced Graphene Oxide as IrO$_2$ Support for Efficient Oxygen Evolution Reaction**

Prerna Joshi$^1$, Hsin-Hui Huang$^2$, Masanori Hara$^1$ and Masamichi Yoshimura$^1$; $^1$Toyota Technological Institute, Japan; $^2$Japan Fine Ceramics Center, Japan

With depleting fossil fuel reserves and increasing environmental problems, novel strategies have been developed based on renewable energies. A major source of renewable energy is water, which can produce hydrogen energy in large amounts. Electrochemical water splitting is an excellent way to produce hydrogen as an energy source. For generation of hydrogen at a specific rate, under ideal conditions, 1.23 V must be supplied to the water electrolyzers to allow hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in a feasible manner. In practice, OER is a complex reaction with slow kinetics and low overpotential, hence, precious metal catalysts such as iridium and ruthenium oxides (IrO$_2$, RuO$_2$) are used to reduce the overpotential for OER. However, their high cost and low natural abundance limit their extensive commercialization. One of the plausible approach can be the reduction of metal loading with the use of conductive support. For metal catalysts, the reduction in size of the catalysts (formation of nanoparticles (nps)) can help in increasing active surface area. Further, for conducting support, doped graphene can be used as a support because it can tune the electronic structure of catalysts to improve specific activity. In the current research, we have studied the electrochemical activity of IrO$_2$ nps catalyst supported on heteroatom-doped reduced graphene oxide (rGO) as the carbon support. Along with alteration of the electronic structure of the IrO$_2$ nps, heteroatom-doping of graphene also promotes ion diffusion at the electrode-electrolyte interface, improving the overall performance of the catalyst.

Graphene oxide (GO) was prepared from synthetic graphite (Sigma Aldrich) by modified Hummers’ method. For boron doping, boric anhydride (B$_2$O$_3$, BA) was used as the precursor. Briefly, BA and GO were mixed together and ultrasonicated in water for 1 hour. The mixture was freeze dried and the obtained powder was pyrolysed at 1000 °C for 60 min in N$_2$ atmosphere. The pyrolysed sample was washed with boiling water and ethanol to yield boron-doped rGO (B-rGO). As the second step, IrO$_2$ nps were decorated onto B-rGO by hydrothermal synthesis at 150 °C for 4 h using H$_2$IrCl$_6$ as the Ir precursor. The synthesized materials were characterized for its chemical composition, morphology and electrocatalytic activity using various analytical techniques such as X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), cyclic voltammetry (CV) and linear sweep voltammetry (LSV).

XPS analysis of the synthesized catalyst, IrO$_2$-B-rGO revealed the presence of all constituent elements at their respective binding energies. The XPS spectra were deconvoluted to obtain the types of constituent C and B. Ir 4f peaks for IrO$_2$-B-rGO were obtained at lower binding energies than the unsupported IrO$_2$ powder confirming the change in electronic states of Ir due to boron doping. Further, EDX analysis indicated B to be present in ~2.0 wt% and Ir in 3.3, 7.1 and 19.6 wt%. TEM results exhibited the uniform dispersion of IrO$_2$ over the wrinkled B-rGO sheets with an average particle diameter of 1.5 nm. Electrochemical analysis in 0.5 M H$_2$SO$_4$ with Ir loading of ~140 µg cm$^{-2}$ on glassy carbon (GC) electrode showed that the onset potential was 1.41 V vs RHE for IrO$_2$-B-rGO which was ~90 mV lower than that of IrO$_2$ decorated on undoped rGO.

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(IrO$_2$-rGO). Despite the low Ir content, higher current density was obtained for B-doped catalyst as compared to the IrO$_2$-rGO. Increase in current density for B-doped catalyst is attributed to charge redistribution in graphene lattice which alters the electronic states for Ir and provides additional active centres for catalysis.


S.EN11.07.08
Investigating Potential Kinetic Limitations to MgB$_2$ Hydrogenation
Lennie Klebanoff$^1$, Yi-Sheng Liu$^2$, Don Cowgill$^1$, Alexander Baker$^3$, Vitalie Stavila$^1$, Keith R. Ray$^3$ and Brandon Wood$^3$; $^1$Sandia National Laboratories, United States; $^2$Lawrence Berkeley National Laboratory, United States; $^3$Lawrence Livermore National Laboratory, United States

We report an investigation of potential kinetic limitations to the rate of hydrogenation of magnesium diboride. The metals Pd, Fe and Ti, known to be proficient at H-H bond dissociation, were introduced into MgB$_2$ by ball milling. Pd and Fe are directly introduced as crystalline metals, whereas Ti metal was introduced via the reaction between TiF$_3$ and MgB$_2$ to form Ti metal and MgF$_2$. XRD, FTIR, XAS and TEM data show that the additives persist as metals in the MgB$_2$ solid, free from significant oxidation of the additive itself (i.e. TiO$_2$, Fe$_2$O$_3$, PdO) as well oxidation of the MgB$_2$ material (i.e. no MgO, B$_2$O$_3$). The Pd in the MgB$_2$ material consists of two morphological forms: Pd particles of a size ~ 2 – 25 nm diameter with a d-spacing essentially the same as bulk Pd, as well as a highly dispersed Pd component within the MgB$_2$ matrix. The Fe additive decorates the MgB$_2$ particles as small particles with sizes ranging from ~ 11 – 34 nm diameter with comparatively little atomic-scale dispersal of the Fe additive. TiF$_3$ reacts with MgB$_2$ to form Ti metal and MgF$_2$, with the Ti and the F smeared out within the MgB$_2$ base solid. Sieverts-acquired MgB$_2$ hydrogenation rates for the Pd, Fe and Ti modified MgB$_2$ are higher than for commercial MgB$_2$, but the improvement is very modest, about a factor of two at most. H-D exchange studies were conducted to confirm H-H bond breaking in these materials. The data shows that H-H bond breaking is slowest for the bulk MgB$_2$ material, but much faster for the Fe, Pd and Ti modified samples for which H-H bond breaking reaches equilibrium in about 20 minutes. This work shows that H-H bond dissociation is not limiting the rate of hydrogenation of MgB$_2$ because extensive H-H bond breaking is already occurring after only 20 minutes whereas the initial hydrogenation to ~0.8 weight percent hydrogen takes about 100 hours. The results also show that surface diffusion cannot be limiting the MgB$_2$ hydrogenation rate because surface diffusion, a requirement for HD generation, is occurring very rapidly. We speculate that it is the intrinsic stability of the B-B extended hexagonal ring structure in MgB$_2$ that hinders the hydrogenation of this material. This supposition was supported by B K-edge TFY XAS measurements of the materials, which showed spectroscopically that the B-B ring was intact in these systems throughout most of the material.

S.EN11.07.09
Graphene- and CNT- Hybrids with Metallic and Metalorganic Framework Nanostructures as Reversible and Sustainable H$_2$ Storage Media
Suresh Kuppireddy, Anish Varghese and Georgios Karanikolos; Khalifa University, United Arab Emirates

H$_2$ storage constitutes a barrier in decarbonizing the energy economy and expanding H$_2$ utilization into large scale. Design of novel nanostructured materials is currently a high research priority toward a permanent solution to this challenging problem, and development of safe, dense, solid state media to substitute cryogenic storage. In this work, we present in-situ grown hybrid nanostructures based on graphene and CNTs supporting metalorganic framework (MOF) and metallic (e.g. Mg) clusters and nanocrystallites exhibiting controlled microstructure, porosity, and interface characteristics. The resulting nanohybrids exhibit increased storage capacity, while the stability of the active sites is preserved through the presence and controlled coating by the graphitic layers.

S.EN11.07.11
Metal-Organic Framework (MOF) Derived Cobalt Oxide and Cobalt Sulfide for Efficient Electrocatalysts in Water Spitting
Jonghyun Choi, Tenzin Insgel, Pawan Kahol and Ram K. Gupta; Pittsburg State University, United States

Increasing global population and advancement in energy-dependent devices have caused increased use of energy in consumer and industrial appliances, electronic devices, and automobiles creating an urgent need for clean and renewable energy sources. Electrochemical water-splitting is one of the greenest ways to generate clean and high-performance fuel. Water-splitting generates hydrogen and oxygen gases. The generated hydrogen gas can be used as fuel whereas evolved oxygen gas can be used in metal-air batteries or released in the atmosphere as a clean gas. The electrocatalytic properties of most of the materials for water splitting depend upon several factors such as morphology, phase purity, defects, etc. We have synthesized
metal-organic framework (MOF) derived cobalt oxide and cobalt sulfide using a facile method for their application in water-splitting as electrocatalysts. 2-methyl imidazole and cobalt nitrate were used for the synthesis of MOF-derived cobalt oxide and MOF-derived cobalt sulfide electrodes. The electrode with MOF-derived cobalt oxide was synthesized via a solvothermal process, while the electrode with MOF-derived cobalt sulfide was prepared through sulfurization using a hydrothermal process. The structural and electrochemical properties of these films were studied in detail. The electrocatalytic activities of the MOF-derived cobalt oxide and sulfide were studied in 1M KOH solution for oxygen evolution and hydrogen evolution reactions. MOF-derived cobalt oxide showed overpotential of 375 mV and 224 mV to achieve a current density of 10 mA/cm² for oxygen and hydrogen evolution processes, respectively. A significant improvement in electrocatalytic properties was observed with the electrode after sulfurization producing MOF-derived cobalt sulfide. MOF-derived cobalt sulfide displayed overpotential of 278 mV and 220 mV at 10 mA/cm² for oxygen and hydrogen evolution processes, respectively. Our results suggest that a facile method of sulfurization of the MOF-derived compound is a way to achieve high electrocatalytic activities for oxygen and hydrogen evolution reactions in the water-splitting process.

S.EN11.07.12
First Principles Investigation of the Influence of Magnetic Moment on Single Atom Earth-Abundant Transition Metal Catalysts for Integrated 3D Graphene Structures Chloe Groome and Regina Ragan; University of California, Irvine, United States

Single atom catalysis (SAC) represents a promising design for the next generation of robust catalysts. These systems, which are commonly single metal atoms stabilized on carbonaceous materials, maximize catalytic performance while simultaneously minimizing the use of expensive and scarce platinum-group metals (PGM). While it is accepted that the molecular environment of a SAC is of crucial consequence to the chemical activity, the exact catalytic sites and chemical pathways responsible have been a matter of some controversy. For industrially practical non-PGM SAC, optimizing the defect environment stabilizing the single metal atom is necessary for enhanced performance. We will present work using a first principles approach for materials discovery to investigate three less studied earth abundant transition metals (V, Mo, Ta) stabilized on single vacancy and pyridinic N-doped defect moieties on graphene substrates to understand the role of electronic transfer, spin state and steric effects on SAC. Our results of all investigated metals demonstrate single atom stability on graphene substrates with both defect moieties. By modeling carbon monoxide oxidation, a common benchmark reaction, facilitated by these defect stabilized SAC with climbing image-nudged elastic band (CI-NEB) calculations, we find that all activation energies for transition metals stabilized on the pyridinic N-doped graphene surface defect are ~0.8 eV or lower. These low activation energy barriers suggest that the CO oxidation reaction would proceed at room temperature with pyridinic N-dopants present in the defect environment. The CI-NEB calculations further illustrate that SAC of Ta and V on pyridinic N doped graphene significantly decrease the activation energy of CO oxidation by 27% and 44%, respectively. Bader charge analysis reveals that the electronic charge transfer is surprisingly similar across the two defect moieties investigated for all four earth-abundant transition metals. However, the pyridinic N-dopant introduces an additional magnetic moment of 0.53 µB on average. Plotting the density of states of CI-NEB transition states shows spin destabilization of O₂ peaks near the Fermi level, suggesting that these imparted magnetic moments could be destabilizing the O₂ bond and hence lowering activation energies for CO oxidation in some cases. We will present results suggesting that magnetic moment could play a significant role in enhancing catalytic performance of SAC on nitrogen doped graphene substrates, as well as more traditionally understood mechanisms such as charge transfer and steric effects. Computational design of materials is used to define processing conditions for three-dimensional porous graphene structures. Fabrication and characterization of macroscopic graphene structures with high surface area and architectures to facilitate mass transport will also be presented.

S.EN11.07.15
3D Interface-Engineered Transition Metal Oxide/Carbon Hybrid Structures for Efficient Bifunctional Oxygen Electrocatalysis in Alkaline and Acidic Environments Simranjit K. Grewal1,2,3, Angela Andrade-Macedo1, Ziqi Liu1 and Dr. Min-Hwan Lee1,2,3, 1University of California, Merced, United States; 2NASA, United States; 3Lawrence Berkeley National Laboratory, United States

Use of regenerative fuel cells (RFC) requires bifunctionality in oxygen electrocatalysis of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) to decrease weight and cost for efficient energy conversion. Many RFC based technologies have used noble metals such as Pt and its alloys (Pt/Ir or Pt/Ru) due to their efficient catalytic activity, selectivity and stability in harsh environments. However, their susceptibility to fast degradation during operation, as a result of catalyst agglomeration and poisoning, has driven research to find alternatives [1]. Non-precious transition metal oxides (TMO) including Fe₂O₄, MnO₂, and Co₃O₄ have attracted significant attention as a potential candidates [2]. We utilized a composite structure where TiO₂, ZrO₂, or CeO₂ are deposited onto conductive 3D carbon structure such as graphene oxide (GO), metal-organic frameworks (MOFs) or a combination of activated carbon (AC) with GO/MOFs. The
use of carbon structures is to leverage their high surface area and excellent electronic conductivity. However, GO contains oxygen-based functional groups on the edges and wrinkles that provides an anchor for nanoparticle binding while its basal plane stays relatively non-reactive. To incur a catalytically active sites between the metal oxides and carbon, we functionalize the basal surface of carbon using phosphoric, hydrobromic and/or oxalic acids. After such treatment, various types of carbon structures were hydrothermally reacted with metal precursors (Ce(NO$_3$)$_3$ or ZrOCl$_2$) or nanoparticles (P25). For MOF structures, due their susceptibility towards degradation after the common step of pyrolysis, a thin film of metal oxides are used. However, to adhere the metal oxides properly onto the MOF, we leverage acid treatment similar to our treatment of GO.

The hydroxylated CeO$_2$/GO hybrids showed the best ORR and OER performance in both alkaline (0.1 M KOH) and acidic media (0.5 M H$_2$SO$_4$), in terms of onset/half-wave potential, electron transfer number, and current density (electrochemical performances) when comparing to the performance of Pt/C (for ORR) and IrO$_2$ (for OER). From a series of material/experimental analyses, a strong tethering of metal oxides upon the basal plane of GO prohibits restacking, and that the particle-carbon interfaces (as oppose to the particle or GO itself) dictates the performance and reaction route, as indicated in density functional theory calculations. In addition, a hybrid catalyst where TiO$_2$ nanodots are uniformly anchored on phosphorylated MOF by atomic layer deposition (ALD) showed an even better ORR and OER performance in 0.1 M KOH when compared the aforementioned CeO$_2$/GO hybrid. Materials characterization emphasizes a strong adhesion of metal oxides upon MOF structures, thus providing ample surface interactions for favorable reaction route is important. In addition, an activation of catalytic sites can be realized by a proper engineering of interfaces in each hybrid systems. Finally, we present a facile route of improving operational durability of TMO/carbon hybrids both in alkaline and acidic media: interfacing with an activated carbon after a proper acid treatment.

This project was funded by NASA Advanced STEM Training and Research (ASTAR) Fellowship.

References:


S.EN11.07.17
**Alkylphosphine as a Ligand for Shape-Controlled Synthesis of Metal Nanostructures** Shutang Chen and Gugang Chen; Honda Research Institute USA Inc., United States

Metal nanoparticles with high index facets and controllable shape have demonstrated excellent catalytic performance because of their unique surface chemistry. Generally, the selection of proper ligand plays an important role for the shape-control of nanoparticles. Here, different kinds of alkylphosphines with high temperature solution reduction method are adopted to synthesize metal nanostructures. With increasing chain length of alkylphosphines, different morphologies of copper nanoparticles were synthesized in a hydrophobic system, such as nanocubes, tetrahedron nanoparticles, nanowires, and nanosheets. All these copper nanostructures demonstrated excellent catalytic performance and selectivity to carbon dioxides reduction reaction. Such simple strategy is also extended to the design of other metal nanoparticles for their potential applications in catalysis, sensor, and electronics.

S.EN11.07.18
**Studies in Pulsed Laser Deposition of FeWO$_4$ Thin Films** Chandler W. Cotton, Braden L. Spiller, Sumner B. Harris and Renato P. Camata; The University of Alabama at Birmingham, United States

Complex metal oxides such as metal tungstates, niobates, cuprates, and vanadates, have long been considered as promising absorber materials for photoelectrochemical (PEC) cells. In particular, the recent demonstration of self-passivated bismuth (Bi)-containing FeWO$_4$ thin films with suitable photovoltage for coupling to a photocathode, suggests significant potential for FeWO$_4$-based photoanodes. In this study, we explore the growth of FeWO$_4$ thin films with the laser plasma control afforded by pulsed laser deposition (PLD). In PLD, thin film growth is mediated by a laser-generated plasma that exhibits rich chemistry and spatiotemporal phenomena. The chemical diversity, variety of gas backgrounds, and shockwave characteristics of the laser plume are highly conducive to kinetic control of materials synthesis. The laser-induced plasma allows wide tunability of plasma parameters. This includes control of the strong gradients of density and temperature that cause deviations from local thermodynamic equilibrium. For all these reasons, synthesis of Bi-containing FeWO$_4$ by PLD
may allow tuning of conductivity, exploration of additional co-doping with other metals, and control of defect concentrations. Using planar and cylindrical Langmuir probes, we have measured the ion density, kinetic energy distribution, and electron temperature in Fe-, W-, and O-rich plumes produced by KrF excimer laser ablation of solid targets that are suitable for growth of FeWO4. These plasma measurements during PLD conditions show that the plasma density can be adjusted over several orders of magnitude in the 10^{18}-10^{20} m^{-3} range, consistent with a correspondingly broad range of deposition rates. Changes in target composition have significant impact in the kinetic energy distribution of ions in the plume. Oxygen-rich targets ablated with a typical 1.4 J/cm^{2} laser fluence and 3.0 mm^{2} spot area, lead to plasmas with wide ion kinetic energy distributions with high fractions of ions in the 80-90 eV range. Similar irradiation conditions for W-rich targets result in plumes dominated by kinetic energies below 5 eV. Thin films grown with changes in laser plasma conditions between these extremes show measurable variation in stoichiometry. We will discuss x-ray photoelectron results on these films that allow correlating changes in W oxidation state with plasma plume composition and kinetic energy. Thin film crystal quality, as measured by x-ray diffraction, will also be discussed in relationship to film stoichiometry and laser plasma characteristics during growth.

S.EN11.07.19
Luminescent Solar Concentrators Based on Self-Contained Silicon Quantum Dots Films for Photovoltaic Applications
Rosendo Lopez-Delgado1, Alejandra J. Cordova-Rubio2, Roberto C. Carrillo-Torres2 and Mario E. Alvarez-Ramos2; 1Cátedras Conacyt - Universidad de Sonora, Mexico; 2Universidad de Sonora, Mexico

The incorporation of energy harvesting systems into architectural elements of buildings is gaining attention as a new possible renewable energy technology for the production of electricity. Luminescent solar concentrators (LSC) represent a promising and cost-effective complement to existing semiconductor photovoltaic (PV) technologies that could be employed as semitransparent windows to contribute to the building’s energy consumption. Typically, an LSC consist of an optical waveguide that collect sunlight from a large-area window and concentrates the emission on the smaller-area edges. The emission is obtained from luminescent materials such as organic dyes, rare earth ions or semiconductor quantum dots in the LSC that absorbs the sunlight and, by a stokes shift, emit photons at wavelengths that are better suitable for absorption by the PV devices coupled at the edges of the LSC, reducing the costs of photovoltaic power generation.

Organic dyes have been the most commonly used luminophores for LSC applications mainly due to their high quantum yield and in some cases its low degradation rate, however, organic dyes no only tend to absorb and convert only a relatively small region of the solar spectrum, but also, they present a large spectral overlap between the absorption and emission regions, which increases the reabsorption losses and prevents the viability of fabrication of large-scale efficient devices. On the other hand, colloidal semiconductor nanoparticles or quantum dots (QDs) exhibit very attractive optical properties and have attracted a lot of attention as potential luminophores for LSC applications. Colloidal QDs are promising candidates since their properties mainly arises from the materials they are made, their size and their surface passivation. Also, QDs can be engineered to manipulate their energy bandgap and the stokes shift values to suppress effectively the reabsorption losses. Here, we report the fabrication of one-pot synthesized and self-contained photoluminescent films based on silicon quantum dots (SiQDs) and its employment on luminescent solar concentrators (SiQDLSC). Silicon quantum dots were synthesized from reduction of (3-aminopropyl) triethoxysilane (APTES) by sodium ascorbate. Besides the reduction of APTES into silicon quantum dots, a silicate matrix host is obtained, which is further employed as the support for the photoluminescent film in the fabrication of the LSC. The size of the synthetized SiQDs were measured by dynamic light scattering and electron microscopy techniques obtaining an average size of 3 nm. Both SiQDs and SiQDLSCs transmittance, absorbance and photoluminescent properties were characterized. The synthesized colloidal SiQDs exhibit an abrupt increase of optical absorption below 425nm extending to the ultraviolet region while emitting photons in a broad band extending from 450 to 600 nm with maximum intensity at 525 nm. SiQDLSC were fabricated in two sets of different dimensions: 1) 50x50x3mm and 2) 25x25x1mm. Set 1 shown a transmittance above 85% while set 2 exhibited above 90% transmittance over the visible region of the electromagnetic spectrum. Both sets shown the absorbance characteristics of the SiQDs decreasing the transmittance (increasing the absorbance) below 425 nm. Photoluminescent properties of the SiQDLSC were measured at the edges of the devices, obtaining broad bands of emission that were slightly blue shifted to around 500nm due to the expected oxidation of the SiQDs surfaces. However, the fabricated SiQDLSC preserve the desired stokes shift that is necessary to prevent reabsorption losses. These results demonstrate a feasible and very attractive method of fabrication of SiQD-based luminescent solar concentrators that presents good transmittance as well as the photoluminescent stokes shift effects desired for their incorporation as PV windows.

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SESSION S.EN12.11: Live Keynote: Materials for Safe and Sustainable Electrochemical Energy Storage  
Session Chairs: Zheng Chen and Hongmei Luo  
Sunday Afternoon, November 29, 2020  
S.EN12

7:15 PM *S.EN12.04.01  
Electrolyte Design for Micro-Sized Si Anodes  
Chunsheng Wang; University of Maryland, United States

Li-ion batteries are the critical enabling technology for the portable devices, electric vehicles (EV), and renewable energy. However, the safety and energy density of current Li-ion batteries still need to be improved to satisfy the requirements for these applications. We systematically investigated the electrochemical performance of the nonflemable fluorinated organic electrolytes and solid state electyrolytes for high energy Li and Li-ion batteries. The Li dendrite formation in liquid electrolyte and solid state Li metal batteries was proposed and validated. The critical issues of these safe electrolytes are also discussed.

7:45 PM *S.EN12.05.04  
The Silicon Electrolyte Interface Stabilization Project  
Anthony Burrell; National Renewable Energy Laboratory, United States

Silicon is a viable alternative to graphitic carbon as an electrode in lithium-ion cells and can theoretically store >3,500 mAh/g. However, lifetime problems have been observed that severely limit its use in practical systems. The major issues appear to involve the stability of the electrolyte and the uncertainty associated with the formation of a stable solid electrolyte interphase (SEI) at the electrode. Recently, calendar-life studies have indicated that the SEI may not be stable even under conditions where the cell is supposedly static. Clearly, a more foundational understanding of the nature of the silicon/electrolyte interface is required if we are to solve these complex stability issues. A multi-lab consortium has been formed to address a critical barrier in implementing a new class of materials used in lithium-ion batteries that will allow for smaller, cheaper, and better performing batteries for electric-drive vehicles. This consortium, named the Silicon Electrolyte Interface Stabilization (SEISta) project, was formed to focus on overcoming the barrier to using such anode materials. Five national laboratories are involved: the National Renewable Energy Laboratory (NREL), Argonne National Laboratory (ANL), Lawrence Berkeley National Laboratory (LBNL), Oak Ridge National Laboratory (ORNL), and Sandia National Laboratories (SNL). The SEISta project was specifically developed to tackle the foundational understanding of the formation and evolution of the solid-electrolyte interphase on silicon. This project will has a primary goal of understanding the reactivity of the silicon and lithiated silicon interface with the electrolyte in lithium-ion systems. The overall objective for
SEISta is to understand the nature and evolution of the SEI on silicon anodes. Several issues must be addressed to enable progress in this area. Materials Standardization is critical to this project and deployment of standardized samples and experimental procedures across the team is a foundation of the project. Full characterization of any new sample that is to be used for SEI studies to ensure reproducibility and full understanding of the material. The materials standardization and model compounds will enable the researchers to systematically investigate the formation of the solid-electrode interphase using a wide variety of the spectroscopy techniques—from different optical, microscopy, and electrochemistry—to determine how the SEI forms based on the nature of the silicon surface, and how it evolves over time. This presentation will detail recent advances that the SEISta team has made to the understanding of the SEI on silicon.

8:15 PM *S.EN12.02.09
Nanoscale Design for High Energy Batteries Yi Cui; Stanford University, United States

The demand from portable electronics and electric vehicles call for high energy batteries beyond the current lithium ion batteries. Here I will present our recent progress on materials and interfacial design to enable much high energy density batteries, which include 1) High capacity Si anodes with success in commercialization; 2) Li metal anodes: host and interface design to over the lithium metal dendrite formation and interfacial instability; 4) Sulfur as an earth abundant material for high capacity cathodes; 4) Our pioneering development of cryogenic electron microscopy for understanding the battery materials and solid-electrolyte interphase down to atomic scale resolution.

SESSION S.EN12.01: Materials for Safe and Sustainable Electrochemical Energy Storage
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN12

5:00 AM *S.EN12.01.01
Unbiased Photoelectrochemical Water Splitting Cell Exceeding >9% Solar-to-Hydrogen Conversion Efficiency with Surface Band-Modified Cu(In,Ga)(S,Se)2 Photocathode and Halide Perovskite Solar Cell Bonhyeong Koo and Byungha Shin; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Efforts to convert sustainable solar energy into a storable form of chemical fuels have generated much interest. Among various technologies, photoelectrochemical (PEC) water splitting, which is capable of producing hydrogen fuel in an environmentally friendly manner, is being intensively studied. Because PEC water splitting has an operating principle similar to that of photovoltaic devices, a good photovoltaic material must be a good candidate for a photoelectrode of PEC solar water splitting. In this talk, I will present the recent research efforts of our laboratory to produce highly efficient and stable photoelectrodes, Cu(In,Ga)Se2 (CIGS)-based heterojunction. First, I will discuss the application of functional overlayers acting as a protective layer and reduced graphene oxide as a catalyst binder to improve long-term stability of the photocathodes.[1], [2] Next, I will present the enhancement of PEC performance of CIGS photocathodes by introducing a greater degree of surface band bending with ZnS/CdS double buffer layers. Finally, we demonstrate a bias-free water splitting PEC cell consisting of the surface band-modified CIGS photocathode with the ZnS/CdS double buffer and a halide perovskite solar cell, and an IrOx anode, with a STH efficiency over 9 %.


5:15 AM S.EN12.01.03
Ionic Pumping and Salt-Rejection by Polyelectrolyte Hydrogel for Continuous Solar Desalination Jian Zeng and Renkun Chen; University of California, San Diego, United States
Efficient water pumping and selective salt rejection is highly desirable for solar or thermally driven seawater desalination, but its realization has been challenging with the typical capillary pumping mechanism. Here we proposed and demonstrated a new liquid supply mechanism, ionic pumping effect, realized using a polyelectrolyte hydrogel foam (PHF) containing poly(sodium acrylate) [P(SA)] embedded in a microporous carbon foam (CF). The PHF simultaneously possesses high osmotic pressure for efficient liquid transport and strong salt-rejection effect. The PHF was able to sustain high water flux of ~ 24 liter per m² per hour (LMH), comparable to the evaporative flux under 15 suns, and a salt rejection ratio over 80%. Compared to the porous carbon foam without the polyelectrolyte hydrogel, i.e., with only the capillary pumping effect, the PHF yielded a 42.4% higher evaporative flux, at ~ 1.6 LMH with DI-water and ~ 1.3 LMH with simulated seawater due to the more efficient ionic liquid pumping. More importantly, thanks to the strong salt-rejection effect, the PHF showed a continuous and stable solar-driven desalination flux of ~ 1.3 LMH under one-sun over 288 hours consecutively using real seawater without salt clogging in the pore and sediment on the surface, which was not achieved before. The successful demonstration of both efficient ionic pumping and strong salt rejection effects makes the PHF an attractive platform for sustainable solar-driven desalination.

Establishing Protocols for Diagnosing Defects in Photoelectrodes Using Structure-Property Analysis

Rodney Smith and Yutong Liu; University of Waterloo, Canada

An inability to routinely identify, quantify and control specific structural defects in photoelectrodes leads to inconsistencies in observed photoelectrocatalytic behavior that inhibit material development. Photophysical analysis of key electron transfer processes in hematite photoanodes, for example, have provided insight into fundamental behavior and properties but have not resolved the persistent variability photoelectrocatalytic performance values reported across the literature. We aim to address such issues by developing simple methodologies to routinely identify and quantify structural defects in photoelectrodes. We initiate this work with structure-property analyses on a series of hematite photoanodes prepared by annealing lepidocrocite films under varied conditions. Raman spectroscopy reveals the presence of a formally Raman inactive vibrational mode in Raman spectra for all hematite samples. The intensity of this feature is dependent on annealing conditions and protocols and is found to correlate with behavioral descriptors extracted from photoelectrochemical, Raman and UV-visible spectroscopic datasets. Specifically, the intensity of this Raman vibrational mode correlates to the measured photocurrent density, to the position of the semiconductor band edges, and to the location of intraband trap states. Observation of such a formally Raman inactive vibration signifies a lattice distortion, and the observed correlations reveal a systematic change in the magnitude of the distortion. Analysis of the full Raman spectrum, X-ray diffraction patterns, and the synthetic conditions lead us to conclude that the lattice distortion is caused by iron vacancies that are themselves induced by the trapping of protons within the crystal lattice. These results provide the foundation for a rapid diagnostic protocol to identify and quantify specific structural defects to guide the optimization of fabrication protocols for photoelectrodes.

Effects of N-Doped Graphene and Carbon Black as Conductive Additives on Sulfur Cathodes in Lithium-Sulfur Batteries

Xiaoxiao Han, Jiyu Cai, Xin Wang, Yongqiang Liu and Xiangbo Meng; University of Arkansas, United States

Lithium-sulfur (Li-S) batteries hold great potential given their theoretic energy density of 2600 Wh/kg, low cost, and S abundance. However, Li-S batteries are currently being retarded from commercialization due to several severe issues. On the S cathode side, S is highly insulating electrically and ionically. Thus, conductive materials are essential to maintain S cathodes accessible to electrons and ions. To date, many carbon materials such as carbon black, carbon nanotubes and graphene are widely used as conductive materials in various battery systems. Nevertheless, there lacks a comparative study on identifying their effects on the electrochemical properties of the S cathode. Knowing that optimizing the configuration and composition of the carbon conductive materials is the most inexpensive and simple way to improve the electrochemical performance of Li-S batteries, we recently conducted a fundamental study on the effects of a carbon black (Super P, SP) and a nitrogen-doped graphene nanosheets (NGS) on S cathodes. Experimental results showed that the S@SP (SSP) cathode and...
S@NGS (SNGS) cathode have different structures, interactions with the active materials and electrochemical impedance spectra, and thus exhibited different electrochemical properties and performance. For SSP, its initial specific capacity is as twice as that of SNGS but fade rapidly. In contrast, SNGS exhibits better capacity retention and rate cyclability. We also found that by simply mixing the SP and NGS mechanically, the S@SP@NGS (SSP/NGS) cathode shows both good capacity and cyclability. The fundamental mechanisms of these phenomena are discussed and a charge transfer model for these electrodes is proposed.

5:10 AM S.EN12.02.04
Influence of Structural Changes on Sodium Storage Mechanism and Electrochemical Performance in Hard Carbons for Sodium-Ion Batteries

Hande Alptekin1, Heather Au1, Anders Jensen2, Alan Drew2 and Magdalena Titirici1; 1Imperial College London, United Kingdom; 2Queen Mary University of London, United Kingdom

Recently, Sodium-ion batteries (NIBs) have emerged as an economical alternative to lithium-ion batteries (LIBs) for large scale energy storage applications and therefore the successful implementation of renewable energy technologies. Developing optimum negative electrodes is of crucial importance to improve the energy density and stability of NIBs. Hard carbons with tunable morphologies are preferred due to their low cost, operating voltage (high energy density) and high reversible capacities.

Here, in our research work, a series of hard carbon anode materials prepared via the Hydrothermal Carbonisation (HTC) followed by high-temperature carbonisation. Applying various carbonization temperatures, templating agents and dopants results in materials with different pore morphologies, functional groups and graphitisation degrees which were characterised by HRTEM, XPS, Raman, gas adsorption, SAXS/WAXS and Total Neutron Scattering. The influence of material morphology and microstructural change during the electrochemical cycling were investigated by in-situ Electrochemical Dilatometry. By tuning the degree of graphitic regions to disordered domains, capacity obtained from slope and plateau regions of the discharge curve adjusted and a capacity up to 300 mAh/g with a very good initial Coulombic efficiency of 83% was achieved. The degree of graphitisation, pore structure, particle size and defects were found to have a significant effect on the storage mechanism and electrochemical performance of the batteries. Being able to design and modify the electrode structure and chemistry allowing us to move closer to electrochemically optimized, high performance and efficient Na-ion batteries.

5:20 AM S.EN12.02.05
A New Cathode Material for Na-Ion Batteries Made Exclusively from Abundant Elements

Arnaud J. Perez, Jacinthe Gamon, Leanne A. Jones, Rhun Morris, Luke Daniels, Tim Veal, Laurence Hardwick, Dyer Matthew, John Claridge and Matthew Rosseinsky; University of Liverpool, United Kingdom

The worldwide development of Li-ion batteries has led to a revolution in the field of consumer electronics and completely transformed the way we access information. It is currently the leading technology for the technological transition towards electricity-powered transportation and large-scale energy storage capabilities. However, it is still unclear whether the cost of Li-ion batteries will meet this challenge, as they contain non-abundant elements such as lithium, nickel, cobalt, which price is bound to vary with market and political decisions. Developing Na-ion batteries as a cheaper alternative is therefore a promising route, as it would help diversifying technology for grid or local storage applications that do not require high energy density.

Recent work on a new anti-perovskite cathode Li$_2$FeOS$_{1.2}$ has shown that oxysulfides represent a promising family of material. Oxysulfides have long been overlooked in the literature due to their complex synthesis conditions and lower voltage compared to oxides. However, they can deliver high capacities using abundant elements. We prepared a new oxysulfide material with a crystallographic structure yet unexplored in cathode materials for Li and Na-ion batteries, by a simple mechanosynthesis method in dry air, and studied its electrochemical properties. Interestingly, the material becomes amorphous upon its initial oxidation but still delivers a reversible capacity of 160 mAh/g between 1.5 and 3 V vs Na+//Na and a good capacity retention upon cycling. To understand the evolution of the material during (de)sodiation, we combined several techniques (X-ray diffraction, X-ray absorption and X-ray photoemission spectroscopies) and obtained insight on the local structure evolution and oxidation/reduction of the different elements in the material. Finally, full Na-ion cells were assembled using hard carbon anodes, showing the possibility to prepare Na-ion batteries with abundant and cheap materials. Oxysulfides, and more generally multiple anion materials, give us an opportunity to control the energy storage properties of electrode materials without relying on non-abundant transition metals.

References:


5:30 AM S.EN12.02.07

**Synergistic Engineering of Defects and Architecture in Metal Chalcogenide towards Fast and Reliable Electrocatalytic Behavior for Lithium-Sulfur Batteries**

Dan Luo, Gaoran Li and Zhongwei Chen; University of Waterloo, Canada

Lithium sulfur (Li-S) batteries deliver great promise to support the next-generation energy storage when the sluggish redox kinetics and polysulfide shuttling can be well addressed. The rational design of sulfur electrode plays key roles in tacking these problems and fulfilling a high-efficiency sulfur electrochemistry. Herein, we demonstrate a synergetic defect and architecture engineering strategy to design highly disordered spinel Ni-Co oxide double-shelled microspheres (NCO-HS), which consists defective spinel NiCo$_2$O$_{4-x}$ ($x=0.9$ if all nickel is Ni$^{2+}$ and cobalt is Co$^{2.13+}$), as the multifunctional sulfur host material. The *in-situ* constructed cation and anion defects endow the NCO-HS with significantly enhanced electronic conductivity and superior polysulfide adsorbability. Meanwhile, the delicate nano-construction offers abundant active interfaces and reduced ion diffusion pathways for efficient Li-S chemistry. Attributed to these synergistic features, the sulfur composite electrode achieved excellent rate performance up to 5 C, remarkable cycling stability over 800 cycles and good areal capacity of 6.3 mAh cm$^{-2}$ under high sulfur loading. This proposed strategy based on synergy engineering is also promising to enlighten the material engineering in related energy storage and conversion fields.

5:40 AM *S.EN12.02.09

**Nanoscale Design for High Energy Batteries**

Yi Cui; Stanford University, United States

The demand from portable electronics and electric vehicles call for high energy batteries beyond the current lithium ion batteries. Here I will present our recent progress on materials and interfacial design to enable much high energy density batteries, which include 1) High capacity Si anodes with success in commercialization; 2) Li metal anodes: host and interface design to over the lithium metal dendrite formation and interfacial instability; 4) Sulfur as an earth abundant material for high capacity cathodes; 4) Our pioneering development of cryogenic electron microscopy for understanding the battery materials and solid-electrolyte interphase down to atomic scale resolution.

5:55 AM S.EN12.02.11

**Harnessing Structural Complexity for the Design of New Lithium-Ion Cathode Materials**

Huiwen Ji$^{1,2}$, Jinpeng Wu$^1$, Zijian Cai$^2$, Jue Liu$^3$, Deok-Hwang Kwon$^1$, Hyunchul Kim$^1$, Alexander Urban$^4$, Joseph K. Papp$^5$, Emily Foley$^5$, Yansen Tian$^2$, Mahalingam Balasubramaniam$^6$, Haegeyeom Kim$^1$, Raphael E. Clement$^1$, Bryan D. McCloskey$^2$, Wanli Yang$^1$ and Gerbrand Ceder$^{2,1}$; $^1$Lawrence Berkeley National Laboratory, United States; $^2$University of California, Berkeley, United States; $^3$Oak Ridge National Laboratory, United States; $^4$Columbia University, United States; $^5$University of California, Santa Barbara, United States; $^6$Argonne National Laboratory, United States

The facile transport of lithium ions in inorganic crystalline materials is a prerequisite for the many electrochemical processes in rechargeable batteries, the production of which is now being rapidly scaled up to electrify vehicles and even enable grid-scale energy storage. Achieving fast ion transport kinetics in electrode materials requires an optimized crystal structure with favorable short-range atomic arrangements, which are, in the meantime, extensively connected in the long range. In conventional electrode materials, wherein a single unit cell exactly repeats its chemistry and geometry into infinity, the two criteria conveniently become one. Such perfectly-ordered structures, though easy to characterize, lack flexibility and impose a narrowed selection in chemistry, causing significant strains on several metal resources, such as cobalt and nickel. In this talk, I will show how strategically introducing compositional and structural disorder into a simple rocksalt lattice can lead to the discovery of novel electrode materials with ultrahigh energy and power density as well as a reversible anion redox process. The design strategies might open up a vast chemical space for the search of new battery materials made from earth-abundant elements.

6:05 AM S.EN12.02.12

**Controllable Fabrication of Pitaya-Like SnO$_2$/N-Doped Carbon Composite Nanospheres for Highly Rate Capability Lithium Storage**

Xiao Liu; Henan University, China
As one of the most important energy storage devices, lithium ion batteries (LIBs) have been widely used in portable electronic devices due to its high energy density and long cycle life. However, for commercial lithium ion batteries with graphite as anode material, a common drawback is the relatively low specific capacity (372mAh g\(^{-1}\)) and the problem of Li plating under high current density. To solve the problems, one of effective strategies is to develop anode materials with high theoretical capacity. Among them, SnO\(_2\), with higher theoretical capacity, low toxicity and natural abundance, is widely studied as the promising alternative anode material for LIBs. However, SnO\(_2\) is accompanied by pulverization and aggregation during charge and discharge process, resulting in its fast capacity fading and poor rate performance. Herein, we have designed and synthesized SnO\(_2\) nanoparticle (\(\approx 10\) nm) uniformly distributing in porous carbon nanosphere with a continuous N-doped carbon shell (denoted as SnO\(_2\)/po-C@NC) via a multistep method. Here, dopamine due to its excellent physicochemical property was adopted as a conductive carbon shell to provide a fast electronic transport framework and thus homogenize lithiation/delithiation, when used as anode material, This architecture demonstrate enhanced capacity and excellent rate performance, SnO\(_2\)/Po-C@NC can deliver a high reversible capacity 936.8 mAh g\(^{-1}\) after 100 cycles at 100 mA g\(^{-1}\), even at the high current density of 3.2 A g\(^{-1}\) an average capacity of 460.0 mA h g\(^{-1}\) can be achieved.

**References**

Polymer electrolyte-based Lithium metal batteries are attractive for safe energy storage with high-energy-density. However, various material challenges present inside, such as interfacial stability with electrodes and low ionic conductivity. In this talk I will present material characterizations and designs to understand and address some challenges inside. Specifically, a combination of stimulated Raman scattering microscopy and AFM measurements first illustrate how mechano-chemical coupling at the lithium/polymer electrolyte interface affect dendrite formation in polymer electrolyte. Second, interfacial designs are developed to suppress the oxidation of PEO electrolyte at the cathode side, and thus long-term cycling is achieved in 4V LCO or NMC-PEO-Li cells. The capacity retention reaches 85% after 200 cycles.

5:15 AM S.EN12.03.02
In-Built Solid-State Polymer Electrolytes for Rechargeable Lithium-Metal Batteries Qing Zhao and Lynden Archer; Cornell University, United States

Rechargeable metal batteries that employ metals, including Li and Na, as anodes have been gained increasing attention in recent years due to their high energy density. However, poor chemical stability of traditional liquid electrolytes in contact with the metal anode limit both the performance and safety of such cells. Solid-state electrolytes are considered particularly promising because of their inherent safety characteristics and potential to prevent dendritic deposition of the metal, in which solid polymer electrolytes (SPEs) are considered attractive from a range of perspectives, including their light-weight characteristics, lower cost, excellent mechanical toughness, and compatibility with roll-to-roll manufacturing processes. In general, a successful SPE is required to have at least two characteristics. Firstly, it should have high bulk ionic conductivity and fast interfacial transport; and secondly it should remain mechanically stable and chemically inert during extended battery cycling.

In present talk, I will present our recent progresses on the preparation of in-built SPEs. Firstly, we found that the ring-opening polymerization of molecular ethers (for example, 1,3-dioxolane) inside an electrochemical cell can produce SPEs with high ionic conductivity at room temperature. These SPEs retain conformal interfacial contact with all cell components and exhibit low interfacial resistances, uniform lithium deposition and high Li plating/striping efficiencies. Secondly, we will report how to further improve cathode-electrolyte interphases of in-built SPEs. In the presence of designed fluorinated nanofillers, the designed SPEs enable the stable cycling performance in high areal capacity and high voltage LiNi0.6Mn0.2Co0.2O2 cathodes. We found the fluorinated nanofillers can play dual role as a Lewis acid catalyst and in building fluoridized interphase to protect both the electrolyte and aluminum current collector from degradation reactions. Finally, we will report how to maintain long-term stability for in-built SPEs by designing plasticizer. The complex kinetics of in-built SPEs with plasticizer results in nonlinear phase behavior, including the appearance of a critical transition to an entangled, solid-like electrolyte state.

References:

5:25 AM S.EN12.03.04
High Density and Ionic Conductivity in Nanostructured Ta-Doped LLZO Synthesized by a Polymer Combustion Method Jon M. Weller and Candace Chan; Arizona State University, United States

Ta-doped LLZO (LLZTO) is of great interest due to its high ionic conductivity, electrochemical stability in contact with metallic lithium, and the fact that doping the Zr-sites with Ta does not block Li-ion conduction as is the case with other common dopants such as Al or Ga, which reside on the Li sublattice. As with most methods for synthesis of LLZO, LLZTO is primarily obtained via the solid-state reaction (SSR) method, incurring a high energy cost and producing bulk powders that require high energy milling after synthesis to promote higher reactivity towards sintering. Other methods such as sol-gel and combustion methods have also been employed seeking smaller particle sizes, but generally do not result in as good of
performance as the SSR method. Herein, a novel non-aqueous polymer combustion method is used to produce LLZTO nanopowders, which enables somewhat better control over synthesis conditions and better reproducibility than conventional nitrate-based combustion methods. Compared to SSR LLZTO, which is generally sintered at temperatures between 1150-1250 °C, as-synthesized LLZTO nanopowders are easily consolidated via conventional pressureless sintering at 1100 °C. This lower sintering temperature is enabled in part by mitigating Li2O volatility and in part by the relatively higher reactivity of nanosized LLZTO compared to coarse LLZTO powders obtained via SSR. LLZTO processed with this method exhibits relative densities up to 93.6 % with ionic conductivities as high as 0.67 mS cm⁻¹, which compares well with dense LLZTO ceramics processed at higher temperatures or via advanced consolidation processes such as hot pressing. This method can be easily extended to other doping schemes, and the ease with which nanosized LLZO can be obtained makes this polymer combustion method promising for producing active fillers for composite polymer electrolytes.

5:35 AM S.EN12.03.05
A Composite NASICON (Na₃Zr₂Si₂PO₁₂) Solid-State Electrolyte with Enhanced Na⁺ Ionic Conductivity by Liquid Phase Sintering Jin An Sam Oh¹,², Li Lu¹ and Kaiyang Zeng¹; ¹National University of Singapore, Singapore; ²Singapore Institute of Manufacturing Technology, Singapore

Solid-state battery is one of the most discussed next generation energy storage devices in both industry and academia. While Li-ion battery has been popularised by the success in mobile electronics, Na-ions battery has higher potential in stationary energy storage system due to the cost and availability of raw materials. Among the solid-state electrolyte, NASICON (NASic Super Ionic CONductor), Na₃Zr₂Si₂O₇PO₇₂₋ₓ, possesses high mechanical strength, large electrochemical stability, and good chemical and thermal stability making it one of the potential materials to be utilised. However, the processing of NASICON involves long exposure at high temperature thermal treatment. In addition, the lower grain boundary ionic conductivity limits the total ionic conductivity to be around 0.64 mS cm⁻¹. In this study, sodium metasilicate, Na₂SiO₃, was added into the NASICON matrix and facilitated the sintering process. The addition of Na₂SiO₃ has effectively reduced the sintering duration and temperature. Furthermore, the diffusion of cation from Na₂SiO₃ into the bulk NASICON resulted in changes in the stoichiometry and improve the bulk ionic conductivity. More importantly, as Na₂SiO₃ melt pool penetrate through the grain boundary, it formed a Si-rich secondary phase that significantly improve the grain boundary ionic conductivity. The highest ionic conductivity measured at room temperature is when 5wt% of Na₂SiO₃ was added into the NASICON at 1.48 mS cm⁻¹. This study has shown facile addition of liquid-phase during sintering can effectively achieve high ionic conductivity.

5:45 AM S.EN12.03.06
Solid-State Materials to Enable Molten Sodium Batteries Erik D. Spoerke, Martha M. Gross, Stephen Percival, Leo J. Small and Amanda Peretti; Sandia National Laboratories, United States

In the expanding search for safe, sustainable, low-cost large scale energy storage solutions, molten sodium batteries have been recognized as an attractive candidate technology. The relatively high operating temperature (near 300°C) of traditional molten sodium-sulfur and sodium-nickel chloride batteries, however, has discouraged the widespread adoption of these battery chemistries. We are developing a new, lower temperature molten sodium battery that operates near 100°C, based on a sodium anode, a solid state separator, and a sodium iodide-based molten halide salt catholyte. This new lower temperature system opens the door to lower materials costs, improved material lifetimes, and simplified, less costly operation. The reduced operating temperature, however, introduces new material and electrochemical challenges to not only the key molten components of the battery, but also critical interfaces and functional materials associated with the solid state separator, the current collectors, and even the material packaging of the battery. Here, we will discuss creative engineering solutions to emergent low temperature-specific problems related to interfacial wetting, ionic conductivity, chemical compatibility, and charge transfer efficiency. We highlight new approaches to solid state separator development, manipulating not only ceramic or composite chemistry but also separator structure and interfacial chemistry to enhance low temperature ionic conductance. Meanwhile, efforts to tailor high surface area, low resistance current collectors show progress toward higher efficiency battery cycling. Addressing the specific solid state materials in this functionally molten battery system allows us to accelerate the development of this potentially safe and sustainable sodium-based energy storage option.


5:55 AM S.EN12.03.07
Electrolyte and Interface Design for High Voltage Solid-State Batteries Xin Li; Harvard University, United States
In this talk, we show how mechanically-induced metastability greatly widens the voltage window and modulates the dynamic interface decomposition of sulfide solid electrolyte at high voltage, going beyond our recent work [1,2, 3]. By comparing ab-initio simulation and XPS measurement, the thermodynamic pathway of decomposition is determined. Beyond this thermodynamic stability window, kinetic effects are also discussed. We show both experimentally and theoretically how the decomposition of LGPS at high voltage is largely prohibited by these effects via mechanical constraint. We further discuss the potential of this effect on the cathode-electrolyte interface design to enable high voltage solid state batteries beyond the commercial level.

Bio-Inspired Nanospiky Metal Particles Enable Thin, Flexible and Responsive Polymer Nanocomposites for Thermal Regulation Mingqian Li and Zheng Chen; University of California, San Diego, United States

Safety issue remains a major obstacle towards large-scale applications of high-energy lithium-ion batteries. Embedding thermo-responsive polymer switching materials (TRPS) into batteries is a potential strategy to prevent thermal runaway, which is a major cause of battery failures. Here, we report thin, flexible, highly responsive polymer nanocomposites enabled by bio-inspired nanospiky metal (Ni) particles. These unique Ni particles were synthesized by a simple aqueous reaction at gram-scale with controlled surface morphology and composition to optimize electrical properties of the nanocomposites. The Ni particles provide TRPS films with a high room-temperature conductivity of up to 300 S cm⁻¹. Such TRPS composites also have a high rate (< 1s) of resistance switching within a narrow temperature range, good reversibility upon on/off switching and a tunable Tc (75 to 170 °C) that can be achieved by tailing their compositions. The small size (~500 nm) of Ni particles enables ready fabrication of thin and flexible TRPS films with thickness approaching 5 µm or less. These features suggest the great potential of using this new type of responsive polymer composites for more effective battery thermal regulation without sacrificing cell performance.

5:35 AM *S.EN12.04.04
Draining over Blocking—Nano-Composite Janus Separators for Mitigating Internal Shorting of Lithium Batteries Matthew Gonzalez, Qizhang Yan, Zhaohui Wu, Hongyao Zhou, Nicholas Patterson, Victoria Petrova, Haodong Liu and Ping Liu; University of California, San Diego (UCSD), United States

Catastrophic battery failure due to internal short is extremely difficult to detect and mitigate. In order to enable next generation lithium-metal batteries, a “fail safe” mechanism for internal short will be highly desirable. We introduce a novel separator design and approach to mitigate the effects of an internal short circuit by limiting the self-discharge current to prevent cell temperature rise. A nano-composite Janus separator—with a fully electronically insulating side contacting the anode and a partially electronically conductive (PEC) coating with tunable conductivity contacting the cathode—is implemented to intercept dendrites, control internal short circuit resistance, and slowly drain cell capacity. Galvanostatic cycling experiments demonstrate Li-metal batteries with the Janus separator perform normally before shorting, which then results in a gradual increase of internal self-discharge over >25 cycles due to PEC mitigated shorting. Abuse charge testing of Li metal batteries containing the Janus separator shows a remarkable ability to reduce short circuit current and heat generated during internal shorting incidents. This new separator design can not only greatly improve battery safety, but also lower battery costs by relaxing manufacturing tolerance and accelerate the adoption of high-energy next-generation batteries.

5:45 AM *S.EN12.04.06
Dual Ion Organic Batteries Based on Conducting Redox Polymers Guiomar Hernández1, Nerea Casado2, Lisa Åkerlund1, Rikard Emanuelsson1, Fernando Ruipérez2, Daniel Brandell1, Maria Strömme1, Martin Sjödin1 and Davis Mecerreyes2; 1Uppsala University, Sweden; 2University of the Basque Country, Spain

The electrochemical performance of lithium-ion batteries has been substantially improved in the last decades. However, with the increasing demand of electrochemical energy storage technologies, other challenges such as scarcity of raw materials, toxicity, and recyclability ought to be considered. In this regard, redox active polymers are promising materials thanks to their abundance, low cost, low toxicity and environmentally friendly disposal.[1-3] In addition, their redox properties can be tailored to be used as negative electrodes storing cations (Li⁺, Na⁺, H⁺) as well as positive electrodes incorporating anions (PF₆⁻, TFSI⁻). However, redox active polymers also possess some limitations, such as dissolution into the electrolytes, poor conductivity and low operational voltage.[4] To overcome some of those limitations, we have investigated different redox active conducting polymers with enhanced conductivity and reduced solubility to be used as positive and negative electrodes. As negative electrode, we have chosen a polypyrrole-polyether block copolymer that combines the versatile redox activity and electronic conductivity of aromatic imide groups with the ion conducting polyether. As positive electrode, we have studied a PEDOT-lignin biopolymer composite combining the PEODT conducting backbone with redox active lignin to increase the capacity. These two materials have been paired to build an all-organic aqueous battery with long cycle life at high current densities.[5] Additionally, another positive electrode based on PEDOT with hydroquinone and pyridine pendant groups has been investigated as a proton trap material. In this system, the redox reaction occurs in the hydroquinone moieties and the protons are transferred to the pyridine sites preventing its diffusion to the electrolyte. This material is very versatile as it can be used in many different electrolytes (conventional liquid electrolytes and ionic liquids), regardless of the coordinating salt (lithium or sodium based).[6]

Overall, redox active polymers can be tailored with specific backbones and redox active moieties to feature the desired properties and to be used as negative and positive electrodes towards more sustainable and environmentally friendlier energy storage technologies.
Exploiting Mechanistic Solvation Kinetics for Dual-Graphite Batteries with High Power Output at Extremely Low Temperature John Holoubek, Ping Liu and Zheng Chen; University of California, San Diego, United States

Improving the extremely low temperature operation of rechargeable batteries is vital to the operation of electronics in extreme environments, where systems capable of high-rate discharge are in short supply. Herein, we demonstrate the holistic design of dual-graphite batteries, which circumvent the sluggish ion desolvation process found in typical lithium-ion batteries during discharge. These batteries were enabled by a novel electrolyte, which simultaneously provided high electrochemical stability and ionic conductivity at low temperature. The dual-graphite cells, when compared to industry-type graphite | LiCoO2 full-cells demonstrated an 11 times increased capacity retention at -60 oC for a 10 C discharge rate, indicative of the superior kinetics of the “dual-ion” storage mechanism. These trends are further supported by GITT and EIS measurements at reduced temperature. This work provides a new design strategy for extreme low-temperature batteries.

Porous Si and CNT@Si@C Microspheres from Self-Assembly of Colloidal SiO2 Nanoparticles as High-Performance Li-Ion Battery Anodes Xiaolin Li, Haiping Jia and Jiguang Zhang; Pacific Northwest National Laboratory, United States

Silicon has been regarded as the most promising high energy density anode for Li-ion batteries. However, it suffers from large volume expansion upon full lithiation and fast capacity fade. Si of porous structure has been known to accommodate the volume change and improve the cycling stability and hence has attracted extensive attention. Here, we report the synthesis of porous Si microspheres by thermite reduction of SiO2 microspheres (500nm to 10 micron) from self-assembly of 70 nm SiO2 colloidal particles. The porous Si microspheres have uniform mesopores and Si crystallites of ~20 nm. The fine primary particles can shorten the Li+ transport route and avoid the pulverization of Si. The obtained porous silicon delivers a reversible capacity of 1900 mAh g-1 at 0.5C and 85% capacity can be retained after 100 cycles. In another effort, CNT@SiO2 coaxial cables were synthesized using sol-gel method and then self-assembled into microspheres in microemulsion. Hierarchical porous CNT@Si@C microspheres obtained after thermite reduction reaction demonstrated excellent electrochemical performance. The anodes deliver 90% capacity retention over 100 cycles at the areal loading of ~3 mAh/cm2. These works represent significant steps in the development of Si anodes and provide guidance for battery material synthesis.

Non-Equilibrium Tungsten Oxide Hydrates via Selective Ion Etching for Aqueous Energy Storage Veronica Augustyn; North Carolina State University, United States

The search for electrochemical energy storage that provides good safety as well as high energy storage performance has reignited interested in materials that operate in aqueous electrolytes. In these electrolytes, protons are increasingly identified as the relevant intercalating species into the vacant sites of transition metal oxide electrodes. Using selective ion etching of a bismuth tungsten oxide, we synthesized a non-equilibrium tungsten oxide hydrate (W2O6*H2O) that exhibits both high proton intercalation capacity (~ 55 mAh/g) and excellent kinetics enabling charge/discharge times of just 12 seconds. The capacity is significantly higher than what can be attained with tungsten oxide hydrates obtained via typical acid precipitation routes or the anhydrous tungsten oxide. Intriguingly, the performance is attained with thick electrodes consisting of large particles tens of microns in diameter. Utilizing a combined experimental and theoretical approach, this talk will discuss how the structure of the non-equilibrium hydrate influences its proton intercalation kinetics. Finally, we will discuss future opportunities in the use of selective-ion etching of transition metal oxides for the synthesis of non-equilibrium structures for energy storage.
Global demand for high-performance energy storage systems has grown tremendously in recent years. The all-solid-state lithium-ion batteries (ASSLIBs) are promising for such storage solutions on account of the lithium metal anodes with high areal capacity and the solid-state electrolytes (SSEs) with critical safety.\textsuperscript{1} However, the interfacial failure of the ASSLIBs posed a major hurdle towards the design of high-performance solid-state batteries.\textsuperscript{2,3,4} Time-resolved in operando techniques (\textit{e.g.} in situ microscopy, synchrotron X-ray tomography) are ideal for the direct and quantitative characterization of the interfacial deteriorations. However, the \textit{in situ} analysis of solid-state batteries is still in its primary stage due to the difficulties in probing the buried interfacial layer. The specific causes of the high interfacial impedance and the lithium dendrite growth that deteriorates the battery in a few cycles remain nebulous.

To this end, we developed a multi-dimensional diagnostic platform that allows the direct probe of the chemical and spatial distribution on the interface while the cell operates. Parameters such as pressure and temperature, which have a strong influence on cell behavior, are also enabled by the platform. Moreover, the platform can be transferred between analytical instruments, including SEM, ToF-SIMS, and Raman, for a synergistic diagnose of the structural and chemical evolutions in solid-state Li batteries. A deeper understanding of interfaces and dendrites evolutions has been acquired by the testing platform, including (1) correlation between void formation and electrolyte decomposition, and (2) creeping mechanical properties of the lithium metal during the cell operations. These in-depth understandings will allow us to effectively optimize and enable further enhancements of solid-state Li batteries.

References

SESSION S.EN12.05: Next-Generation and Beyond Li
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-EN12

5:00 AM *S.EN12.05.01
\textbf{Sustainable Energy Storage Technologies Beyond Li-Ion Batteries} Jie Xiao and Chaojiang Niu; Pacific Northwest National Laboratory, United States

\textbf{Abstract:} The thermodynamically instable nature of lithium metal in liquid electrolytes significantly plagues the implementation of the high-energy rechargeable lithium battery technology in electrical vehicles. Although many approaches have been proposed to rescue Li metal anodes, most of the work are performed in small-scale coinellsand tested in the conditions drastically different from the reality. A full knowledge of Li metal activities at the cell level is lacking but extremely critical for the success of developing next-generation rechargeable Li metal batteries. This talk will discuss the fundamental challenges of utilizing Li metal anode in at cell-level and demonstrate a prototypic 350 Wh/kg lithium metal pouch cell > 250 stable cycling.

5:15 AM *S.EN12.05.02
\textbf{Controlled Synthesis of Disordered Carbon Anodes for Na-Ion Battery} Yaxiang Lu, Yuruo Qi, Chenglong Zhao, Qingshi Meng, Yuqi Li, Hong Li, Xuejie Huang, Liuan Chen and Yong-Sheng Hu; Chinese Academy of Sciences, China

Na-ion batteries (NIBs) have been recently reconsidered for storing the electricity from renewable energy due to the abundant sodium resources and low cost. The progress of NIBs intensively relies on the application of appropriate cathode and anode materials, especially, the anode side has become the main bottleneck in enhancing the batteries’ performance. Among all available anode candidates, disordered carbon still shows the best overall performance in terms of capacity, cycling stability and cost. In this talk, I will present several superior low cost disordered carbon anodes made from pitch, focusing on the strategies adopted to suppress the graphitization degree of pitch-derived carbon at high carbonization temperature. Besides,
pore structures of a porous biomass-derived carbon are regulated to enhance the Na storage performance. Furthermore, two kinds of carbon anodes demonstrate a high Na storage capacity ≥400 mAh/g through controlled synthesis, which help unravel the Na storage mechanism in disordered carbon. The understanding gained potentially provides reference for the design and development of high-performance disordered carbon materials for NIBs.

References
Li, Y.Q.; Lu, Y.X.*; …; Hu, Y.-S.* Advanced Energy Materials 2019, accepted.

5:30 AM *S.EN12.05.04
The Silicon Electrolyte Interface Stabilization Project Anthony Burrell; National Renewable Energy Laboratory, United States

Silicon is a viable alternative to graphitic carbon as an electrode in lithium-ion cells and can theoretically store >3,500 mAh/g. However, lifetime problems have been observed that severely limit its use in practical systems. The major issues appear to involve the stability of the electrolyte and the uncertainty associated with the formation of a stable solid electrolyte interphase (SEI) at the electrode. Recently, calendar-life studies have indicated that the SEI may not be stable even under conditions where the cell is supposedly static. Clearly, a more foundational understanding of the nature of the silicon/electrolyte interface is required if we are to solve these complex stability issues. A multi-lab consortium has been formed to address a critical barrier in implementing a new class of materials used in lithium-ion batteries that will allow for smaller, cheaper, and better performing batteries for electric-drive vehicles. This consortium, named the Silicon Electrolyte Interface Stabilization (SEISta) project, was formed to focus on overcoming the barrier to using such anode materials. Five national laboratories are involved: the National Renewable Energy Laboratory (NREL), Argonne National Laboratory (ANL), Lawrence Berkeley National Laboratory (LBNL), Oak Ridge National Laboratory (ORNL), and Sandia National Laboratories (SNL). The SEISta project was specifically developed to tackle the foundational understanding of the formation and evolution of the solid-electrolyte interphase on silicon. This project will has a primary goal of understanding the reactivity of the silicon and lithiated silicon interface with the electrolyte in lithium-ion systems. The overall objective for SEISta is to understand the nature and evolution of the SEI on silicon anodes.

Several issues must be addressed to enable progress in this area. Materials Standardization is critical to this project and deployment of standardized samples and experimental procedures across the team is a foundation of the project. Full characterization of any new sample that is to be used for SEI studies to ensure reproducibility and full understanding of the material. The materials standardization and model compounds will enable the researchers to systematically investigate the formation of the solid-electrode interphase using a wide variety of the spectroscopy techniques—from different optical, microscopy, and electrochemistry—to determine how the SEI forms based on the nature of the silicon surface, and how it evolves over time. This presentation will detail recent advances that the SEISta team has made to the understanding of the SEI on silicon.

5:45 AM S.EN12.05.08
Low-Temperature Formation of Lithium Conducting Garnets via Basic Molten Salt Synthesis Jon M. Weller and Candace Chan; Arizona State University, United States

Lithium conducting garnets in the family of lithium lanthanum zirconate (nominally Li7La3Zr2O12, LLZO) are of great interest as oxide solid electrolytes for solid-state lithium-metal batteries. Various synthetic approaches have been investigated to date, including sol-gel, co-precipitation, thin film deposition, spray pyrolysis, combustion, and molten salt synthesis, not to mention the standard solid-state reaction (SSR) method. Most of the aforementioned methods can generate LLZO with expected good properties, but nearly all have drawbacks including cost, high processing temperatures, complexity, poor properties (in the case of vacuum deposition of thin films), or difficulty of producing fine powders for thin films of LLZO, which are necessary for practical solid-state batteries. Thus, despite the promising properties of LLZO in terms of electrochemical stability and ionic conductivity, processing of garnet powders into dense solid electrolytes in practically useful forms is still a challenge. Herein, submicron (200-500 nm) powders of doped LLZO of nominal composition Li1-xLa2-xZr2Ti1-xTa0.5O12 are demonstrated to form at an unprecedented low temperature of 400 °C using a basic molten salt synthetic approach, ameliorating two main challenges of processing temperature and particle size. However, a curious
phenomenon is observed: the composition of individual LLZO particles can vary considerably from the nominal composition, producing a distribution in the ratio of Zr and Ta that is difficult to detect during routine characterization (requiring the high spatial resolution of analytical transmission electron microscopy) but may have deleterious consequences on performance. Indeed, LLZTO synthesized via SSR exhibits higher ionic conductivity despite comparable relative density and sintering conditions. Backscatter electron imaging and energy dispersive spectroscopy shows that this compositional inhomogeneity persists even after sintering at high temperatures, indicating that interdiffusion between Zr and Ta does not go to completion at relevant sintering times if a distribution in composition exists in the feedstock powder. Variation in composition between individual grains implicates subcritical doping in some percentage of grains in a dense ceramic as the source of poorer performance relative to SSR LLZTO. The thermodynamic and kinetic origins of compositional inhomogeneity are discussed in Ta-doped LLZO and addressed by use of novel elementally homogeneous precursors. Implications of compositional inhomogeneity on performance of garnet solid electrolytes via this and other common synthesis methods are discussed.

5:55 AM S.EN12.05.09
Development of High Potential Negative Electrode for Lithium-Ion Batteries

Benjamin Mercier-Guyon, Jean-François Colin and Sebastien Martinet; Univ. Grenoble Alpes, CEA, LITEN, France

Rechargeable lithium ion batteries (LiBs) are commonly used as power sources, and they became the dominant energy storage technology for various range of applications including portable electronic, electrical vehicles, and large-scale energy storage.

Used as negative electrode for most of commercial cells because of its low cost and good theoretical capacity (372 mAh.g⁻¹), graphite, suffers from important stability issues.

The passivating layer formed on graphite electrode, well-known as solid electrolyte interphase (SEI), occurring because of the decomposition of organic liquid electrolyte can lead to capacity fading, electrolyte consumption and low lifetime. Despite the presence of the “stable” SEI layer, lithium plating, dendrite formation and in some case thermal run away may occur depending on the charging conditions. This poor interface, especially sensitive to low temperature and high currents poses an important challenge for the development of electric vehicles (EVs).

For some years, with safety and performance in mind, titanates composites have been studied as anode material. The lithium titanate spinel Li₄Ti₅O₁₂ (LTO) has drawn attention of many research groups, due to its high operating voltage preventing lithium plating, its long cycle life and its ultra-low volume change during the lithium insertion. This material might have been perfect for hybrid electric vehicles requiring high rate cycling and fast charge even with low temperature. However, a low specific capacity (175mAh.g⁻¹) leading to a low energy density associated as well with a gassing phenomenon drastically hinder the deployment of this material.

Another family of material exhibiting Wadsley-Roth shear structures, mainly composed of mixed Ti and Nb was introduced during the 50s and has shown the ability to intercalate lithium ions [1]. Later, Goodenough et al. showed in 2011 that TiNb₂O₇ (TNO) can be used as negative electrode material in a full cell system [2], keeping LTO’s advantages (high working potential and safety) but offering a theoretical capacity of 387.6 mAh.g⁻¹ that is comparable to the one of graphite.

Many groups report advanced ways to synthesize this material such as solvothermal synthesis [3] and spray drying [4] but only little consideration was given to the study of the lithiation and degradation mechanisms [5]. In this work, we report that TNO electrodes present important differences of performances at high rates following their cycling history. Indeed, we notice that, when previously cycled at low rate (C/10 or below), the material exhibits less than the half of the discharge capacity obtained when directly cycled at high rate.

To understand this phenomenon, many investigations have been carried, in particular using in situ and post-mortem X-ray diffraction. In situ and operando X-ray diffraction can be a powerful tool to characterize crystalline evolution upon cycling and pushing forward the understanding of lithiation reactions.

We used a cell fitted with thin beryllium windows, with a mix of TNO and black carbon, a lithium metal as counter electrode and using EC/PC/DMC (1/1/3v) +1M LiPF₆ electrolyte.

Different conditions of cycling where used and diffractograms obtained were compared for a same lithiation rate. Clear and important evolutions of peak positions, shapes and intensities can be followed all along the lithiation process and allowed us to refine the lattice parameter.

We have been able to follow the lithiation process in the materials at different cycling conditions. We also try to stabilize and improve the comportment of the material with different solutions such as carbon coating or doping and we will present the results of these studies.

Among electrical energy storage (EES) systems, sodium-ion batteries (SIBs) are very promising and have been attracting an ever-growing research interest in the past decade, due to the low cost and natural abundance of sodium element. Compared to the success of cathodes in SIBs, one main challenge is seeking high-performance anodes. To this end, in this work we investigated copper(I) sulfide (Cu$_2$S) as a promising SIB anode through mixing with nitrogen-doped graphene nanosheets (NGS) via a facile high-energy ball milling route. The resultant Cu$_2$S@NGS composite could achieve a sustainable high capacity of 300 mAh g$^{-1}$ over 500 cycles and accomplish a high rate capability up to 10 C ($1$C = 337 mA/g). Compared to all studies reported so far, our Cu$_2$S@NGS composite electrodes demonstrated the highest electrode capacity. Our analyses revealed that the substitution of NGS for carbon black has produced multiple beneficial effects: (i) inhibiting polysulfide shuttling effect, (ii) suppressing the formation of SEI layer, (iii) offering high electron and ion conductivity, and (iv) enhancing mechanical integrity of electrodes. We also systematically investigated the effects of voltage windows and surface coatings on enhancing the stable electrochemical performance of Cu$_2$S@NGS composite electrodes. This work represents a great advance in seeking high-performance anodes in SIBs.

SESSION S.EN12.06: Li-Metal Anodes
On Demand Abstracts Available for Viewing Starting Saturday
Morning, November 21, 2020
S-EN12

5:00 AM *S.EN12.06.02
Design and Architecture of Solid-Electrolyte Interphase for Stable Lithium-Metal Anode Donghai Wang; The Pennsylvania State University, United States

Li metal anode materials are the most promising anodes for next-generation Li batteries. The poor interfacial stability in the battery has been the primary issue hindering their practical application. In this talk, I will present approaches developed in my group to design and architect the solid-electrolyte interphase (SEI), particularly using a chemically and electrochemically active organic makers. The maker coated on the Li surface can generate the SEI by preferentially chemically occupying the Li surface site and subsequently electrochemically self-decomposing at the interface. The maker-derived SEI presented desirable ionic conductivity, density, homogeneity, and mechanical strength. The SEI reinforced by the organic maker shows much better stability than the SEI reinforced by electrolyte additive strategy, which is the current state-of-art and commercially used solution to SEI stability issue. Our findings open a new way to design stable electrochemical interfaces for battery materials.

SESSION S.EN12.07: Sustainable Technologies
On Demand Abstracts Available for Viewing Starting Saturday
Morning, November 21, 2020
S-EN12

5:00 AM *S.EN12.07.01
Material Design for Electrochemical Devices with Better Energy-Storage-Conversion Performance Yunfeng Lu; University of California, Los Angeles, United States

There are increasing demands for high-performance electrochemical-energy-storage devices, such as lithium ion batteries and fuel cells, for microelectronics, electrical vehicles, and other applications. Generally, such devices are operated through charge separation in one electrode, during which electrons and ions are transported respectively through the external circuit
and the electrolyte and recombined in the other electrode, accomplished through the redox reactions occurred in the electrodes. Material design that lead to better charge separation, transport, and recombination, in this context, holds great promise towards better electrochemical-energy-storage devices. In this presentation, the design of electrode materials and electrolytes, which lead to better performance lithium-ion batteries, lead acid batteries, and fuel cells will be discussed.

5:15 AM *S.EN12.07.02
Direct Recycling of Lithium-Ion Battery Materials
Jack Vaughey, Anthony Montoya and Fulya Dogan; Argonne National Lab, United States

Lithium-ion batteries have been manufactured for nearly three decades and represent an excellent example of the role steady improvements in design and science can have on end users and research opportunities. As more uses become viable the number of cells produced increases and puts a strain on the metals and mining industry to maintain the supplies of component metals, such as cobalt. Some reports have noted that for cobalt, almost 25% of the worlds yearly output is used in lithium ion batteries creating the need to vary the amount of metals used and identify new compositions made of more abundant materials. In addition to new supplies, the opportunity exists with previously manufactured lithium ion cells to recover and reuse the metals and components. As with the lead-acid battery industry, collection of end-of-life lithium ion cells (automotive, consumer, or medical) can act as a supply of reusable materials. In this talk we will discuss the role Direct Recycling has on these pathways and highlight methods to relithiate lithium-deficient samples and deal with the need for compositional changes as market needs change over time with advances in chemistry and technology.

5:30 AM *S.EN12.07.03
Towards Safe and Sustainable Energy Storage by New Approaches and Materials for Future Dual-Ion Batteries
Jens M. Wrogemann1, Martin Winter2,1 and Tobias Placke1; 1University of Münster, Germany; 2Forschungszentrum Jülich GmbH, Germany

Lithium-ion batteries are the dominating energy storage technology for various applications, especially in the field of portable electronics as well as for large scale applications like electric mobility, due to an outstanding mix of high energy density, high power density and long cycle life. However, a growing demand of rechargeable batteries for automotive and stationary applications raises also concerns about resources, growing costs, and sustainability aspects. Especially for stationary grid storage and large-scale applications, sustainability aspects and low installation and lifetime costs are mandatory requirements in order to compete with other energy storage technologies.[1] Driven by that motivation, a huge number of several alternative energy storage technologies rised up in the last decade. One prominent candidate are dual-ion batteries (DIBs), which gained increased attention as alternative energy storage recently. [2] DIBs are characterized by the simultaneous uptake of both, anions and cations from the electrolyte into the respective host materials during charge and their release during discharge. This working principle allows to use non-lithium as well as non-heavy metal containing positive electrode materials like graphite, organic cathodes or even metal organic frameworks for anion storage. [2-4] Due to the promising high working potential of graphite for anion intercalation of ≥4.5 V vs. Li|Li⁺ especially dual-graphite batteries (DGB) achieved an increased attention in the last years. However, the high working potential generates new issues and requirements like high oxidative stability of the electrolyte. Therefore, ionic liquids as well as highly concentrated electrolytes were studied and show promising results. [2,5] However, in terms of cost, safety and sustainability these cell chemistries need further improvement.

The presented work shows first approaches by introducing water-based electrolytes in DIBs as well as new electrode materials for anion insertion. In the first part, a water-based DIB using graphite as cathode material is presented. The impact of different anode materials on the electrochemical performance as well as structural changes during charge and discharge are systematically investigated by ex situ studies as well as in situ X-Ray diffraction and other techniques. In a second part, new organic/inorganic positive electrode materials for reversible anion insertion are presented and evaluated for application in DIB cells with regard to their electrochemical and structural properties.

References:
SESSION S.EN12.08: Characterization and Mechanistics
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
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5:00 AM *S.EN12.08.01
Advanced Characterization and Diagnosis of Sulfide Based Solid Electrolytes and Their Interfaces Y. Shirley Meng; University of California, San Diego, United States
Enabling long cyclability of high-voltage oxide cathodes is a persistent challenge for all-solid-state batteries, largely due to their poor interfacial stabilities against sulfide solid electrolytes. While protective oxide coating layers such as LiNbO3 (LNO) have been proposed, its precise working mechanisms are still not fully understood. Existing literature attributes reductions in interfacial impedance growth to the coating’s ability to prevent interfacial reactions. However, its true nature is more complex, with cathode interfacial reactions and electrolyte electrochemical decomposition occurring simultaneously, making it difficult to decouple each effect. Herein, we utilized various advanced characterization tools and first-principles calculations to probe the interfacial phenomenon between solid electrolyte and high-voltage cathode. We segregated the effects of spontaneous reaction between the electrode and electrolyte at the interface and quantified the intrinsic electrochemical decomposition of LPSCI during cell cycling. We will also discuss a few important aspects related to the mechanical compatibility of electrode and electrolyte in all solid state batteries.

5:15 AM *S.EN12.08.03
Developing Materials and Structural-Chemical-Mechanical Diagnostics Tools for Understanding Interface Evolutions in Solid-State Metal Batteries Yan Yao; University of Houston, United States

The performance deterioration of a solid-state Li battery is the result of a combination of interfacial events. Characterization of these interfaces has been an ongoing challenge, and solid-state batteries are considered by some as a “black box”. Only during the past few years has there been exponential growth in the efforts to apply a variety of microscopic and spectroscopic techniques to characterizing solid-state batteries, but the interfacial phenomena are still far from being well understood. We will report the progress of establishing a structural-chemical-mechanical diagnostics toolset to investigate the interface evolutions in solid-state Li batteries. We will acquire detailed information of interfaces and dendrites evolutions including but not limited to (1) real-time visualization of Li dendrites growth within the whole thickness of electrolyte layer, (2) chemical composition, mechanical property, and evolution of electrolyte decomposition products, including intermediate and metastable ones, at both cathode and anode interfaces, and, (3) quantitative correlation between electrolyte decomposition, void formation, and cell performance. These in-depth understandings will allow us to effectively predict and optimize the physical and chemical changes of components within solid-state Li batteries during charge and discharge. In addition to tool development, we have studied new cathode and electrolyte materials that form reversible cathode-electrolyte interfacial resistance evolution during cycling as the result of the reversible conversion between the superionic conductor Na3PS4 and the resistive oxidation products Na2P2S6/Na2P2S8. Structural and mechanical analyses further showed that a low-modulus cathode material like PTO (Young’s modulus = 4.2 ± 0.2 GPa) can effectively accommodate interfacial stress and maintain intimate interfacial contact with solid electrolytes. The reversible electrolyte decomposition, revealed by time-of-flight secondary ion mass spectrometry (ToF-SIMS), the consistently intimate interfacial contact, visualized by focused ion beam-scanning electron microscopy (FIB-SEM), and the soft nature of cathode material, characterized by nanoindentation, are all first-time reports in the field of solid-state batteries, and they have collectively led to a high specific energy (587 Wh kg-1) at the active-material level and an 89% capacity retention over 500 cycles, a record cycling stability among all-solid-state Na batteries.

5:30 AM S.EN12.08.04
Atomic-Scale Reactivity and Degradation of Electrode Materials During Liquid-Phase Electrochemical Reactions through In Situ/Operando Transmission Electron Microscopy Rui Filipe Serra Maia and Eric A. Stach; University of Pennsylvania, United States

Liquid-phase Transmission Electron Microscopy (TEM) provides a unique platform to perform time-resolved analysis of
materials and chemical processes in realistic experimental conditions at the atomic scale. However, the resolution of liquid-phase TEM is strongly hindered by the thickness of liquid that must be traversed by the electron beam, which increases spatial and chromatic broadening. This effect negatively impacts imaging resolution and elemental analysis in liquid-phase conditions. We have developed a new technique to achieve atomic-scale resolution while keeping the sample in liquid condition. To do that, we use a chip equipped with active electrodes to generate a gas bubble through electrochemical water splitting and have shown that this leaves only a thin layer of liquid covering the sample. The thin-film liquid layer permits atomic-scale image resolution and elemental analysis through Electron Energy Loss Spectroscopy (EELS), which makes this technique very appealing for \textit{in situ} operando studies. Electrochemical analysis indicates that the remaining thin-film liquid layer exhibits good ion transport and electrical conductivity. We recently used this method to study the dissolution of platinum when it is subjected to an oxidizing electrochemical potential in an aqueous electrolyte, which allowed us to identify new ways to decelerate the degradation of platinum during oxygen evolution reaction (OER) conditions. We are also using this method to determine the active sites for hydrogen and oxygen evolution at the atomic scale in a variety of electrode surfaces, including polycrystalline platinum (Pt), monolayer molybdenum disulfide (MoS$_2$) and gold nanoprisms (Au). The approach here developed opens the opportunity to study and develop nanomaterials with enhanced performance in applications with worldwide impact, such as ion batteries, hydrogen fuel cells and reduction of CO$_2$ to biofuels. Moreover, the liquid thin-film is achieved without any damage to the sample in study, which makes this technique also suitable for sensitive samples, such as organic materials and biological samples.

5:40 AM *S.EN12.08.08

\textbf{Stability and Evolution of Solid Electrolyte Interphase on Lithium-Ion Anodes} Chunmei Ban; University of Colorado Boulder, United States

Solid electrolyte interphase (SEI), which forms at the interface between the electrolyte and the electrode, can passivate the surface of graphite anodes and finally facilitate the intercalation of lithium ions into graphite electrodes. The concept of using SEI protects the electrode surface from the reductive electrolyte has been used for developing other Lithium-ion (Li-ion) anodes, such as intermetallic silicon (Si) anodes. Different from the intercalation chemistry in graphite anodes, Si anodes experience alloying/dealloying reactions during electrochemical process, leading to phase transformation, morphology and volumetric changes. It generates great complexity in understanding the formation and the structural/composition evolution of the SEI layer during electrochemical process. Considering the high theoretical capacity Si anodes can offer, the investigation of SEI behavior on Si anodes is critical for developing next-generation anode materials. This presentation, which is based on recent results from advanced electrochemical and spectroscopy characterization, systematically elaborates the chemical and physical properties of SEI chemistry, towards developing mitigation strategies for stabilizing SEI on Li-ion anodes.

5:55 AM *S.EN12.08.09

\textbf{Synthesis of High-Ni Cathode Materials by Design} Feng Wang; Brookhaven National Laboratory, United States

Electrode performance is largely determined by the structure of active materials, and thus can be advanced by synthesis of phase-pure materials, and control of their stoichiometry, morphology, surface properties. However, synthesizing materials with desired structure and properties has been difficult due to the complexity associated with chemical reaction and involvement of metastable intermediates. Additional challenge comes from the fact that synthesis is often undertaken under non-equilibrium conditions, making it hard to predict the synthesis process by theoretical computations. Herein, we report development and application of \textit{in situ} spectroscopy techniques for real-time studies of synthesis to capture intermediates, thereby elucidating how synthesis parameters affect the kinetic reaction pathways and, consequently, the structural properties of the final products both in the bulk and at particle surface. By coupling with electrochemical characterization of the synthesized materials, such studies elucidate how structure, composition and synthesis affect electrochemical performance and therefore provide a basis for synthesis of cathode materials by design. Specific examples will be given on developing LiNi$_{0.8}$Mn$_{0.1}$Co$_{0.1}$ (NMC811) and other high-Ni cathodes for Li-ion batteries.

\textbf{ACKNOWLEDGMENT.} This work was supported by the U.S. Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office, Contract No. DE-SC0012704.

6:10 AM S.EN12.08.11

\textbf{The Formation of Li-Mg-Si Zintl Phase by Magnesium Coating on Si Thin-Film as Anode for Lithium-Ion Batteries} Zhifei Li$^{1,2}$, Caleb Stetson$^{1,2}$, Glenn Teeter$^1$, Andrew Norman$^1$, Bertrand Tremolet de Villers$^1$, Yeyoung Ha$^1$, Zoey Huey$^{1,2}$, Sang-Don Han$^1$, Chun-sheng Jiang$^1$, Anthony Burrell$^1$ and Andriy Zakutayev$^1$; $^1$National Renewable Energy Laboratory, United States; $^2$Colorado School of Mines, United States
Si anode with high theoretical capacity has shown its promise as the next generation anode for high energy density lithium ion batteries. The large volume change of Si anode during cycling has been well accepted as the main reason that leads to its poor cycling stability. However, the high reactivity of lithiated Si, namely Li_xSi, is also responsible for the fast consumption of electrolyte and therefore, the quick capacity decay. To address this issue, we coated Si anode with Mg where the Mg can diffuse into the bulk Si anode and involve in the formation of ternary Li-Mg-Si Zintl phase upon lithiation. The ternary Zintl phase had been proved to be more stable toward electrolyte than Li_xSi. The formation of this new phase by Mg coating suppressed the decomposition of electrolyte, altered the solid electrolyte interphase, and resulted in a significantly improved cycling performance of Si anode. This work provides a new approach to tuning the compositions and properties of Si anodes.

6:20 AM S.EN12.08.12
Change in the Crystal Structure of Lithium-Intercalated Graphite at Elevated Temperature Studied by Synchrotron X-Ray Diffraction
Hideaki Oka, Yoshinari Makimura, Chikaaki Okuda, Takamasa Nonaka, Takeshi Uyama and Tsuyoshi Sasaki; Toyota Central R&D Labs., Inc., Japan

The growth of the lithium-ion battery market is being fueled by the expansion of its use in electric vehicles. To achieve long cycle life and high reliability, lithium-ion batteries have to be operated in the limited conditions as for voltage, current, and temperature. Above all, it is important for using lithium-ion batteries safety that understanding and improvement of the thermal stabilities of active materials with electrolyte under elevated temperature. In this study, the thermal stability of the graphite electrode used in Li-ion batteries was studied by in-situ X-ray diffraction (XRD) during elevating the temperature. The in-situ XRD measurements clarified that phase transitions from C_6Li to C_12Li and from C_12Li to graphite occured in the temperature range of 250-305 degree C and 305-320 degree C, respectively, which corresponds to the exothermic behaviors detected by differential scanning calorimetry. The de-lithiation behavior under anomalous elevated temperature might be passed with an intermediate state between C_6Li and C_12Li, which is not observed in electrochemical processes.

6:30 AM *S.EN12.08.13
Emerging Electron Microscopy Techniques for Probing Interfaces in Battery Materials
Miaofang Chi; Oak Ridge National Laboratory, United States

Interfaces play a fundamental role in defining the performance of batteries, regardless of the type of battery configuration. However, the localized nature of interfaces requires high spatial resolution characterization techniques to fully understand their structure and properties. State-of-the-art atomic-resolution and/or in situ scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) are indispensable tools for characterizing the local structure and chemistry of materials but they are difficult to use to measure many properties that dictate the cycling performance of batteries. For example, it is challenging to directly observe the lithium distribution at lattice sites, to probe electrostatic potential drop at interfaces, to measure electronic and ionic conductivity of local features, and to detect interfacial dynamic evolution under in situ electrochemical cycling conditions. Further, current techniques are largely limited to electron-beam irradiation and samples that do not contain liquids. Here, we outline emerging electron microscopy techniques that allow us to overcome these limitations and highlight several recent studies that have been enabled by techniques such as 4D-STEM, monochromated EELS, cryo-STEM, and new integrated in situ stages. The limitations of these techniques and the pitfalls in data interpretations will be discussed. We provide a perspective as to how these methods can be paired to deliver new insights into the static and dynamic behavior of functional interfaces in batteries.

Acknowledgement
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SESSION S.EN12.09: Safety and Sustainable Technologies
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
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5:00 AM *S.EN12.09.01
Battery Safety Enabled by Super-Concentrated Electrolytes
Kang Xu; U.S. Army Research Laboratory, United States
Under the influences from both classical analytical electrochemistry pursuing ideal ionic behavior at infinitely diluted state and classical physical electrochemistry pursuing the most conductive ionicics, the study of non-aqueous electrolytes have been confined within the narrow concentrations around 1 molarity. This confinement was only breached in recent years when investigators discovered that unexpected properties often arise from excessively concentrated electrolytes, benefitting mechanical, thermal, transport, interfacial structure as well as interphasial chemistries. The most extreme examples of the super-concentrated electrolytes include the high voltage (4 V) aqueous electrolytes and non-aqueous electrolytes that enables highly aggressive battery chemistries (Li-metal, high NMC, etc). Aside from their various novelties in physical, transport and electrochemical/interphasial properties, super-concentrated electrolytes enhances the overall safety of batteries, primarily because solvent molecules therein were bound by new liquid structures that never exists previously. In this talk, I will briefly summarize the current status of these battery chemistries.

5:15 AM *S.EN12.09.02
Does Spinel Serve as a Rigid Framework for Oxygen Redox? Xiang-Mei Shi¹, Kosuke Kawai¹, Eriko Watanabe¹, Masashi Okubo¹² and Atsuo Yamada¹²; ¹The University of Tokyo, Japan; ²Kyoto University, Japan

The discovery of a large-capacity cathode material is a major task for developing batteries of high energy density, and an additional oxygen redox capacity has recently been regarded as a new impetus. From the electronic-structure point of view, lithium-rich layered oxides, typical oxygen-redox cathode materials, possess oxide ions with a nonbonding O 2p state along the Li-O-Li coordination axis, which provides the oxygen redox activity. After oxygen oxidation, either a π-type M t2g-O 2p interaction (M: transition metal) or a O-O bond formation should stabilize oxidized oxide ions. However, the layer structure is generally unstable after extracting an excess amount of Li ions, leading to the capacity fade and potential decay upon cycling. Therefore, for achieving the stable additional oxygen-redox capacity, of particular importance is to implement oxide ions with nonbonding O 2p state into a stable host framework against excess Li-ion extraction. As layerd to spinel transformation has been claimed as a origin of a voltage drop and the latter have a stable three-dimensional framework, it is attractive to explore for spinel oxides capable of the oxygen-redox reactions. Here, we diagnose the oxygen-redox activity of spinel oxides with combined experimental and density functional theory (DFT) calculations. Li4Mn5O12 and LiMg0.5Mn1.5O4 is employed as a model material, as its spinel structure is expected to have oxide ions with nonbonding O 2p state owing to the existence of ionic Li⁺ or Mg⁡2⁺ in the framework. The electronic structure change and phase stability during the oxygen-redox reaction is compared with that of a typical Li-rich layered oxide (Li2MnO3).

5:30 AM S.EN12.09.03
Temperature Effect and Thermal Analysis of Battery Package for Harsh Space Environment Amani Alhammadi, Amarsingh Bhabu Kanagaraj, Prerna Chaturvedi, Hamda Alshibli and Daniel Choi; Khalifa University, United Arab Emirates

The main challenge that hinders the use of Li-ion batteries in space applications is its low performance at ultra-low temperatures. This is due to the low ionic conductivity and freezing of the electrolyte which leads to the loss of battery’s capacity. Another challenge is the moisture absorption of the electrodes and polymer electrolyte. In this research, a protective packaged case is designed and fabricated using 3D printing technique to enhance the ionic conductivity and restrict moisture absorption from the surrounding. This pack is made of polyether–ether–ketone (PEEK) which can withstand temperature range from -100 to 260°C and hence improve the ionic conductivity and prevent freezing of the electrolyte. Furthermore, the full cell battery is coated with a protective layer made of polydopamine to decrease the moisture absorption and improve the performance and lifetime of the battery. The battery case is simulated using COMSOL software to study the thermal and mechanical effect under space environment. In addition, the full cell packaged battery will be tested in terms of mechanical, electrical, and electrochemical performance using battery test setup. Moreover, thermal and radiation tests will be conducted in the vacuum thermal chamber to analyze the battery’s performance in harsh space environment. Parameters such as weight, lifetime and capacity loss are taken into consideration.

5:40 AM S.EN12.09.04
Co-intercalation for Increased Performance of Dual-Carbon Battery Using Mixed Salt Electrolyte Tatsumi Ishihara, Kotaro Nakamura, Jun Tae Song and Taner Akbay; Kyushu University, Japan

Long cycle life, high rate properties, sustainable active materials, reduced manufacturing cost, and improved safety aspects of dual-carbon batteries (DCBs) make them promising alternatives for the state-of-the-art rechargeable battery technologies. The DCB chemistry exploits the redox-amphoteric host capability of graphite as both electrodes for Faradaic charge storage
by intercalating active species such as alkaline cations (typically Li+) and fluorinated anions (e.g. PF6-) into anode and cathode respectively. Recently, as part of the quest for elevating discharge potentials of DCBs, intercalation properties of larger sized anions such as bis(trifluoromethanesulfonyl)imide (TFSI-) into the graphitic carbon cathode have been investigated. However, rather low coulombic efficiency values obtained by using the LiTFSI salts in DCBs prove to be a greater challenge.

Co-intercalation of PF6- and TFSI- anions as a result of the use of a mixed salt of LiPF6 and LiTFSI was studied for the increased performance of a dual-carbon battery (DCB). Unlike the fluorine- or the imide-based anions (eg. PF6- and TFSI-), the cluster formation between co-intercalated PF6- and TFSI- in the positive electrode of a dual carbon battery resulted in achieving high discharge capacities with significant increased cycle properties. A reversible discharge capacity of 90 mAh/g-cathode over 350 cycles with no significant degradation is presented. The Coulombic efficiency of almost 100% is reached after the initial 10 cycles and suitable rate property is also observed. F-NMR analysis on graphitic carbon intercalated with PF6- and TFSI suggested the interaction between two anions resulting in the increased stability of the intercalated structure which is also supported by first principles calculations. Gas formation at high potential during charge step is also suppressed by using mixed salt of LiPF6-LiTFSI.

SESSION S.EN12.10: Poster Session: Materials for Safe and Sustainable Electrochemical Energy Storage
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
5:00 AM - 8:00 AM
S-EN12

S.EN12.10.01 Nicotinamide Cofactor as an Energy Storage Compound for Biologically Inspired Rechargeable Batteries Sunghyun Ko1, Jihyeon Kim2, Chanwoo Noh2, Heechan Kim2, Sechan Lee2, Dodam Kim2, Hyeokjun Park2, Gyun Kwon2, Gyeon Son1, Jong Wan Ko2, YoonJoon Jung2, Dongwhan Lee2, Chan Beum Park1 and Kisuk Kang2; 1Korea Advanced Institute of Science and Technology (KAIST), Korea (the Republic of); 2Seoul National University, Korea (the Republic of); 3Korea Institute of Industrial Technology, Korea (the Republic of)

Rising concerns on sustainability have brought great interest for ecofriendly energy storage solutions and motivated searching for sustainable electrode chemistry for lithium ion batteries (LIBs), most widely used portable power sources. Organic materials, which are derived from biomass or naturally abundant resources, are attractive electrode candidates for LIBs due to their minimal environmental footprint. The chemical tunability of organic materials can additionally allow a design flexibility required for electrodes in various types of rechargeable batteries. Especially, exploiting redox-active molecules in biological energy transduction, which have been optimized over many years of natural selection, is an appealing approach to green energy storage combined with the demonstrated efficiency. Biological energy transductions share many aspects with rechargeable battery operation in underlying redox mechanism with respect to unidirectional transportation of charged ions (H+ or Li+) and electrons to a redox-active center, resulting in reversible energy storage. This analogy suggests a potential feasibility for utilizing new redox center from biological reactions to energy storage in rechargeable batteries.

Nicotinamide adenine dinucleotide (NAD+) is one of the most well-known redox cofactors carrying electrons. The redox-active NAD+ motif is involved in over 80 % of all biotransformations and electron transfer reactions in natural systems by carrying charged ions and electrons from one reaction to another. The versatility of NAD+ motif may present promises in its electrochemical activity in other energy storage systems such as LIBs. Nevertheless, the exploration of its applicability as an electrode in conventional LIB setup is not trivial, since its charged state (NAD+) and the dissolved nature are not compatible with the electrode fabrication requirements, where active compounds are generally in neutral state and ready for process into solid electrode. While significant portion of the energy carrying molecules are in charged states and/or dissolved states in the biocells, a general fixation strategy would aid in expediting the exploration of these bio redox molecules.

Herein, we exploited the NAD+ motif, one of the most versatile redox centers in nature, to facilitate reversible electrochemical energy storage in LIB system for the first time. To exploit the redox reaction of NAD+ motif in LIBs, nicotinamide cofactor was modified into a simple structure bearing the redox-active part to produce nicotinamide analogue (mNAD+). The charged mNAD+ were crystallized using counter anions such as I-, Br-, and Cl-, resulting in a neutral and solid-state powder. It is demonstrated that these NAD+-derivatives (mNAD-X, X=I-, Br-, and Cl-) are capable of reversibly facilitating lithium coupled electron transfer in solid electrode form, exhibiting the intrinsic redox capability of NAD+.
Combined experimental and theoretical calculations revealed that mNAD-X retains the intrinsic redox activity of natural NAD\(^+\) motif, accompanying lithium coupled electron transfer which is similar to the proton-coupled electron transfer mechanism in the biological systems. Furthermore, the operating voltage and capacity are tunable by altering the anchoring anion species without modifying the redox center itself. This work not only demonstrates the redox capability of NAD\(^+\), but also suggests that anchoring the charged molecules with anion incorporation is a viable new approach to exploit various charged biological cofactors in rechargeable battery systems.

**S.EN12.10.02**

**Bio-Templated Tubular MCo_2O_4 (M= Mn, Ni, Cr) Microstructure and Their Electrochemical Performance**

Deepa Guragain¹, Camila Zequine², Sanjay R. Mishra¹ and Ram K. Gupta²; ¹University of Memphis, United States; ²Pittsburg State University, United States

Binary oxides with novel nanoarchitectures are increasingly explored for their application in energy storage devices. The nanoarchitecture of these oxides is usually varied via synthesis route, which usually requires complex technologies, expensive equipment, and harmful organic reagents or surfactants, which might further hinder their application. Hence, it is highly desirable to explore facile synthesis strategies, which are cost-effective, simple, and environmentally friendly to get “green” nanomaterials. Recently, bio-templating has emerged as a promising technique for the synthesis of Co_3O_4 capacitors [i]. Nature offers us various and excellent bio-templates[ii],[iii],[iv] such as bamboo, pig bone, crab shells, lotus pollen grains, bacteria [v], leaf [vi], sorghum straw [vii], butterfly wing [viii], jute fibers [ix], and cotton [ix]. Such bio-templates exhibit precise widths and lengths, complex exterior and interior surfaces, and uniform geometries, all of which have inspired researchers to produce multiscale hybrid inorganic materials that exhibit hierarchical morphologies.

In this work, we present a comparative study of the electrochemical performance of tubular MCo_2O_4 (M= Mn, Ni, Cr) microstructures prepared using cotton fiber as a biotemplate. The as-obtained templated MCo_2O_4(M= Mn, Ni, Cr) structures inherit the morphology and microstructure of cotton fiber. The electrochemical performance of the electrode made up of tubular MCo_2O_4(M= Mn, Ni, Cr) structure was evaluated in 3M KOH aqueous electrolytes. The large-surface-area of tubular MCo_2O_4(M= Mn, Ni, Cr) microstructures has a noticeable pseudocapacitive performance with a capacitance of 161 F/g, 190 F/g, and 231 F/g at 1 A/g current density and 378.13 F/g, 407.16 F/g, and 403.39 F/g at 2 mV/s scan rate for MnCo_2O_4, NiCo_2O_4, and CrCo_2O_4 respectively. These obtained tubular MCo_2O_4(M= Mn, Ni, Cr) microstructure display superior electrochemical performance in aqueous 3M KOH electrolyte with peak power density reaching 295.5 W/Kg, 296.3 W/Kg, and 293.5 W/Kg, and energy density 7.8 Wh/kg, 9.3 Wh/kg, and 11.1 Wh/kg, for MnCo_2O_4, NiCo_2O_4, and CrCo_2O_4 respectively. The superior performance of tubular MCo_2O_4(M= Mn, Ni, Cr) microstructure electrode is attributed to their high surface area and adequate pore volume distribution, which allows effective redox reaction and diffusion of hydrated ions.


Facile Synthesis of Bio-Templated Tubular Co$_3$O$_4$ Microstructure and Its Electrochemical Performance in Aqueous Electrolytes

Deepa Guragain, Camila Zequine, Tej P. Poudel, Dipesh Neupane, Sanjay R. Mishra and Ram K. Gupta; 1University of Memphis, United States; 2Pittsburg State University, United States

The preparation of transition metal oxides has attracted the interest of many research groups in recent years because of their unique properties and envisioned applications in electronics, optics, magnetic materials, and energy storage devices. Co$_3$O$_4$ belongs to a class of complex oxides known as spinels with the chemical formulas of AB$_2$O$_4$ in which A ions are generally divalent cations occupying tetrahedral sites, and B ions are trivalent cations in octahedral sites. Co$_3$O$_4$ has been explored for its good pseudocapacitance along with other established materials, in which charge is stored using redox-based Faradic reactions. Many synthesis techniques such as solvothermal synthesis\[i\], sol-gel method \[ii\], electrospinning method \[iii\] and lithography technique \[iv\], a hydrothermal technique\[v],[vi], have been explored for the synthesis of nanostructured materials. However, many of these strategies generally require complex technologies, expensive equipment, and harmful organic reagents or surfactants, which might further hinder their application. In the present work, we used a one-step facile procedure for the synthesis of biomorphic Co$_3$O$_4$ using cotton fiber as a bio-template.

Template-assisted facile synthesis of tubular Co$_3$O$_4$ microstructures and its electrochemical performance was studied to understand its use as a potential electrode material for supercapacitors. Tubular porous Co$_3$O$_4$ microstructures were synthesized using cotton fibers as bio-template. The as-obtained templated Co$_3$O$_4$ structure inherits the morphology and microstructure of cotton fiber. The electrochemical performance of the electrode made up of tubular Co$_3$O$_4$ structure was evaluated in 3M KOH, NaOH, and LiOH aqueous electrolytes. The large-surface-area of tubular Co$_3$O$_4$ microstructure has a noticeable pseudocapacitive performance with a capacitance of 401 F/g at 1 A/g and 828 F/g at 2 mV/s, a Coulombic efficiency averaging ~100%, and excellent cycling stability with capacitance retention of about 80% after 5,000 cycles. Overall, the tubular Co$_3$O$_4$ microstructure displayed superior electrochemical performance in 3M KOH electrolyte with peak power density reaching 5,500 Wh/kg and energy density exceeding 22 Wh/kg. The superior performance of tubular Co$_3$O$_4$ microstructure electrode is attributed to its high surface area and adequate pore volume distribution, which allows effective redox reaction and diffusion of hydrated ions. The facile synthesis method can be adapted for preparing various metal oxide microstructures for possible applications in catalysis, electrochemical, sensors, and fuel cells applications.

S.EN12.10.04
Morphological and Theoretical Study of Ni$_{1-x}$Ca$_x$Co$_2$O$_4$ (0 ≤ x ≤ 0.8) Nanostructures as High-Performance Electrode Materials for Supercapacitors
Deepa Guragain$^1$, Camila Zequine$^2$, Romakanta Bhattarai$^1$, Jonghyun Choi$^2$, Ram K. Gupta$^2$ and Sanjay R. Mishra$^1$; $^1$University of Memphis, United States; $^2$Pittsburg State University, United States

Nowadays the binary metal oxides are highly used as supercapacitor electrodes in energy storing devices. Particularly NiCo$_2$O$_4$ has shown promising electrocapacitive performance with high specific capacitance and energy density. The electrocapacitive performance of these oxides largely depends on their morphology and electrical properties governed by their energy band-gaps and defects. The morphological structure of NiCo$_2$O$_4$ can be altered via synthesis route while energy band-gap could be altered by doping. Also, doping can enhance crystal stability and bring in grain refinement, which can further enhance the much-needed surface area for high specific capacitance. In view of the above, this study evaluates the electrochemical performance of Ca-doped Ni$_{1-x}$Ca$_x$Co$_2$O$_4$ (0 ≤ x ≤ 0.8) compounds. The Ni$_{1-x}$Ca$_x$Co$_2$O$_4$ samples were prepared via a facile and cost-effective hydrothermal technique by varying Ca to Ni molar ratio. Physical, morphological, and electrochemical properties of Ni$_{1-x}$Ca$_x$Co$_2$O$_4$ were observed on the variation of Ca. The increase of Ca concentration in Ni$_{1-x}$Ca$_x$Co$_2$O$_4$ leads to the morphological transformation from nanoplates to urchin-like structure with an increase in the surface area reaching up to 73.2 m$^2$/g for x=0.2. The higher specific capacitance of 247.5 F/g at a current density of 1 A/g, 934.4 F/g at 2 mV/s scan rate, the energy density of 14.8 Wh/kg and power density of 136.3 W/kg in 3M KOH electrolyte was observed for x = 0.6 sample. An increased retention capacity ~255% measured at 5 A/g current density and Coulombic efficiency of 99%. The density functional theory (DFT) calculations of the electronic density of states identified Ni$_{1-x}$Ca$_x$Co$_2$O$_4$ with optimal band-gap varies from 2.67 eV to 3.88 eV for x=0 to x=0.8. Such impressive electrocatalytic activity results in the high intrinsic electronic conductivity and can largely improve the interfacial electroactive sites as well as charge transfer rates. This work of doping NiCo$_2$O$_4$ by calcium is very novel which will stipulate promising applications for electrodes in future supercapacitors.

S.EN12.10.06
NOEL—Innovative Nanostructured Electrodes for Energy Storage Concepts
Maria Bernechea$^1$, M. Pilar Lobera$^{1,2}$, Robert Dominko$^4$, Alen Vizintin$^4$, Elzbieta Frackowiak$^5$ and Krzysztof Fic$^5$; $^1$INA - Institute of Nanoscience of Aragon, Spain; $^2$Networking Biomedical Research Centre of Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), Spain; $^3$ARAID, Spain; $^4$National Institute of Chemistry, Slovenia; $^5$Poznan University of Technology, Poland

Energy Storage Systems (ESS) will play a central role in reducing fossil fuel consumption and greenhouse gas emissions by providing solutions to store energy produced from renewable sources and to implement electrical vehicles. Graphite is the traditional material employed in standard rechargeable batteries or hybrid electrochemical capacitors, but it shows restrictions because of its limited intrinsic capacity, moderate Li-ion intercalation and capacity rate. Also, Li and Co, all standard materials for hybrid capacitors and Li-ion batteries, are limited resources, and the European Union (EU) is dependent on external supply.

To solve these shortcomings, NOEL aims at developing new, low-cost and environmentally friendly layered semiconductor-carbon composites for their use as innovative electrodes in the next generation of batteries or supercapacitors. Specifically, NOEL will provide new carbon substrates and carbons decorated with layered sulfide nanoparticles and will test their performance as electrodes for supercapacitors and post-Li batteries (Na, Mg, or Ca), looking for improved performance, low price, high material availability being locally produced in EU, and environmentally friendly properties.

For that purpose, NOEL consists of 2 European universities (Zaragoza University, UNIZAR, in Spain, and Poznan University of Technology, PUT, in Poland), and 1 European research institution (National Institute of Chemistry, NIC, in Slovenia). The balancing expertise includes development and characterization of nanomaterials (UNIZAR), and manufacture and testing of batteries (NIC), or supercapacitors (PUT).

S.EN12.10.07
Nanocoﬁned Iron (III) Fluoride Cathode in NaDFOB Electrolyte towards High-Performance Sodium-Ion Batteries
Zifei Sun, Wenbin Fu, Michael Liu, Peilin Lu, Enbo Zhao, Alexandre Magasinski, Mengting Liu, Shunrui Luo, Jesse McDaniel and Gleb Yushin; Georgia Institute of Technology, United States

Iron (III) fluoride (FeF$_3$) is considered as a potential cathode for sodium-ion batteries (SIBs) due to its high capacity and low cost. However, the particle pulverization upon cycling generally results in rapid degradations in its structure and capacity.
Here, we introduce a free-standing nanoconfined FeF$_3$ cathode and a novel electrolyte salt sodium-difluoro(oxalato)borate (NaDFOB) for SIBs. The assembled cells show high discharge capacity up to ~230 mAh g$^{-1}$ at the rate of 20 mA g$^{-1}$ (~200 mAh g$^{-1}$ at 100 mA g$^{-1}$) and capacity retention up to ~70% after 100 cycles, which represent the best results reported on FeF$_3$ in Na-ion electrolytes. The achieved high performance can be attributed to the synergic protection provided by the nanoconfined FeF$_3$ electrode and the NaDFOB electrolyte. Post-mortem analysis and quantum mechanics show that DFOB anion facilitated the formation of a thin cathode electrolyte interphase (CEI) at the surface of FeF$_3$-carbon nanofibers (CNFs) via oligomerization.

S.EN12.10.08
Upgrading Coal to Multifunctional Graphene-Based Materials by Direct Laser Scribing Chi Zhang and Jian Lin; University of Missouri-Columbia, United States

Despite much progress, developing a cost-effective and environmental-friendly method to upgrade earth-abundant coal into high value-added products is still a grand challenge. Here, we report a one-step facile approach to synthesize graphene based materials from coal under ambient conditions via direct CO$_2$ laser scribing. The obtained laser scribed graphene from coal (C-LSG) has been well characterized, showing good electrical conductivity (12U/square), high electrochemical sensitivity and ion storage properties. These properties make C-LSG a multifunctional material for applications in Joule heating, electrochemical dopamine sensing, and supercapacitors. Moreover, when electrochemically deposited with FeNi hydroxide, the hybridized FeNi/C-LSG shows impressive electrocatalysis performance toward oxygen evolution reaction. As such, this direct laser scribing of coal into graphene based materials can not only potentially expands new business opportunities by adding coal into the value-chain of industries that usually do not use coal as the starting materials in their manufacturing processes but also brings down the cost of the graphene based materials, which would make their deployment in various fields more economically attractive.

S.EN12.10.10
Facile Fabrication of a Polyaniline Electrode with a Hierarchical, 3-D Porous Network for High Performance Supercapacitors Hyung-Jun Koo$^1$, Ji-Hye Kim$^1$, Ju-Hee So$^2$ and Sung-Kon Kim$^3$; 1Seoul National University of Science & Technology, Korea (the Republic of); 2Korea Institute of Industrial Technology, Korea (the Republic of); 3Chonbuk National University, Korea (the Republic of)

Since any electrochemical reactions occur at the interface between electrodes and electrolytes, an electrode with well-defined open pores and high surface area is preferred for an efficient electrochemical system, such as supercapacitors and batteries. Recently, it has been reported that a conducting polymer, polyaniline, can be crosslinked by phytic acid, to form a conducting hydrogel with hierarchical open pores. Here, we present a facile fabrication method of a conducting porous electrode, by a doctor-blading technique of the polyaniline hydrogel paste and successive dehydration process. We carefully investigated the effect of compositions in preparation of PANI on its pore morphology and electrical property. It turns out that as initiator/crosslinker contents increase or monomer content decreases, the PANI conducting hydrogel has denser morphology with decreased pore size, resulting in higher electrical conductivity. Notably, hierarchical pores, ranging from 300 to 1 micrometers in size, are well developed, even in the dense porous PANI film. Due to its characteristic pore morphology and redox activity, the PANI film could serve as an efficient electrode for a pseudo-capacitor. In the 3-electrode configuration, the porous PANI electrode prepared at the optimized composition, in the pristine form without any conducting additive, exhibited ~690 F/cm$^3$ of volumetric capacitance, which is much higher than those of the PANI based capacitors reported so far. Finally, we fabricated a practical capacitor with two symmetric PANI hydrogel electrodes, which shows 110 mF/cm$^3$ of volumetric capacitance with improved cycle stability of 80% retention rate for 5000 cycles.

S.EN12.10.14
Molten Salt Catholytes for Low-Temperature Molten Sodium Batteries Leo J. Small, Stephen Percival, Martha M. Gross and Erik D. Spoerke; Sandia National Laboratories, United States

Molten sodium batteries offer a promising technology for grid scale energy storage. The molten sodium anode minimizes dendrite formation, while the elevated operating temperature minimizes hazards associated with assembly of MWh capacities at room temperature. Typical molten sodium battery chemistries such as Na-S and Na-NiCl$_2$ (ZEBRA) operate near 300 and 200 °C, respectively. Driving operating temperatures down to 100 °C would decrease operating costs, minimize materials aging effects, and enable use of low temperature polymeric seals. Successful development of a molten sodium battery that operates near 100 °C, however, requires significant reengineering of the catholyte. Besides being molten at 100 °C, such a catholyte must possess (1) electrochemically reversibility, (2) chemical stability, (3) high ionic conductivity, and (4) minimal reactivity to molten sodium metal. Herein we describe the development of fully inorganic molten salt catholytes based on...
mixture of NaI and group 13 halide salts that satisfy these requirements. The NaI enables use of the facile, energy-dense I\textsuperscript{-}/I\textsubscript{3} redox couple, while targeted group 13 halide salts engender sufficiently low melting points over a wide range of NaI concentrations. These molten salts demonstrate good electrochemical I\textsuperscript{-}/I\textsubscript{3} reversibility and at high I\textsuperscript{-} concentrations near 100 °C, without use of any organic solvent. We characterize the ionic conductivity and electrochemical kinetics of these salts for a variety of compositions and electrode materials. Full cell cycling using a molten sodium anode and a ceramic NaSICON separator demonstrates promising performance and indicates points for further electrolyte refinement. Together, these molten salts offer a pathway for safe, reliable, grid-scale energy storage.


S.EN12.10.21
Fabrication and Characterization of Glassy Carbon on Flexible Substrate Interdigitated Supercapacitor Omar Nunez Cuacuas, Sammuel Kassegne and Surabhi Nimbalkar; San Diego State University, United States

Improved energy storage technologies have received intense attention since there is a fast-growing market for portable electronic devices such as the internet of things. Micro-supercapacitors possess a remarkable feature of high electrochemical performance and relatively small volume in which they can reach high power density and fast charge-discharge rates. In contrast to batteries, these next-generation energy storage devices are fast, efficient and environmentally friendly with longer life cycles without losing performance. We developed a novel integrated, flexible glassy carbon micro-supercapacitor technology with 30 interdigitated fingers as seen in figure 1. We compacted the complete electrical routing path and contact pads within the device’s area, utilizing through-via bottom electrodes. The glassy carbon electrode achieved a surface area of 0.1655 and mass of 0.278 mg. The device showed a specific capacitance of 963.979 uf/cm\textsuperscript{2} for a scan rate of 0.1 v/s, which is greater than the values reported for vertically aligned carbon nanotubes. In addition, it achieved an energy density of, and a power density of higher than those reported from multilayer reduced graphene oxide [2].


S.EN12.10.24
Ni\textsubscript{1-x}Al\textsubscript{x}Co\textsubscript{2}O\textsubscript{4} (0 ≤ x ≤ 0.8) Nanostructures as High-Performance Supercapacitor Applications—Theoretical and Morphological Study Deepa Guragain1, Jonghyun Choi2, Wang Lin2, Subash C. Bhandari1, Ram K. Gupta2 and Sanjay R. Mishra1, 1The University of Memphis, United States; 2Pittsburg State University, United States

Nowadays nickel cobaltite, NiCo\textsubscript{2}O\textsubscript{4} with excellent electrochemical properties has become good source of energy storage electrode for electrochemical supercapacitor. NiCo\textsubscript{2}O\textsubscript{4} has shown promising electrocapacitive performance with high specific capacitance and energy density. The electrocapacitive performance of these oxides highly depends on their morphology and electrical properties governed by their energy band-gaps and defects. The variation of morphological structure can be occur via synthesis route, on the other hand energy band-gap could be changed by doping. Also, doping can enhance crystal stability and bring in grain refinement, which can further enhance the much-needed surface area for high specific capacitance. This study evaluates the electrochemical performance of Al-doped Ni\textsubscript{1-x}Al\textsubscript{x}Co\textsubscript{2}O\textsubscript{4} (0 ≤ x ≤ 0.8) compounds. These Ni\textsubscript{1-x}Al\textsubscript{x}Co\textsubscript{2}O\textsubscript{4} samples were prepared via a hydrothermal technique by varying Al to Ni in molar ratio. Physical, morphological, and electrochemical properties of Ni\textsubscript{1-x}Al\textsubscript{x}Co\textsubscript{2}O\textsubscript{4} were observed on the variation of Al. The characterization was performed by using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Quantachrome Instrument, and X-Ray Photoelectron Spectroscopy (XPS). XRD confirms the formation of phase pure Ni\textsubscript{1-x}Al\textsubscript{x}Co\textsubscript{2}O\textsubscript{4} (0 ≤ x ≤ 0.8). The increase of Al concentration in Ni\textsubscript{1-x}Al\textsubscript{x}Co\textsubscript{2}O\textsubscript{4} leads to the morphological transformation from urchin like spheres to nanoplates like structure with an increase in the surface area reaching up to 107.2 m\textsuperscript{2}/g for x=0.4. XPS give the elemental composition of Al doping Ni\textsubscript{1-x}Al\textsubscript{x}Co\textsubscript{2}O\textsubscript{4} (0 ≤ x ≤ 0.8). The electrochemical performance was observed using Cyclic Voltammetry (CV), Galvanostatic Charge Discharge (GCD), and Electrochemical Impedance Spectroscopy (EIS) measurement. The higher specific capacitance of 511.5 F/g at 2 mV/s scan rate, 267.9 F/g at a current density of 0.5 A/g, and the energy density of 12.4 Wh/kg in 3M KOH electrolyte was observed for x = 0.0 sample. The power density of 4660.4 W/kg was observed for x = 0.8 sample. The capacitance retention ∼97%, 108.52% and Coulombic efficiency of 100%,
99.24% for x=0.0 and x=0.8 respectively. All these results indicate Al dope NiCo2O4 composites electrode shows promising electrocatalytic activity results in the high intrinsic electronic conductivity, can largely improve the interfacial electroactive sites, increase charge transfer rates and help to stabilize the structure of compound.

**S.EN12.10.25**

*Synthesis of NiCo2O4 Nanoparticles Decorated with g-C3N4 by Using Urea as a High-Performance Electrode Material for Supercapacitor*

Deepa Guragain, Subash C. Bhandari and Sanjay R. Mishra; University of Memphis, United States

Transition metal oxides have been extensively studies as an electrode material for the energy storage devices including fuel cell, Li-ion batteries, and electrochemical capacitors. Nowadays, it has been found that ternary metal oxides with two different metal cations exhibit much higher electrochemical activities because of their complex chemical composition and effect of multiple metal ions [[1]]. NiCo2O4 urchin like Nano-flower are decorated by graphitic carbon nitride (g-C3N4). Graphitic carbon nitride is a graphene derivative, has been explored due to its interesting electronic feature, low price, and high environmental-friendly features [2], [3]. We have prepared first NiCo2O4 by hydrothermal method and decorated NiCo2O4 by g-C3N4 composite material by calcination of urea. The structural property of NiCo2O4 was confirmed by X-ray diffraction (XRD) and found phase pure crystalline structure. On the other hand, presence of g-C3N4 is confirmed by Scanning Electron Microscopy (SEM) which show the NiCo2O4 with g-C3N4 have thicker urchin Nano-flowers compare to NiCo2O4 without it. X-ray Photoelectron Spectroscopy (XPS) confirm the presence of graphitic carbon on NiCo2O4 composition. The obtained surface area by using Quanta-chrome surface area analyzer is 40.1 m²/gm for NiCo2O4 and 63.7 m²/gm for NiCo2O4 decorated with g-C3N4. Higher surface area could provide more channels for the access of hydrated electrolyte ions, so we can assume that g-C3N4 decorated NiCo2O4 have shown better electrochemical performance compare to NiCo2O4 alone. The electrochemical performance was observed using Cyclic Voltammetry (CV), Galvanostatic Charge Discharge (GCD), and Electrochemical Impedance Spectroscopy (EIS) measurement. The higher specific capacitance of 601 F/g and 712 F/g at 2 mV/s scan rate, specific capacitance of 289 F/g and 394 F/g at a current density of 0.5 A/g, and the energy density of 13 Wh/kg and 14.5 Wh/kg observed for NiCo2O4 and g-3N4 decorated NiCo2O4 respectively, when measure in 3M KOH electrolyte. Furthermore, the observed power density of 4740 W/kg and 5010 W/Kg, capacitance retention ∼97% and 99% and Coulombic efficiency of 97% and 99.5% for NiCo2O4 and g-3N4 decorated NiCo2O4 respectively. This project will be promising for future energy storing devices.


**S.EN12.10.28**

*Fabrication and Characterization of Flexible MWCNTs/LTO Nanocomposites-Based Electrodes for Battery Applications*

Prerna Chaturvedi1, Amarsingh Bhabu Kanagaraj1, Aman Alhammadi1, Mariam S. Al Nahyan1, Hamda Alishibli1, Boohyun An1, Sultan Al Dahmani2, Hamed Fadaq2 and Daniel Choi1; 1Khalifa University of Science and Technology, United Arab Emirates; 2United Arab Emirates Space Agency, Space Missions’ Science and Technology Directorate, United Arab Emirates

The investigation and development of flexible power sources has motivated the development of flexible, lightweight, binder and current-collector-free electrodes for Li-ion batteries (LIB). For the fabrication of conventional LIB electrode, binder and current collector are introduced to inhibit the collapse of the active materials and maintain the electrode conductivity, respectively. The usage of binders and current collectors contributes nothing but dead weight to the lithium storage, which decreases the energy density of LIBs. Free-standing carbon nanotube ‘buckypaper’ can be fabricated by using both single-walled carbon nanotubes and multi-walled carbon nanotubes (MWCNTs), and their composites with other active electrode materials and then can be used as working electrodes for LIBs. Compared with conventional electrode material in the bulky form, free-standing paper type electrodes have several advantages. First of all, with the removal of the binders and current
collector, the dead weight of an electrode is decreased, leading to the increase of usable capacity and specific energy density for the overall battery design. Secondly, the ease of handling the ‘buckypaper’ makes them readily shaped into various forms required in a variety of flexible and lightweight electronic devices. Here, we are proposing the fabrication of free-standing, flexible and foldable MWCNTs/ lithium titanate oxide (Li4Ti5O12, LTO) based composite ‘buckypaper’ by a facile, scalable, cost-effective and environmental friendly surface-engineered tape casting (SETC) method. The SETC technique has several advantages such as tunable length, thickness, density, composition and implementation in both batch and roll to roll process. The composite ‘buckypaper’ is demonstrated as anode material for LIB. Electrical conductivity was found to be $4.4 \times 10^2$ Scm$^{-1}$ at room temperature. The composite electrode shows the specific capacity of $\sim 150$ mAhg$^{-1}$ at 0.2 C rate which is mainly attributed to enhanced electric and ionic transfer during electrochemical reactions.

Acknowledgements
This project is part of the implementation plan for the United Arab Emirates Space Agency’s ST&I Roadmap and it falls under Level 1 ST&I area of "space power and energy storage” and level 2 "energy storage”. The project is aimed at developing enabling technologies for promising mission and system concept; in particular, an in-house prototype of lithium-ion battery. The project can potentially result in a commercially viable lithium-ion battery technology for spacecrafts/satellites. This work is funded by the United Arab Emirates Space Agency, Space Missions’ Science and Technology Directorate, Reference M04-2016-001.

S.EN12.10.32
Fabrication of Freestanding Mn$_2$O$_3$ Web Electrode for Supercapacitor Applications
Molly Brockway and Jack L. Skinner; Montana Tech, United States

Supercapacitors have the potential to bridge the gap between traditional capacitors and secondary batteries, providing high power and energy densities that may be used for clean energy storage, hybrid vehicles, and other applications. Manganese oxides, including Mn$_2$O$_3$, are inexpensive, environmentally benign materials that have shown promising performances as supercapacitor electrodes. Inherent low conductivity limits application of Mn$_2$O$_3$ in bulk form; however, nanostructured oxides demonstrate enhanced charge-transfer capabilities that render them feasible electrode materials. Additionally, the increased specific surface areas of nanomaterials provide a route for further enhancement of electrode performance, as electrochemical capacitors store charge through surface interactions with the electrolyte. However, in the fabrication of electrodes from nanostructured manganese oxides, the active materials are mixed with binders and conductive agents before pasting onto a charge-collecting substrate. By eliminating additives, mass can be minimized, and the specific capacitance of assembled devices can be improved. Free-standing web electrodes have been reported in several materials systems but have primarily been carbon-fiber based. A similarly independent structure for manganese oxides may improve performance to allow for enhanced widespread use.

In this work, a free-standing Mn$_2$O$_3$ web electrode is fabricated directly onto a charge collector using a facile, two-step electrospinning and thermal treatment process. To fabricate freestanding web electrodes, polymer fibers containing manganese salts are electrospun directly onto foil charge collecting substrates. The fibers are calcined in air to remove the carrier polymer and convert the manganese salts to an oxide. X-ray diffraction is used to confirm the oxide phase produced during calcination so that comparison of electrochemical performance to literature values may be performed. The fabricated electrodes are imaged with scanning electron microscopy; fiber mat morphology and structure are qualitatively observed, while quantitative image analysis is used to calculate the active mass of oxide in the electrodes. The web electrodes are tested in an electrochemical system using cyclic voltammetry and galvanostatic charge-discharge to measure specific capacitance and capacity fading over many cycles. Contact angle measurements are performed to analyze electrode wettability and determine whether poor wettability and the accompanying reduced interfacial area present a barrier to optimized capacitance. After electrochemical cycling, the electrodes are again imaged with electron microscopy, and morphological changes are qualified with electron microscopy and comparison to the as-fabricated structures. Electrodes prepared using pre-calcination processing steps such as hot-pressing and chemical melting are examined alongside untreated fiber mats to determine the effects of multiple processing steps on final manganese oxide electrode morphology and performance.

S.EN12.10.33
Decoding the Oil Dependent Properties of Soot’s Composition and Optimization Strategies for Its Application in EDLC Supercapacitors
Anurag Tyagi$^1$, Manish Gupta$^1$, Chetna Gola$^2$, Surender K. Sharma$^1$, Vivek Shukla$^1$ and Chhaya Ravikant$^1$; $^1$Gautam Buddha University, India; $^2$Indira Gandhi Delhi Technical University for Women, India

EDLC supercapacitors have drawn wide-ranging consideration and significant scientific interest in recent years due to their rapid charging and discharging capabilities, high energy density, large capacity and better performance in terms of...
Supercapacitors are emerging as an alternative to batteries particularly for applications where rapid charging/discharging is needed. Another reason for their advent is their increased energy density that is approaching to the leading competitive technology of lithium ion battery. However the major drawback of lithium-ion cell is its electrochemistry that causes the rapid degradation in its performance in addition to its high failure rate that puts the user at high risk. On the other hand the energy storage mechanism of EDLC supercapacitors does not involve any electrochemical reaction therefore it offers more charging discharging cycles and more safe operation compared to Li-Ion batteries. However a key component of their performance is activated carbon whose electrical and morphological property plays a crucial role in governing the performance of supercapacitor. The newer techniques to synthesize activated carbonaceous material having a precise control on their morphological and electrical properties could be more useful for improvement in their capacity and energy density. In present investigations use of carbonaceous materials with different dimensions and aspect ratio obtained from soot generated by controlled burning of various oils derived from plant/animal sources such as coconut oil, mustard oil, olive oil, wax, kerosene etc are explored for their application in EDLC supercapacitor. A systematic study has been carried out to understand the dependence of soot’s composition and its properties on composition of oil and further optimizing the properties of as obtained soot by several measures including its activation to accomplish the improved performance. Although the present study is focused on supercapacitor application, the work may have broad technological scope because the soot synthesized in this work has potential to be used in various other applications also such as sensors, conductive additives for EMI shielding applications etc.

3D-Printed Flexible Energy Storage for Soft Robotics Christian Romero; University of Bristol, United Kingdom

Novel methods to fabricate bendable and stretchable energy storage devices with improved performance for flexible and wearable electronics are of great current interest. Scalable manufacturing procedures are crucial for practical application in the fabrication of complete functional electronic devices.[1] Here we report a scalable hybrid fabrication process of 3D printing combined with laser engraving to construct highly flexible and stretchable supercapacitors. CAD-designed supercapacitors were manufactured with a customized commercial 3D-printer equipped with a 460 nm commercial laser. In addition, we present our route to the development, formulation and preparation of the main components required for a fully 3D-printed flexible and stretchable supercapacitor. A range of functional 3D-printable inks were developed to enable printing of the current collectors, electroactive electrode materials, the electrolytes, as well as the flexible and stretchable housing. In addition to the development of such inks, we have combined printing with laser-scribing of the functional inks. Specifically, high areal capacitance is achieved with conductive current collectors obtained by simple laser-scribing reduction of graphene oxide (GO) flakes in a 3D-printed polyethylene oxide (PEO)/GO-based material.[2],[3] The resulting reduced GO-based 3D microstructures are transferred onto a commercial UV-curable silicon rubber to obtain flexible current collectors.[4] The flexible conductive collectors were coated with a 3D-printed PEO/polyaniline-based electroactive material.[5] These component are integrated with a polyvinyl alcohol/sulphuric acid-based gel electrolyte to obtain a flexible and stretchable supercapacitor.

References:

Impacts of Oxygen on the SEI Formation and Electrochemical Cycling of Si Anodes Zhifei Li, Glenn Teeter, Anthony Burrell and Andriy Zakutayev; National Renewable Energy Laboratory, United States

Si anodes are one of the most promising anodes for the next generation high energy density lithium-ion batteries (LIBs) because of its high theoretical capacity, low operating potential and high abundance of Si. However, the large volume expansion and continuous electrolyte consumption during lithiation and delithiation leads to a poor cycling performance of Si anodes. It is critical to understand how the electrolyte is consumed, how to stabilize the interface and form a stable solid electrolyte interphase (SEI) in order to develop Si anodes with good cycling stability. Oxygen is almost inevitable in Si anodes where the surface of Si forms a native oxide layer when it exposes to air. In addition, the different preparation
processes of Si anodes may also lead to different levels of oxygen content [1,2]. Thus, a better understanding about how the oxygen would affect the surface SEI formation, (ir)reversible capacity, and electrochemical cycling of Si anodes is needed.

In this study, we synthesized a series of model Si anodes with different oxygen levels by sputtering on Cu foils, to investigate SEI formation and electrochemical cycling in GEN-2 electrolyte with FEC additive in half-cells configuration with Li-metal counter electrode. The obtained Si anodes clearly showed different lithiation/delithiation behaviors and cycling performance with different oxygen level, where higher oxygen level leads to a longer plateau at around 0.6 V during the first lithiation and better cycling performance. Via comprehensive in situ and ex situ characterization techniques, such as XPS, AFM and EQCM, we revealed how oxygen affects the SEI formation and electrochemical performance of Si anodes.


S.EN12.10.38
Role of Thin and Uniform Solid Electrolyte Interface in High-Rate Sodium Storage of Sb2Te3/CNT and Sb2Se3/CNT Composite Anodes Muhammad Ihsan Ul Haq, Baoling Huang and Jang Kyo Kim; The Hong Kong University of Science and Technology, Hong Kong

Metal chalcogenides (MCs) are widely studied for low cost and high performance sodium ion batteries (SIBs).[1-3] However, the thickness and morphology of solid electrolyte interface (SEI) formed on MC based electrodes still remain to be elucidated because the formation of SEI is highly sensitive to ambient conditions and electron beam in vacuum.[4] Herein, two Sb-based MCs, Sb2Te3 and Sb2Se3, are selected to study the SEI formed on their pristine particles and composites assembled with functionalized CNTs through high energy ball milling. The ex-situ cryogenic electron microscope (cryo-EM) is employed to distinguish the morphologies and dimensions of the SEI layers formed on pristine Sb2Te3, Sb2Se3 and their composite electrodes. Uniform and thin SEI layers of ~19.1 and ~35.7 nm are observed for the Sb2Te3/CNT and Sb2Se3/CNT composite electrodes, respectively. In contrast, irregular SEI films with maximum thicknesses of ~67.3 and ~71.8 nm are revealed for the pristine Sb2Te3 and Sb2Se3 electrodes, respectively. The ex-situ electrochemical impedance spectroscopy (EIS) analysis corroborates the effect of thin and uniform SEI on reduced charge transfer resistances of 126.9 and 290 Ω for the Sb2Te3/CNT and Sb2Se3/CNT composite electrodes, which are much lower than 556.1 and 466.3 Ω of the pristine Sb2Te3 and Sb2Se3 counterparts, respectively. The significant increase in electrochemical kinetics of the composite electrodes results in outstanding high-rate capabilities. The sodium-ion full cells (SIFCs) are assembled by pairing the Sb2Te3/CNT and Sb2Se3/CNT composite anodes with a Na3V2(PO4)2F3 cathode, which deliver high energy densities of ~229 and ~176 Wh kg⁻¹, respectively, at 0.5 C together with remarkable power densities of 5384 W kg⁻¹ at 40 C and 5760 W kg⁻¹ at 80 C. These findings may shed new insight into the important role played by the optimal SEI layers on the rationally designed composite electrodes in giving rise to high-rate capabilities.

S.EN12.10.39
Three-Dimensional Sn-Based Anodes for All-Solid-State Rechargeable Batteries Arailym Nurpeissova¹, Gulnur Kalimuldinav² and Zhumbay Bakenov¹,²;¹National Laboratory Astana, Kazakhstan; ²Nazarbayev University, Kazakhstan

Recently a rapid technological progress in various fields of industry and daily life has been driven by miniaturization of electronics. Components such as medical devices, logic and memory circuits, and various sensors have been drastically reduced to smaller dimensions with vastly improved performance. Limited performance of batteries is one of the most critical problems to be tackled for sustainable technological advances and to allow for further development of novel and future technologies.

Lithium-ion batteries (LIBs) exhibit excellent cycle performance and high energy capacity and thus are the best choice to power miniaturized devices. However, the current architecture used in LIBs’ electrodes limits the energy and power densities in electrodes. Furthermore, safety issues arising from flammable liquid electrolytes and lithium dendrite growth upon cycling still remain as the major challenges for implementation of LIBs in this area. Advanced architectures and materials are needed to design high performance LIBs with increased energy storage capacity per unit volume while maintaining a small footprint area.

A three-dimensional (3D) architecture design of the battery electrodes is believed to enhance the energy and power densities of conventional LIBs. In this regard, we report a unique 3D architecture anode designed for all-solid battery and fabricated by electrodeposition of ultrathin Ni₃Sn₄ intermetallic alloy onto a commercially available nickel foam current collector from an aqueous electrolyte. The X-ray diffraction results obtained from three-dimensional electrodes indicated that the main phase of
electrodeposited alloys was Ni$_3$Sn$_4$. The designed three-dimensional electrode demonstrated a high discharge capacity of 843,75 mAh g$^{-1}$ during initial cycles and an improved cycle performance over 100 cycles. The high surface area of the electrode and short Li$^+$-ions diffusion paths along with suppression of volume expansion provided by the proposed 3D structure and Ni inactive matrix play a key role in improving the performance of the electrode.

Acknowledgements

This work was supported by the CRP research grant “Three-Dimensional All Solid State Rechargeable Batteries” from Nazarbayev University.

References


S.EN12.10.40

Efficient and Stable TiN$_x$O$_y$ Thin-Film Catalysts for Oxygen Evolution Reaction

Nikhil R. Mucha$^1$, Jacob Som$^1$, Surabhi Shaji$^1$, Felipe Martins Desouza$^2$, Ram K. Gupta$^2$, Corson Cramer$^3$, Harry Meyer$^3$, Amy Elliott$^3$ and Dhananjay Kumar$^1$; $^1$North Carolina A&T State University, United States; $^2$Pittsburg State University, United States; $^3$Oakridge National Laboratory, United States

A TiN$_x$O$_y$ (TiNO) material system has been synthesized in a thin film form using a pulsed laser deposition process with a wide range of x and y realized by varying the oxygen pressure from 5 to 50 mTorr. X-ray diffraction, x-ray photoelectron spectroscopy, and transmission electron microscopy measurements have been carried out to confirm the phase purity, partial oxidation, and chemical bonding information. The XPS compositions of the TiNO film deposited in 5, 15, 25, and 50 mTorr oxygen pressures were found to be TiN$_{0.57}$O$_{0.76}$, TiN$_{0.44}$O$_{0.99}$, TiN$_{0.37}$O$_{1.19}$, and TiN$_{0.29}$O$_{1.25}$ after 15 seconds of Ar-ions surface etch which was performed to remove carbon as well physically adsorbed O 1s and N 1s signals. The XPS depth profile study has shown that O and N profiles act opposite, i.e., when the O goes down, N goes up; when O goes up, N goes down. The electrocatalytic activities of these films were performed in 1M KOH solution for oxygen evolution reaction. It was observed that the electrocatalytic activities of these films depend on the growth conditions. Films grown under low oxygen partial pressure (5 mTorr) showed an overpotential of 390 mV to achieve a current density of 10 mA/cm$^2$, whereas the TiNO film grown under high oxygen partial pressure of 50 mTorr displayed the lowest overpotential of 320 mV at 10 mA/cm$^2$. This range of overpotential observed in this study is among the lowest values reported for any oxynitride systems. In addition to low overpotentials, these TiNO based films showed a stable electrocatalytic performance over 24 hours of chronoamperometric testing. Thus, our results suggest that a very high level electrocatalytic activity can be accomplished in TiNO films for the oxygen evolution reaction in the water-splitting process by controlling the substitutional defects in the starting TiN material.

S.EN12.10.45

Definition of Redox Centers in Reactions of Lithium-Intercalation in Li$_3$RuO$_4$ Polymorphs

Haifeng Li$^1$, Srinivasan Ramakrishnan$^2$, John Freeland$^3$, Bryan D. McCloskey$^2$ and Jordi Cabana$^1$; $^1$University of Illinois at Chicago, United States; $^2$University of California, Berkeley, United States; $^3$Argonne National Laboratory, United States

Cathodes based on layered LiMO$_2$ are the limiting components in the path toward Li-ion batteries with high energy density. Introducing an over-stoichiometry of Li increases storage capacity beyond a conventional mechanism of formal transition metal redox. Yet the role and fate of the oxide ligands in such intriguing additional capacity remain unclear. This reactivity is hypothesized in Li$_3$Ru$_5^+$O$_4$, making it a valuable model system. A comprehensive analysis of the redox activity of both Ru and O under different electrochemical conditions was carried out, and the effect of Li/Ru ordering was evaluated. Li$_3$Ru$_4$O$_4$ displays highly reversible Li intercalation to Li$_3$Ru$_2$O$_4$ below 2.5 V vs. Li$^+$/Li$^0$, with conventional reactivity through the formal Ru$^{3+}$-Ru$^{4+}$ couple. In turn, it can also undergo anodic Li extraction at 3.9 V, which involves of O states to a much greater extent than Ru. Although the associated capacity is reversible, reintercalation subsequently unlocks a conventional pathway involving the formal Ru$^{3+}$-Ru$^{4+}$ couple despite operating above 2.5 V, leading to chemical hysteresis. This new pathway is both chemically and electrochemically reversible. This work exemplifies both the challenge of stabilizing highly depleted O states, and the ability of solids to access the same redox couple at very different potential windows depending
on the underlying structural changes. It highlights the importance of properly defining the covalency of oxides when defining charge compensation in view of the design of materials with high capacity for Li storage.

S.EN12.10.46
One-Step Low Temperature Synthesis of Carbon Free Pure Phase Orthorhombic Li2MnSiO4 and Its Electrochemical Activity
Meetesh Singh, Nagesh Kumar and Yogesh Sharma; Indian Institute of Technology Roorkee, India

Li2MnSiO4 (LMS) offers a promising opportunity as a high capacity potential cathode for next generation lithium ion battery because of its high theoretical capacity 333 mAhg⁻¹ which is ascribed to the possible deintercalation/intercalation of two lithium ions per formula unit through the excursion of MnII/MnIII and MnIII/MnIV redox couples within the voltage range of used electrolyte (1 M LiPF₆ in EC: DC, 1:1 vol. %) However, the main drawbacks associated with LMS is its poor electronic conductivity (5x10⁻¹⁶ Scm⁻¹), low Li-ion diffusion coefficient (10⁻¹⁷-10⁻₁₈ cm²s⁻¹), unstable crystallographic structure, and poor cyclability, which hinder its possibility to be used as a commercial cathode material. Additionally, only a small difference in the formation energy of its polymorphisms, namely, orthorhombic Pmn2₁, Pmnb, and monoclinic P2₁/n, further challenges its pure phase synthesis, and the investigation of its electrochemical behaviour. In view of this, although various synthesis approaches have been adopted in the recent past to get reproducible pure phase LMS yet still not facile, and the formation of some impure phases such as MnO, Li₂SiO₃, and Mn₂SiO₄ usually appear along with LMS phase. In most of the reported synthesis approaches, a little amount of carbon has been used, which suppresses the growth of impurity phases in the sample. In this study, carbon free pure phase orthorhombic Li₂MnSiO₄ cathode with space group Pmn2₁ has been prepared at low temperature (180 °C) via facile one-step hydrothermal approach. The pure phase formation has been confirmed by Rietveld refinement followed by other characterizations like TGA, FE-SEM, EDAX, XPS, HR-TEM, FTIR, Raman, and EPR at room temperature. Further, the electrochemical activity of such synthesized LMS as a prospective cathode for LIBs has been investigated thoroughly via galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). We believe our findings can be utilized in exploring the possible commercial utility of the Li₂MnSiO₄ as cathode material for Li-ion batteries.

References:

S.EN12.10.48
Nanostructured Low Bandgap Perovskite Oxides for Artificial Photosynthesis
Pawan Kumar¹, Sheng Zeng², Suresh Mulmi², Kazi Alam¹, Venkataraman Thangadurai² and Karthik Shankar¹; ¹University of Alberta, Canada; ²University of Calgary, Canada

YMnO₃ (and related compositions) is a multiferroic perovskite oxide, which is recently attracting attention as a visible light driven photocatalyst due to optical absorption that extends to ~900 nm. Similarly, quinary and senary non-stoichiometric double perovskite oxides such as BCNF (Absorption edge ~800 nm) have been used for gas sensing, solid-state ionics and thermochemical CO₂ reduction. Herein, we examined the potential of both non-stoichiometric YMnO₃ and BCNF-family of compounds, as narrow bandgap semiconductors for use in solar energy harvesting.

Both YMnO₃ and BCNF showed p-type conduction and a distinct photoresponse up to red wavelengths. Due to poor carrier transport in these materials, these perovskite oxides need to be nanostructured in order to ensure that the critical dimension is roughly comparable to the minority carrier diffusion length. While YMnO₃ was nanostructured through solvothermal processing, BCNF was nanostructured by forming composites with few-layer sheets of g-C₃N₄. For both types of nanostructured perovskites, scanning Kevinn probe force microscopy (KPFM) and photoluminescence measurements indicated efficient charge separation following visible light illumination. In this poster, we will be presenting our preliminary results exploiting these materials in photocatalytic CO₂ reduction and photoelectrochemical water splitting.
Selective and Efficient Gd-Doped BiVO₄ Photoanode for Two-Electron Water Oxidation to H₂O₂

Thomas Gill, Jihyun Baek and Xiaolin Zheng; Stanford University, United States

Photoelectrochemical oxidation of water presents a pathway for sustainable production of hydrogen peroxide (H₂O₂). Two-electron water oxidation toward H₂O₂, however, competes with the popular four-electron process to form oxygen and one-electron water oxidation to form OH radical. To date, bismuth vanadate (BiVO₄) has been shown to exhibit promising selectivity toward H₂O₂, especially under illumination, but it suffers from high overpotential and notoriously poor stability. Herein, using density functional theory calculations, we predict that doping BiVO₄ with optimal concentrations of gadolinium (Gd) not only enhances its activity for H₂O₂ production but also improves its stability. Experimentally, we demonstrate that intermediate amounts of Gd doping (6–12%) reduce the onset potential of BiVO₄ for H₂O₂ production by ∼110 mV while achieving a Faradaic efficiency of ∼99.5% under illumination and prolonging the catalytic lifetime by more than a factor of 20 at 2.0 V vs RHE under illumination.

Influence of the Solvent and Precursors in the Formation of CuS and CuInS₂ Nanoparticles by Controlled Precipitation

Daniela E. Ortiz Ramos¹ and Luis Alfredo González-López²; ¹Universidad Autonoma de Coahuila, Mexico; ²CINVESTAV Saltillo, Mexico

Nowadays, many applications of optoelectronics require materials with tailored properties. Chalcogenide metallic materials have become an important research field in order to get semiconductors. Specifically, CuS and CuIn₂ are a promising materials for device applications like in solar energy conversion, lighting, display technology, or biolabelling. However, is important to avoid the use of toxic heavy metals as cadmium or lead, one of the possible alternatives are copper sulfide and Copper indium disulfide.

Copper sulfide is a p-type semiconductor with a bandgap in the range of 2.0-2.36 eV and a low resistivity with a value of 1×10⁴ Ωcm, has a covellite structure with a hexagonal arrangement. Copper indium disulfide (CuInS₂), a direct semiconductor with a bandgap in the bulk of 1.45 eV, it has a chalcopyrite type crystalline structure, this metal chalcogenide has a high absorption coefficient of 10⁵ cm⁻¹.

Here, we show preliminary results of the influence of the solvent in the formation of CuS and CuInS₂ nanoparticles by controlled precipitation, also we studied de influence of the metallic precursors and the source of the sulfur ions in the formation of the nanoparticles. The solvents used were ethanol, ethylene glycol and deionized water. The metal precursors were Cu(NO₃)₂·2.5H₂O and CuCl₂·H₂O for CuS nanoparticles, Cu(NO₃)₂·2.5H₂O , CuCl₂·H₂O, In(C₂H₃O₂)₃ and InCl₃ for CuInS₂ nanoparticles. Sulfur ion sources were CH₃CSNH₂, NaS₂·9H₂O and NaSH·xH₂O at low temperature 80°C and 1 hour stirring. It is important to note that the addition of the solution containing the sulfur ions to the solution containing the metal ions should be drop by drop, otherwise an abrupt reaction and rapid precipitation occurs, resulting in metal oxides and sulfur ions not react with copper ions.

First, a formulation was made to obtain CuS nanoparticles, using Cu(NO₃)₂·2.5H₂O as a metal salt and a variation of the sulfur ion precursor was made CH₃CSNH₂, NaS₂·9H₂O and NaSH·xH₂O using water and ethanol as solvents, with the objective of obtaining CuS with covellite crystalline structure. The results obtained by an XRD analysis show that when using NaS₂·9H₂O as a source of sulfur ions, the desired crystalline structure for CuS is obtained. Subsequently ethylene glycol was used as a solvent, to obtain CuS and CuInS₂, the characterization by DRX and EDAX in the nanoparticles of CuS and CuInS₂ showed contamination by oxides and in the case of CuInS₂ showed low content of atomic In%. Finally, deionized water was used as a solvent, in this case the optical properties, the crystalline structure and the morphology of the CuS and CuInS₂ nanoparticles are related to the results reported in the literature. The objective was achieved, the nanoparticles were analyzed structurally, morphologically and optically to study the effect of using different sources of metal ions and vary the solvent used in the obtention of CuS and CuInS₂ nanoparticles.
SESSION S.NM01.11: Live Keynote: Nanodiamond
Session Chair: Edward Chow
Saturday Morning, November 28, 2020
S.NM01

10:15 AM *S.NM01.13.01
Nanodiamond Production and Surface Manipulation Oliver A. Williams, Soumen Mandal and Laia Gines; Cardiff University, United Kingdom

Diamond nanoparticles have a diverse array of applications from single photon sources and biomarkers to the seeds for diamond growth. Although there are a wide range of commercial suppliers, the purity of diamond nanoparticles is insufficient for some specific applications such as optical levitation and Coherent Anti-Stokes Raman Spectroscopy (CARS). There is also no commercial supplier for nanodiamonds containing the silicon vacancy centre or newer single photon sources. In this work the production and purification of novel diamond nanoparticles containing custom colour centres will be detailed. First a diamond film containing NV/SiV centres was grown onto a substrate. Colour centre incorporation was confirmed by Photoluminescence and Hanbury Brown and Twiss measurements. The resulting diamond film was removed from the substrate and milled using a planetary mill based on either steel or SiN. The milled material was purified by acid reflux. To measure particle sizes, different slurries containing the diamond nanoparticles obtained were prepared and characterized by using Dynamic Light Scattering (DLS) and Nanoparticle Tracking Analysis (NTA). XPS was also used to qualify the milling process contamination.

The control of surface sp² and zeta potential will also be demonstrated. Positive zeta potentials in hydrogenated nano-structured carbons could be explained due to the presence of basal planes of graphite which can become protonated. At the same time, sp² carbon creation on diamond nanoparticles surface eases low temperature (500°C) diamond nanoparticles hydrogenation and amination, previously demonstrated for detonation diamond (5nm). Applications of the positive zeta potential in nanodiamond will be proposed.

10:45 AM *S.NM01.07.01
Measuring and Controlling Temperature at The Nanoscale—Current Strategies and Future Challenges Carlo Bradac; Trent University, Canada

Color centers in solids are the fundamental building blocks of various applications ranging from lasers to light emitting diodes and sensors, as well as the foundation of advanced quantum information and communication technologies. Their photoluminescence properties are usually studied under Stokes excitation, in which the emitted photons are at a lower energy than the excitation ones. We explore the opposite Anti-Stokes process, where excitation is performed with lower energy photons. The process is sufficiently efficient to excite even a single quantum system—the germanium-vacancy center in diamond. As a proof of concept, we propose using Anti-Stokes excitation of diamond color centers for nanoscale thermometry. We leverage the temperature-dependent, phonon-assisted mechanism to realize an all-optical nanoscale thermometry scheme that outperforms any homologous optical method employed to date. We discuss other potential applications and show that our results frame a promising approach for exploring fundamental light-matter interactions in isolated quantum systems.

11:15 AM *S.NM01.09.01
Nanodiamonds in Biological Environment—From Selective Cell Targeting to Control of Cell Signalling Petr Cigler; Institute of Organic Chemistry and Biochemistry of the CAS, Czechia

Nanodiamond is a biocompatible nanomaterial which can accommodate various photoluminescent crystal defects. Nitrogen-vacancy (NV) centers show particularly high photostability and unique electronic sensitivity to magnetic and electric fields. Their spin properties can be read by optical means, which enables construction of various probes based on quantum mechanical interactions. For application in biological environment, a proper interface of the particles is required. Two conceptually different design of nanodiamond surface design will be discussed [1-3]. These includes polymer and biomimetic lipid terminations enabling further modification by chemically reactive groups. Selectivity of cell surface receptors targeting will be discussed.

Furthermore, specific and efficient regulation of the family of extracellular signaling molecules known as fibroblast growth factors (FGFs) using positively charged detonation nanodiamonds without any synthetically installed (bio)organic interface will be presented [4]. The FGF-based regulation of cell signalling using nanodiamonds can be performed in full sera. This nanotherapeutic approach can be potentially applied to mitigation of pathological FGF signaling and neutralization of disease-related activities of FGFs.

References

11:45 AM *S.NM01.06.02
Surface Reactivity of Hydrogenated Nanodiamonds in Water Franziska Buchner¹, Christoph Merschjann¹, Robert Seidel¹, Benjamin Kiendl², Peter Knittel¹, Hugues Girard³, Jean-Charles Arnault⁴, Anke Krueger² and Tristan Petit¹; ¹Helmholtz Zentrum Berlin, Germany; ²Julius-Maximilians-Universität Würzburg, Germany; ³Fraunhofer Institute for Applied Solid State Physics (IAF), Germany; ⁴CEA, LIST, Diamond Sensors Laboratory, France

The nanodiamond-water interface plays a central role in nanodiamond reactivity in aqueous environment, which is relevant for nanomedicine, photocatalysis or environmental applications. Especially, the generation of solvated electrons can trigger N₂ or CO₂ reduction in aqueous environment, and probably strongly depend on the nanodiamond-water interface.

In this presentation, our latest results related to different spectroscopic approaches to probe the nanodiamond-water interface will be shown. In particular, the different surface reactivity with water related to hydrogen-termination will be compared to oxidized nanodiamond surfaces.

First, the vibrational and electronic structures of water molecules around nanodiamonds were probed by Fourier Transform Infrared spectroscopy (FTIR) and X-ray absorption spectroscopy (XAS) directly in aqueous environment.¹ X-ray Photoelectron Spectroscopy (XPS) was also applied under near ambient pressure conditions (few mbar of water) to probe changes of the surface chemistry of nanostructured diamond upon exposure to water.

Finally, transient absorption spectroscopy (TAS) was applied to nanodiamond dispersions. The evolution of the visible light absorption spectra over time with a sub-picosecond time resolution was monitored after excitation of electrons into the diamond valence band using a UV laser pulse. This enables the observation of the emission of solvated electrons from nanodiamonds in water. The effect of surface chemistry on the electron emission will also be discussed.

This work has received funding from the European Union’s Horizon 2020 Program under Grant Agreement number 665085 (DIACAT).

SESSION S.NM01.12: Live Panel Discussion: Future of Nanodiamond
Session Chair: Shery Chang
Sunday Afternoon, November 29, 2020
S.NM01

7:15 PM S.NM01.01.06
Controlled Production of a Vibrant Color Spectrum of Fluorescent Diamond Particles Olga A. Shenderova1, Nicholas Nunn1, Marco Torelli1, Alexander I. Shames2 and Alexandre Zaitsev3; 1Adamas Nanotechnologies, United States; 2Ben-Gurion University of the Negev, Israel; 3College of Staten Island, United States

We will report on a breakthrough method of production of multicolor diamond particulates using a rapid thermal annealing (RTA) approach with precise temperature and time control, enabling annealing of diamond particulates up to 2100 °C without extensive graphitization. The RTA method generates conditions which allow formation of one-, two- and three-atom nitrogen complexes with vacancies in electron irradiated type Ib synthetic diamond, providing vibrant luminescence in the red, green and blue spectral ranges, correspondingly. We will demonstrate opportunities for particulate diamond in a plethora of fluorescence imaging applications in biological and industrial fields based on controlled and highly reproducible formation of specific color centers previously not possible in type Ib synthetic diamond particles in micron- and nanometer size ranges.

7:30 PM PANEL DISCUSSION: MANUFACTURING

7:45 PM MANUFACTURING AND APPLICATIONS OF DETONATION NANODIAMOND—HISAYOSHI ITO

8:00 PM PANEL DISCUSSION: APPLICATIONS OF DETONATION NANODIAMOND

8:15 PM *S.NM01.05.01
Progress in Nanodiamonds for Novel Composites and Biomedical Applications Vadym Mochalin; Missouri University of Science and Technology, United States

Nanodiamond powders produced by detonation synthesis offer a great potential in many applications1, including novel nanocomposites2 and biomedical applications3. In the area of nanocomposites, much of work has been focused on polymer matrix composites, while significantly less has been done with other matrices, such as ceramics and metals4. At the same time, nanodiamonds have great potential in reinforcing as well as improving optical properties and wear behavior of metal- and ceramic-matrix composites.

We will review our progress in developing well dispersed nanodiamonds5 for composite applications with emphasis on novel and less studied nanodiamond-ceramic and nanodiamond-metal composites. Manufacturing and processing techniques, as well as properties of the composites will be discussed.

Another hot area of applications for nanodiamond is biomedical imaging and drug delivery. We will discuss our recent progress in drug delivery with nanodiamonds, emphasizing the effects of nanodiamond surface chemistry, and present novel processing techniques to produce luminescent nanodiamond particles from HPHT luminescent diamond for bioimaging, labeling, and other applications.


8:30 PM PANEL DISCUSSION: COMPOSITE AND BIO-APPLLICATIONS

8:45 PM BIOMEDICAL APPLICATIONS OF NANODIAMONDS—EDWARD KAI-HUA CHOW
9:00 PM PANEL DISCUSSION: FUTURE BIOMEDICAL APPLICATIONS

SESSION S.NM01.01: Frontiers in Nanodiamond Properties and Applications

On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday
Morning, November 21, 2020
S-NM01

5:00 AM *S.NM01.01.02
Dynamic Nuclear Polarization of 13C Spins in Diamond Nanoparticles Carlos Meriles¹ and Ashok Ajoy²; ¹The City College of New York, United States; ²University of California, Berkeley, United States

Diamond particles hosting negatively charged nitrogen vacancy (NV-) centers have recently emerged as an intriguing platform to dynamically polarize nuclear spins both inside and outside the crystal lattice. This presentation surveys some recent work on the topic by our groups including the development and implementation of spin polarization methods insensitive to the orientation of the diamond particles, as well as proof-of-principle applications such as dual fluorescence and magnetic resonance imaging of diamond particles arrays. Further, we introduce recent observations using particles of varying dimensions down to nm sizes, and show that diamond annealing at elevated temperatures has important effects on the hyperpolarization levels, enhancing them by above an order of magnitude over materials annealed through conventional means. Electron and nuclear spin resonance measurements show this response correlates with NV- and 13C relaxation and coherence times, which points to improved recovery of the diamond lattice from radiation damage.

5:15 AM *S.NM01.01.03
Diamond Magnetometry with Nanodiamonds in Cells Romana Schirhagl; Groningen University, University Medical Center Groningen, Netherlands

Diamond magnetometry has led to impressive results in physics. The technique provides magnetic resonance signals with nanoscale resolution. It is so sensitive that even the faint signal of single electrons can be detected. Here we have first applied the technique to measure free radical generation in cells. These radicals play a critical role in the natural metabolism of cells. Examples of processes relying on radicals include, signalling, immune responses or cell death or ageing. However, they are also involved in numerous processes which indicate disease. Diseases where radicals play a key role includes cancer, cardiovascular diseases, bacterial or viral infection or arthritis. Despite their relevance and prevalence, we know very little about free radical generation. The reason is that they are small, short lived and reactive and thus difficult to measure for the state of the art.

For diamond magnetometry they are well visible due to their free electron spin. With this new technology we are able to detect stimulation and inhibition of radical production with subcellular resolution. On top of that we can differentiate different knock out cells (where certain metabolic processes have been turned off) as well as different production in mitochondria compared to the cytosol. The signals we receive are in principle equivalent to conventional MRI signals. However, the resolution and sensitivity are significantly improved

5:30 AM *S.NM01.01.04
Optically Hyperpolarized Nanodiamonds—New Avenues for Signal Enhanced NMR and MRI Ashok Ajoy¹,²; ¹UC Berkeley, United States; ²Carnegie Mellon University, United States

I will describe new quantum-assisted modalities to deliver enormous signal enhancements in conventional MRI and NMR mediated by quantum defects in nanodiamond powder. This relies on the use of Nitrogen-Vacancy (NV) center spins within the diamond particles that can be optically polarized at room temperature with modest laser powers. This polarization can be transferred to nuclei surrounding the NV spins to hyperpolarize them to levels far above Boltzmann levels, manifesting in a highly enhanced NMR signature. Nanodiamonds are particularly suited for this task, given their large surface areas, and the ability to arrange for close physical contact between the polarized NVs and analyte molecules of interest.

I will discuss our experimental effort in this direction, particularly focusing on the ability for ¹³C hyperpolarized nanodiamonds to serve as dual-mode (optical and MRI) imaging agents, and as transduced and deployable magnetometers.
Beyond Superlubricity—Manipulating Friction and Wear at an Unprecedented Level
Anirudha Sumant; Argonne National Laboratory, United States

The mechanical energy dissipation between two sliding objects at macroscopic level leads to friction and wear and is explained by Amonton’s law where friction is directly proportional to the load applied but independent of the contact area. However, at nanoscale, contact area becomes dominant factor in controlling friction due to the nanoscale interactions at single asperity level and therefore interpretation of friction at nanoscale and macroscale has always been somewhat ambiguous due to the missing mesoscopic link that bridges nanoscale phenomenon with that of macroscopic world. Our research at CNM has always been focused on understanding atomic scale origin of the friction and how that can be linked to the macroscopic world. Our recent work utilizing combination of 2D materials and nanodiamond as a nanoscale lubricant have broken that barrier between nanoscale and macroscale world demonstrating near zero friction (superlubricity) at engineering scale for the first time [1-2]. We have further shown that it is possible to control friction at macroscale by manipulating nanoscale interactions at the tribological interface involving combination of various 2D materials and nanoparticles that generates superlubric tribolayer within the wear track resulting in near zero friction and negligible wear [3-4]. With the help of newly installed multifunctional tribometer at CNM in the superlubricity lab, we systematically study evolution of tribochemical changes in the wear track using integrated Raman spectroscopy and 3D confocal microscopy and wear debris using HRTEM and EELS techniques. Combining that with the molecular dynamic simulation we elucidate the mechanism of friction and show possible pathways to manipulate friction at nanoscale that can directly influence friction at macroscale. The implications of this discovery are profound and already demonstrating its potential for some commercial applications that we are exploring with the industry. I’ll also discuss some new results on achieving superlubricity in rolling/sliding contacts [5] that will have great potential in bearings industry.

References:
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Controlled Production of a Vibrant Color Spectrum of Fluorescent Diamond Particles
Olga A. Shenderova1, Nicholas Nunn1, Marco Torelli1, Alexander I. Shames2 and Alexandre Zaitsev3; 1Adamas Nanotechnologies, United States; 2Ben-Gurion University of the Negev, Israel; 3College of Staten Island, United States

We will report on a breakthrough method of production of multicolor diamond particulates using a rapid thermal annealing (RTA) approach with precise temperature and time control, enabling annealing of diamond particulates up to 2100 °C without extensive graphitization. The RTA method generates conditions which allow formation of one-, two- and three-atom nitrogen complexes with vacancies in electron irradiated type Ib synthetic diamond, providing vibrant luminescence in the red, green and blue spectral ranges, correspondingly. We will demonstrate opportunities for particulate diamond in a plethora of fluorescence imaging applications in biological and industrial fields based on controlled and highly reproducible formation of specific color centers previously not possible in type Ib synthetic diamond particles in micron- and nanometer size ranges.

SESSION S.NM01.02: Colloids and Self-Assembly of Nanodiamonds
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM01

Self-Assembly of Elementary Diamond Nanoparticles from their Aqueous Solutions #2—Hybrid Ultra-Thin Films of Fatty Acid and Diamond Nanoparticles
Yasuhiro F. Miura1, Yoshiya Akagi1, Toshihiko Tanaka2,3, Tetsuya Aoyama3, Kazunori Miyamoto3, Masaya Nemoto2, Masanobu Uchiyama3,4 and Eiji Osawa5; 1Hamamatsu University School of Medicine, Japan; 2Center for Medical Biotechnology, National Institute of Technology, Fukushima College, Japan; 3RIKEN Cluster for Pioneering Research (CPR), Japan; 4National Institute of Technology, Fukushima College, Japan; 5The University of Tokyo, Japan; 6NanoCarbon Research Institute Co., Ltd., Japan

2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
Detonation nanodiamonds (DNDs) attract much attention due to the exceptional colloidal properties in aqueous media. In particular, the elementary particles of detonation nanodiamonds (EPDNDs), whose size is within a lower single-digit nanometer, should be a promising component in various fields that include nanoscale medicine. Whereas the characterization of EPDNDs is progressing rapidly, one of the remaining subjects is the fabrications of organized films of EPDNDs to confirm the agglutination mechanism as predicted based on the interfacial Coulombic interactions and to obtain clues to identify the surface structure. Furthermore, it is also beneficial if we can make heterojunctions between organized two-dimensional assemblies of EPDNDs and those of other chemical species.

We have already reported that nanosheets of DNDs are formed at the air/water interface by injecting a well-dispersed solution of DNDs (NanoAmando®) below a Langmuir monolayer of arachidic acid (CH₃(CH₂)₁₈COOH, C₂₀) at the interface. We have also reported that the floating nanosheets can be transferred onto solid substrates, such as glass, quartz or Si wafers by the modified horizontal lifting method, during which the substrate is lifted up below the nanosheets keeping the substrate surface horizontally to the air/water interface. Since each nanosheet is strip-like or rectangular in shape and is birefringent, we postulate that they are of colloidal crystals of EPDNDs.

By our fabrication technique reported so far, however, we were not able to fabricate continuous films based on EPDNDs (each nanosheet is isolated on the substrate surface). Therefore, it was practically impossible to perform layer-by-layer depositions to make multi-layered structures. Here we report a successful layer-by-layer depositions of the hybrid EPDND-C₂₀ films onto solid substrates by the Langmuir-Schaefer method, where the substrate is lowered toward the floating film keeping the substrate surface horizontally to the air/water interface and after the substrate touches the film surface, the substrate is lifted up. We would like to discuss the structure and properties of the hybrid EPDND-C₂₀ film based on FT-IR and Raman spectra together with morphological characterizations by atomic force microscopy and optical microscopy.


5:10 AM S.NM01.02.02
Top-Down Fabrication of High-Uniformity Nanodiamonds by Self-Assembled Block Copolymer Masks
Benjamin Lienhard¹, Jiabo Zheng¹, Gregory S. Doerk², Mircea Cotlet², Eric Bersin¹, Harrison S. Kim³, Young-Chul Byun⁴, Chang-Yong Nam⁴, Jiyoung Kim³, Charles T. Black² and Dirk R. Englund¹; ¹Massachusetts Institute of Technology, United States; ²Brookhaven National Laboratory, United States; ³The University of Texas at Dallas, United States

Over the past two decades, solid-state defects have emerged as one of the leading systems for a wide variety of quantum technologies. Solid-state hosts such as diamond are well studied, and a wide spectrum of fluorescing crystal defects have been identified and characterized. Nanodiamonds enable efficient control and readout of color centers within. Furthermore, nanodiamonds offer surface functionalization, nanometer-scale spatial positioning, and the compatibility with optical levitation. The fabrication of non-aggregated and uniformly-sized nanodiamonds with systematic integration of single quantum emitters has so far been lacking. Here, we present a top-down fabrication method to produce ~30 nm uniformly-sized single-crystal nanodiamonds by block copolymer self-assembled nanomask patterning together with directional and isotropic reactive ion etching. We show detected emission from bright single nitrogen vacancy centers hosted in the fabricated nanodiamonds. The lithographically precise patterning of large areas of diamond by self-assembled masks and their release into uniformly sized nanodiamonds open up new possibilities for quantum information processing and sensing. (Scientific Reports 9, 6914 (2019))

Research carried out in part at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-SC0012704.

5:20 AM S.NM01.02.03
Enhancing the Strength of Polyester with Nanodiamonds
Taylor Sloop, Nathan Sunbury, Dithi Ganjam, Red Willow Coleman and Albert Dato; Harvey Mudd College, United States

Polyester is used as a matrix material in fiber-reinforced composites that have a wide range of applications, which include naval vessels, storage tanks, and pipelines. Improving the strength of polyester is highly desirable in these applications. Detonation nanodiamond is a promising filler material for polymer reinforcement because of its superior mechanical
properties, small size, and chemical stability. Here we show that incorporating low concentrations (0.1 wt%) of commercially-available detonation nanodiamonds (3-10 nm in diameter) into isophthalic polyester results in significant enhancements in the strength of the polymer. A facile method of fabricating nanodiamond-polyester composites will be discussed. The method does not require additional nanodiamond purification steps or surface modification strategies to enhance the bonding of nanodiamond to polyester. Results from the uniaxial tensile testing of nanodiamond-polyester composites will be presented, and scanning electron microscopy images of specimen fracture surfaces will be shown. The results reveal the mechanical properties, dispersion, and possible strengthening mechanisms of nanodiamond-polyester composites.

5:30 AM S.NM01.02.04
Self-Assembly of Elementary Diamond Nanoparticles from Their Aqueous Solutions #1—Anisotropy of Whiskers or Nanosheets Toshihiko Tanaka1,2, Yasuhiro F. Miura3, Tetsuya Aoyama2, Kazunori Miyamoto4, Yoshiya Akagi5, Masaya Nemoto1,2, Masanobu Uchiyama1,2 and Eiji Osawa2; 1National Institute of Technology, Fukushima College, Japan; 2RIKEN, Japan; 3Hamamatsu University School of Medicine, Japan; 4The University of Tokyo, Japan; 5Nano Carbon Research Institute Ltd., Japan

The anisotropy of the precipitates from nanodiamond (ND) solutions suggests the existence of elementary diamond nanoparticles (EDIANs). The rectangular shapes of whiskers [1], nanocrystals[2], sheets[3], or nanosheets[4-6] should be formed from the particles being similar both in shape and size. We believe that there is a peculiar kind of similarity in the colloidal particles consisting the precipitates and that hydrated colloidal crystals are formed from them. We demonstrate herein two kinds of the rectangular precipitates, the whiskers and the nanosheets both of which were prepared from the solutions of NanoAmando® (Nano Carbon Research Institute Ltd.).

The former was prepared at the three-phase contact between air, an ND solution, and glass on the sidewall of its tubes[4]. The whiskers have the fine geometry of rectangular shapes as well as uniaxial uniform optical anisotropy. A laser microscopy image exhibited the surprisingly fine shape and crossed nicol polarized microscopic observations with a Berek compensator demonstrate the uniaxial birefringence of Δn=0.0016. The curvature of the sidewall is needed to show the birefringence and recent procedures furthermore provided a small ring (φ~7 mm) of a curved whisker on the wall. Although the ring was brittle, it was slightly elastic, being able to deform a little without breaking.

The nanosheets were crystallized from a diluted ND solution to the adsorbed ND particles on a Langmuir monolayer of arachidic acid (C19H39COOH). After opening the trough of the monolayer, we found innumerable ultra thin rectangular sheets on the water surface [4-6]. We postulate that the monolayer induces the crystallization under the PTFE bars of a Langmuir trough and that the precipitates of ultrathin rectangular nanosheets (~26 nm thick) are squeezed out from the undersurface of the bars to the water surface. Raman spectra showed that the nanosheets contain a negligible amount of the acid and such a process should result in the low content of it.

We think that the quality of NanoAmando® contributes to the self-assembly; recent small diameter values (2.6 nm) from dynamic light scattering (DLS) measurements also suggest its appreciable content of EDIANs, considering that Raileigh scattering should force us to overestimate the diameters. We will discuss the origin of the self-assembly with respect to the colloidal nature of the multi-polar ND polyhedrons predicted by DFT calculations [7].


Corresponding Author:Toshihiko Tanaka, Tanaka/Tel: +81-246-46-0810/E-mail: 3116566701@jcom.home.ne.jp

5:40 AM S.NM01.02.05
Three-Dimensional Imaging of Self-Assembled Lacey Network of Detonation Nanodiamond in Water Shery Chang, Dwight Williams, Toby Sanders and Christian Dwyer; Arizona State University, United States

Detonation nanodiamonds (DND) are diamond nanoparticles synthesized through detonation process with sizes ranging 3-5nm. It's small size, non-toxic and biocompatibility has drawn huge interests, particularly in the biomedical field. In order to capitalize the large total surface areas afforded by the small particle size, dispersing DND have been one of the endeavor for the better utilizing DND for its applications. The consensus of DND dispersion has been that detonation nanodiamond is mono-dispersed single digit nanoparticles in water, largely based on the dynamic light scattering (DLS) measurements.
We have recently shown that DND dispersion in water, without any surface modification, exhibit striking lacey network, formed dynamically by self-assembled chain-like superstructure. This discovery was carried out by a combination of DLS, small-angle x-ray scattering (SAXS) as well as cryo-TEM imaging. Our analysis shows that the superstructure morphology has strong size and particle shape dependence.

To further understand the three dimensional distribution of the lacey network, electron tomography was conducted on the plunge-freezing samples of DND dispersion. Using a cryo-TEM (Krios) equipped with a single-electron-detection camera, a series of 65 images with specimen tilts ranging from -65°to +65° was acquired, with a dose rate of 3 e-/pixel/sec to avoid melting of the vitreous ice. Our initial result suggests that there is a preferential orientation of the chain-superstructure. We speculate that the reason behind the oriented chains is the screening effect from the interactions between water molecules surrounding the nanodiamond chains.

5:50 AM *S.NM01.02.06
Self-Assembly of Diamond-Gold Conjugates for Plasmonic Enhancement of NV Centers Davida Simpson1, Nedah Basravi1, Karen Lopez1, Camron Stokes1, Trisha Fabillaran1, Camilla Hanson1, Virginia Altoe2, D. Nordlund3 and Abraham Wolcott1; 1San Jose State University, United States; 2Lawrence Berkeley National Laboratory, United States; 3SLAC National Accelerator Laboratory, United States

Nitrogen vacancy center (NVC) nanodiamonds (NDs) are useful for applications in biolabeling and biosensing due to their electron spin properties, biocompatibility and photostability. However, NVC imaging requires high photon fluxes (1 mW/um²), increasing autofluorescence from cells and tissues and reducing signal-to-noise ratios. Generating gold-diamond nanoarchitectures in a hexagonal packing geometry can lead to a 200X fold increase in fluorescence based on finite-dimension time-domain (FDTD) simulations. For maximum fluorescence enhancement these simulations also require a dielectric (SiO₂) to separate the diamond-gold assembly. Here, we satisfy these conditions using a core-shell diamond-SiO₂ nanoparticle using self assembly to generate a gold-nanodiamond heterostructures that is driven by gold-thiolate bond formation. Here we use 65nm gold nanoparticles to plasmonically enhance the far field emission of NV centers. Au NPs were synthesized via a seeded growth mechanism to yield 60-80nm citrate capped AuNPs. 15nm SiO₂ shells were synthesized on nanodiamond cores with sulfyl-hydryl and stabilizing moieties to provide a chemically inert dielectric platform. Both AuNPs and SiO₂ coated nanodiamonds were imaged via scanning electron microscopy (SEM) and probed in-situ via Dynamic Light Scattering (DLS). Self-assembly was found to be driven by entropic forces and the ratio of gold-chelating ligands to stabilizing moieties is discussed. These fundamental findings are a key metric in designing, preparing and deploying nanoscale NV diamond under low-light conditions.

SESSION S.NM01.03: Synthesis of Nanodiamonds and Nanocrystalline Diamonds
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM01

5:00 AM *S.NM01.03.01
Nanodiamond Production and Surface Manipulation Oliver A. Williams, Soumen Mandal and Laia Gines; Cardiff University, United Kingdom

Diamond nanoparticles have a diverse array of applications from single photon sources and biomarkers to the seeds for diamond growth. Although there are a wide range of commercial suppliers, the purity of diamond nanoparticles is insufficient for some specific applications such as optical levitation and Coherent Anti-Stokes Raman Spectroscopy (CARS). There is also no commercial supplier for nanodiamonds containing the silicon vacancy centre or newer single photon sources. In this work the production and purification of novel diamond nanoparticles containing custom colour centres will be detailed. First a diamond film containing NV/SiV centres was grown onto a substrate. Colour centre incorporation was confirmed by Photoluminescence and Hanbury Brown and Twiss measurements. The resulting diamond film was removed from the substrate and milled using a planetary mill based on either steel or SiN. The milled material was purified by acid reflux. To measure particle sizes, different slurries containing the diamond nanoparticles obtained were prepared and characterized by using Dynamic Light Scattering (DLS) and Nanoparticle Tracking Analysis (NTA). XPS was also used to qualify the milling process contamination.
The control of surface sp² and zeta potential will also be demonstrated. Positive zeta potentials in hydrogenated nanostructured carbons could be explained due to the presence of basal planes of graphite which can become protonated. At the same time, sp² carbon creation on diamond nanoparticles surface eases low temperature (500°C) diamond nanoparticles hydrogenation and amination, previously demonstrated for detonation diamond (5nm). Applications of the positive zeta potential in nanodiamond will be proposed.

5:15 AM S.NM01.03.03
Degradation of Perfluorooctane Sulfonate by Sub-Bandgap Irradiation of Hydrogen Terminated Detonation Nanodiamond William A. Maza, Vanessa M. Breslin, Tatyana Feygelson, Paul DeSario, Bradford B. Pate, Jeffrey C. Owrtusky and Albert Epshteyn; US Naval Research Laboratory, United States

The extraordinary stability of the C-F bond imparts many commercially useful properties to poly- and per-fluoroalkyl substances (PFASs). Among the properties imparted by the stability of the C-F bond is a high resistance to degradation via traditional oxidative/reductive processes. As a consequence PFAS is a persistent contaminant upon environmental exposure; especially in water. In this work, we examine the impact of nanodiamond photochemistry on the degradation of one of the more resilient in the class of PFASs, perfluorooctane sulfonate (PFOS). Using nanosecond transient absorption we find that hydrated electrons result by photodetachment from hydrogen-terminated (negative electron affinity) detonation nanodiamond (HDND) suspensions in water upon sub-bandgap (266nm) irradiation. Hydrated electron photogeneration from oxygen-terminated (positive electron affinity) detonation nanodiamond (ODND), on the other hand, is not observed. The transient absorption data suggest the presence of an interaction between PFOS and HDND and, more so, an interaction between PFOS and the hydrated electrons. Finally, we show that prolonged sub-bandgap (254nm) irradiation of aqueous HDND in the presence of PFOS leads to full decomposition of PFOS by reductive fragmentation, consistent with hydrated electron reductive chemistry.

5:25 AM S.NM01.03.04
Sonication-Assisted Hydrolysis of Ozone Oxidized Detonation Nanodiamond Atsushi Kume1,2 and Vadym Mochalin2; 1Daicel Corporation, Japan; 2Missouri University of Science and Technology, United States

Detonation of TNT/RDX in oxygen-deficient conditions produces nanodiamonds terminated by various oxygen containing surface functional groups, which enable single digit state dispersion in aqueous media via deaggregation methods such as zirconia micro bead milling. We quantitatively investigated ozone oxidized DNDs by acid-base back potentiometric titration and XPS, revealing a large amount of oxygen containing surface groups in comparison to air oxidized DNDs. The most prominent feature of the ozone oxidized DNDs is its high tolerance to re-aggregation during horn sonication process, allowing longer sonication times to produce smaller particles (down to a single digit DND dispersion) without any milling media. Additionally, the deaggregated DNDs were investigated by UV-Raman and FTIR, suggesting that a large number of oxygen-containing surface groups (mainly anhydrides) produced by ozonation were further hydrolyzed to COOH during horn sonication. We will introduce the sonication-assisted hydrolysis of ozone oxidized DND as potentially a commercially viable technique to obtain single-digit COOH-terminated DND colloids due to a better control, milder conditions, and a lower burn-off of the smallest DND particles as compared to air oxidation.

SESSION S.NM01.04: Fluorescent Nanodiamonds
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM01

5:00 AM *S.NM01.04.01
Bottom Up Molecular Doping Approach to Synthesizing HPHT Color Centers in Nanostructured Diamond Abbie Ganas1, Matthew J. Crane1, Ryan A. Beck1, Alessio Petrone2, Yue Huang1, Rhonda M. Stroud1, Xiaosong Li1 and Peter Pauzauskie1; 1University of Washington, United States; 2Università di Napoli Federico II, Italy; 3U.S. Naval Research Laboratory, United States

Applications of optically active point defects, or color centers, in nanodiamond encompass a wide range of disciplines including biofluorescent imaging of cellular components, quantum information data storage, and temperature, pressure, and magnetic sensing. Among the >100 different color centers in nanodiamond, the negatively charged silicon divacancy (SiV⁻) is
Current technologies employ a top down approach of chemical vapor deposition grown (CVD) diamond in combination with ion irradiation and implantation to form the desired color center. CVD grown diamond is very pure, but because of the high energies of the implantation technique, the diamond crystal lattice becomes damaged which requires post processing techniques to correct. Doping diamond at high temperatures and pressures is also difficult due to diamond’s compact atomic lattice and low atomic diffusivities. In this work, we demonstrate a versatile, bottom-up approach to SiV$^-$ fabrication based on molecular doping of amorphous carbonaceous precursors which are converted to diamond at high-pressure, high-temperature (HPHT) conditions (>15 GPa, >1800K) within a laser-heated diamond anvil cell. A molecular dopant, tetraethyl orthosilicate (TEOS), incorporates silicon heteroatoms into the HPHT grown nanodiamond compared to non-doped samples fabricated under similar conditions. Pressure dependent photoluminescence confirms not only the formation of SiV$^-$ (λ $\sim$ 738 nm), it also provides experimental juxtaposition for ab initio quantum cluster calculations modeling the pressure dependence of the center’s zero phonon line (~0.9 meV/GPa). Aberration corrected scanning transmission electron microscopy provides images of the silicon heteroatoms on the surface and the interior of converted diamond material. Scanning transmission x-ray absorption microscopy (STXM) measurements, along with electron energy loss spectroscopy (EELS), suggest limited graphitic surface reconstruction of the diamond nanocrystals, as compared to other nanodiamond synthetic avenues. Ab initio quantum cluster calculations also support the possibility of a graphitic reconstruction of the diamond nanocrystal’s surface along with significant distortions of the cubic diamond crystal lattice adjacent to the reconstruction. These results demonstrate the versatility of this approach to doping diamond and that it can be extended to the formation of more complex color centers in diamond.

**5:15 AM S.NM01.04.02**

**Biological Impact and Selective Optical Detection of Functionalized and Luminescent Nanodiamond**

Robert J. Hamers$^1$, Kelly Zhang$^1$, Zachary Jones$^1$, Natalie Hudson-Smith$^2$, Christy Haynes$^3$ and Olga A. Shenderova$^5$; $^1$University of Wisconsin-Madison, United States; $^2$University of Minnesota Twin Cities, United States; $^3$Adamas Nanotechnologies, United States

The biological impact of nanoparticles is largely controlled by the properties of their surfaces. However, on times scales relevant to most biological studies most nanoparticles undergo chemical changes, including oxidation and loss of surface functional groups. Nanodiamond is a nearly ideal system for investigation of nano-bio interactions because diamond can be functionalized with a wide range of organic molecules via "all-carbon" scaffolding with unprecedented chemical stability, and because defects such as Nv centers in nanodiamond provide a way to detect nanodiamond via optical methods. In this talk I will present recent results investigating how the chemical structure of surface ligands affects the interaction of nanodiamond with cells and model membranes, and recent efforts using magnetically modulated Nv imaging to selectively identify nanoparticles within complex matrices. Together, the ability to functionalize nanodiamond and observe it with high selectivity and high sensitivity provides a nearly idea system for understanding nano-bio interactions in environmental systems.

**5:30 AM S.NM01.04.03**

**Effect of Surface Treatment to the Optical Properties of Nitrogen-Vacancy Containing Fluorescent Nanodiamond**

Particles Haotian Wen$^1$, Huan-Cheng Chang$^2$, Christian Dwyer$^4$ and Shery L-Y Chang$^6$; $^1$Arizona State University, United States; $^2$Academia Sinica, Taiwan

Fluorescent nanodiamonds (FNDs) are diamond nanoparticles containing color centers that emit visible light at room temperature. Among the color centers in FNDs, the negatively charged nitrogen-vacancy centers (NV$^-$) have drawn the most attention due to its excellent optical properties and great prospect in sensing and biomedical diagnostic applications. Thus, it is of great significance to further expand the potential of the NV$^-$ centers in FNDs by understanding the effect of various factors including the NV distribution, particle morphology and surface properties of the particles.

Recently, it has been reported that the brightness of the FND particles can be increased by etching the particles with molten salt (KNO$_3$). The increase of the brightness was attributed to the roundness and smoothness of the FND surface, as well as the removal of non-sp$^3$ species after the surface treatment. In order to understand how the surface treatment impacts the surface structure and particle morphology, high-resolution transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) were employed to reveal the detailed surface atomic and electronic structures.

We have previously demonstrated that it is possible to measure the electronic transitions of the NV center in nanodiamond using high-energy resolution EELS in a scanning transmission electron microscope (STEM). Using a crushed type 1a natural diamond with a nominal size of 70 nm, we detected signals at the ~1.3 and 2.16 eV assigned to [NVN]$^-$ and [NV]$^0$. The high
Spatial resolution afforded by this STEM also allows us to observe the atomic structure of the particles. Here, we compare the different surface processing methods for FND (irradiation, acid treatment, molten salt treatment), and correlate the photoluminescence (PL) mapping with the transmission electron microscope (TEM) mapping of the same area. In addition, high-energy resolution EELS in a STEM at low voltage (30-60 kV) was used to measure the surface state of the FND particles, in combination with the high-resolution TEM images on the same particles. Our initial finding from the PL and TEM mappings suggests that most of the molten salt (KNO₃) treated FND particles are photoluminescent, and the PL intensity has a correlation with particle size: the bigger the particle the higher PL intensity. High-resolution imaging shows that the molten salt (KNO₃) treated FND particles tend to have less rough surfaces, with fewer sharp-angle edges and less surface unevenness. The particle morphology population displays more round and polygonal shaped particles compared to the non-molten salt treated particles. However, we found a thin layer (1-2 nm) of amorphous carbon and graphite layers present on the particle surfaces. The EELS mapping also confirms this finding.

5:40 AM S.NM01.04.04
Alkyl-Bromide Formation on HPHT Surfaces Enables Room Temperature Catalyst-Free Functionalization Chemistry Jorge Rosas¹, Cynthia Melendrez¹, Jocelyn Valenzuela¹, Tyanna Supreme¹, Daniel Labunsky¹, James Titus², Sang-Jun Lee³, Virginia Altoe⁴, D. Nordlund⁴, Kent Irwin² and Abraham Wolcott¹; ¹San Jose State University, United States; ²Stanford University, United States; ³SLAC National Accelerator Laboratory, United States; ⁴Lawrence Berkeley National Laboratory, United States

Bulk and nanoscale diamond host the nitrogen vacancy center, a unique atomic defect, a photostable emitter that has been used for magnetometry, electrometry and quantum computation. Wet chemical modification of 25-50 nm diamond surfaces, the typical host for nitrogen vacancy centers, is challenging and carboxylate moieties are the common target of nucleophiles for chemical protocols. Here we produce a carbocation-rich diamond surface by converting high-pressure high-temperature nanoscale diamond with tertiary-alcohols to highly reactive alkyl-bromides. The chemical reactivity of the brominated surface allows for carbon-nitrogen bond formation at room temperature without catalysts using low-cost amine precursors. We report that alkyl-bromine moieties are highly labile on diamond, prone to hydrolysis and intracrystallite Williamson ether-type reactions occur. Additionally, in contrast to traditional organic chemistry reactivity, alkyl-bromides on nanoscale diamond are more reactive than acyl-bromides and an explanation is given. The chemical lability of the alkyl-bromide surface leads to efficient amination with NH₃-THF at 298 K and weak conversion rates with condensed NH₃ at 195K. Other amine precursors were also probed to guage a range of nucleophilicities. Overlapping surface sensitive spectroscopies confirm our chemical assignments. Peptide bond formation with FND-NH₂ and folic acid was demonstrated using sulfo-NHS/EDC coupling reagents and reveals that chemical reactivity is maintained. Our work demonstrates that a robust pathway now exists to transform a chemically inert diamond surface into a highly reactive surface at room temperature and broadens the pathways of carbon-heteroatom covalent bond formation.

SESSION S.NM01.05: Nanodiamonds for Nanomedicine
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM01

5:00 AM *S.NM01.05.01
Progress in Nanodiamonds for Novel Composites and Biomedical Applications Vadym Mochalin; Missouri University of Science and Technology, United States

Nanodiamond powders produced by detonation synthesis offer a great potential in many applications¹, including novel nanocomposites² and biomedical applications³. In the area of nanocomposites, much of work has been focused on polymer matrix composites, while significantly less has been done with other matrices, such as ceramics and metals⁴. At the same time, nanodiamonds have great potential in reinforcing as well as improving optical properties and wear behavior of metal- and ceramic-matrix composites. We will review our progress in developing well dispersed nanodiamonds⁵ for composite applications with emphasis on novel and less studied nanodiamond-ceramic and nanodiamond-metal composites. Manufacturing and processing techniques, as well as properties of the composites will be discussed.
Another hot area of applications for nanodiamond is biomedical imaging and drug delivery. We will discuss our recent progress in drug delivery with nanodiamonds, emphasizing the effects of nanodiamond surface chemistry, and present novel processing techniques to produce luminescent nanodiamond particles from HPHT luminescent diamond for bioimaging, labeling, and other applications.


5:15 AM *S.NM01.05.02*

**Polyglycerol Grafted Nanodiamond Avoids Protein Corona Formation, Evades Macrophage Uptake and Images Tumor Fluorescently**

Naoki Komatsu and Yajuan Zou; Kyoto Univ, Japan

In biological fluids, proteins are adsorbed onto the surface of nanoparticles (NPs) to form a coating known as protein corona. Most of the corona proteins act as opsonin which activates the macrophage from immune system to uptake NPs, leading to the rapid removal of NPs. This restricts the development of nanomedicine. Although conjugation with linear polyethylene glycol (PEG) is the standard approach to reduce protein attachment and to avoid non-specific uptake, it cannot fully prevent the opsonization. On the other hand, we have demonstrated polyglycerol (PG) as a promising alternative to PEG, because PG enhanced the aqueous dispersibility and gave stealth effect to NPs [1]. In order to understand the role of PG, we compare protein affinity and macrophage uptake of PG and PEG grafted nanodiamond (ND-PG and ND-PEG, respectively) with different polymer content in this paper. Protein analyses by sodium dodecyl sulfate-polyacylamide gel electrophoresis (SDS-PAGE) indicated that PG was much more resistant than PEG to adsorption of the opsonin proteins such as IgG and complement protein. In particular, there was almost no protein on the PG layer with high content. In addition, almost no ND-PG was observed in the TEM images of U937 macrophage, while there was ND-PEG in the macrophage. This indicates that PG has much better stealth effect than PEG [2]. Finally, the stealth effect was confirmed in vivo by preferential tumor accumulation of the ND-PG functionalized with near infrared fluorescence dye (Cy7) [3].


5:30 AM *S.NM01.05.03*

**Synergistic Integration of Ultrananocrystalline Diamond (UNCD)-Coatings on Chemical Mechanical Surface Nano-Structured Titanium-Based Dental Implants**

G. Bahar Basin1, Debashish Sur1, Orlando Auciello2, Pablo Tirado2 and Jesus Alcantar2; 1University of Florida, United States; 2The University of Texas at Dallas, United States

This paper focuses on describing a synergistic combination of ultrananocrystalline diamond (UNCD) coating on chemical mechanical nanostructured metallic dental implants to optimize the biocompatibility by a synergistic integration of both processes to optimize the performance of the particular implant.

UNCD films, with grain size in the range of 3-5 nm, exhibit excellent biocompatibility in addition to a unique set of complementary properties including much smoother surface as compared to microcrystalline and nanocrystalline diamond (NCD) (10-100 nm grain size), a superior conformal growth on 3-D structures such as the dental implants and protection of the coated metal-based implants from the chemical attack by oral fluids, enabling enhanced hermeticity [1]. Chemical mechanical nano-structuring (CMNS) is a new complementary technique that can be synergistically utilized to induce nano-scale smoothness or nano/micro-scale roughness on the bioimplant surfaces [2]. Furthermore, implementation of the CMNS process on titanium bio-implants helps cleaning the implant surface from potentially contaminated surface layers by removing a nano-scale top layer, limits any further contamination by creating a non-porous and continuous protective oxide film to minimize the risk of infection and prevent corrosion.

It is demonstrated by surface characterization through SEM imaging and Raman analyses that the CMNS process can be effectively implemented before the UNCD coating to modify surface roughness. Electrochemical evaluations in the simulated...
body fluid were also performed to demonstrate corrosion resistance improvements in addition to enhanced biocompatibility by adjustable surface nano-structuring, depending on the cell attachment requirements on the various parts of the dental implants.


The nanodiamond-water interface plays a central role in nanodiamond reactivity in aqueous environment, which is relevant for nanomedicine, photocatalysis or environmental applications. Especially, the generation of solvated electrons can trigger N₂ or CO₂ reduction in aqueous environment, and probably strongly depend on the nanodiamond-water interface. In this presentation, our latest results related to different spectroscopic approaches to probe the nanodiamond-water interface will be shown. In particular, the different surface reactivity with water related to hydrogen-termination will be compared to oxidized nanodiamond surfaces.

First, the vibrational and electronic structures of water molecules around nanodiamonds were probed by Fourier Transform Infrared spectroscopy (FTIR) and X-ray absorption spectroscopy (XAS) directly in aqueous environment. X-ray Photoelectron Spectroscopy (XPS) was also applied under near ambient pressure conditions (few mbar of water) to probe changes of the surface chemistry of nanostructured diamond upon exposure to water.

Finally, transient absorption spectroscopy (TAS) was applied to nanodiamond dispersions. The evolution of the visible light absorption spectra over time with a sub-picosecond time resolution was monitored after excitation of electrons into the diamond valence band using a UV laser pulse. This enables the observation of the emission of solvated electrons from nanodiamonds in water. The effect of surface chemistry on the electron emission will also be discussed.

This work has received funding from the European Union’s Horizon 2020 Program under Grant Agreement number 665085 (DIACAT).

Color centers in solids are the fundamental building blocks of various applications ranging from lasers to light emitting diodes and sensors, as well as the foundation of advanced quantum information and communication technologies. Their photoluminescence properties are usually studied under Stokes excitation, in which the emitted photons are at a lower energy than the excitation ones.

We explore the opposite Anti-Stokes process, where excitation is performed with lower energy photons. The process is sufficiently efficient to excite even a single quantum system—the germanium-vacancy center in diamond.

As a proof of concept, we propose using Anti-Stokes excitation of diamond color centers for nanoscale thermometry. We leverage the temperature-dependent, phonon-assisted mechanism to realize an all-optical nanoscale thermometry scheme that outperforms any homologous optical method employed to date. We discuss other potential applications and show that our results frame a promising approach for exploring fundamental light-matter interactions in isolated quantum systems.

5:15 AM *S.NM01.07.02
Nanodiamond Quantum Sensing and Its Application to Biological Thermometry Masazumi Fujiwara; Osaka City University, Japan

Fluorescent nanodiamonds (FNDs) have a great promise as robust and biocompatible fluorescent probes. Their most distinct property is the optically detected magnetic resonance of nitrogen vacancy color centers, which enables nanoscale sensing of surrounding physical properties, such as magnetic field, electric field and temperature.

I will talk about our recent activity to build up such microscope-based thermometry for biological applications. Temperature is a fundamental physical parameter of any biological activity, and in most cases, current biology assumes that temperature is uniform over the living space (including organisms themselves). However recent studies have revealed that sub-cellular temperature information is crucial to understand various biological events, such as embryogenesis, physiological thermogenesis, and thermotaxis. The FND quantum thermometry may tackle these biological issues.

I first present our effort to understand the basic spin properties of FND sensors when they are surface treated [1] or placed in various pH and ionic-strength solutions to quantify the sensor stability [2]. Second, we present a bio-dedicated ODMR measurement system to perform quantum thermometry assay for number of biological specimens [3]. Third, with these development, we demonstrate real-time subcellular quantum thermometry of live worms of C. elegans [4].


5:30 AM S.NM01.07.03
Fabrication Technique, Mechanical and Optical Properties of Nanodiamond-Silica Glass Composite Ibrahim M. Abdullahi and Vadym Mochalin; Missouri University of Science and Technology, United States

Due to the high refractive index and unique optical and mechanical properties of diamond, the nanodiamond (ND) glass composites are of great interest for advanced photonic devices and other applications [1]. However, it is difficult to employ conventional processing techniques to achieve good dispersion of NDs in glass. This is because most of these techniques start from solid powder precursors that may result in serious ND aggregation, leading to degradation of the properties of the composites.

In this presentation, an alternative fabrication method for ND-silica glass composites via sol-gel chemistry will be discussed. Optical and mechanical properties of the resulting ND-silica glass composites at various ND contents will be presented. Single digit (~4-10 nm) ND colloidal solutions in water were prepared by salt assisted ultrasonic deaggregation (SAUD) technique [2]. These colloidal solutions were then used to produce excellent dispersions of ND in ND-silica aerogels that were subsequently sintered into glass at 1100 °C. This proposed method for the integration of ND into silica glass has great potential for fabrication of ND-silica glass composites and could be extended to other nanoparticles and materials produced via sol gel chemistry. The improvements in mechanical properties, optical transmittance in ultraviolet (UV) and visible regions of the spectrum, as well as the refractive index of the ND-silica glass composites at various ND contents will be further discussed.
SESSION S.NM01.08: Nanodiamonds for Radical Production
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM01

5:00 AM S.NM01.08.03
Nanodiamond NanoMRI for Intracellular Detection of Free Radical Species Alina Sigaeva, Felipe Perona, Nikos Mougios and Romana Schirhagl; Department of Biomedical Engineering, University Medical Center Groningen, Netherlands

Free radicals, by definition containing unpaired electrons, constitute one of the major sources of magnetic signal in live cells. While these molecules are usually considered to be deleterious and are associated with ageing and pathological conditions, certain types of free radicals, such as nitric oxide (NO), perform important signaling functions in live systems. One of the major challenges in understanding the role of free radicals in health and disease is their high reactivity, which makes it hard to detect these molecules with desired spatial and temporal resolution. Moreover, the majority of methods of free radical detection rely on the reaction between the radical and the probe, thus interfering with the natural effects of the radicals [1]. Nitrogen vacancy (NV) centers of nanodiamonds allow for direct optical quantum-based sensing of the magnetic signal coming from the radicals. We apply nanodiamond magnetometry for intracellular sensing of free radical production. As FNDs possess excellent biocompatibility and can be internalized by live cells [2], they can be used for in situ detection of radicals (nanoMRI on subcellular level). As a proof-of-concept model, we used J774 murine macrophages, which produce large amounts of free radicals as part of the normal immune response. One of these radical species is NO, which is generated by a specific enzyme, inducible nitric oxide synthase (iNOS). iNOS activity can be inhibited, resulting in lower levels of NO present in the cell. We have for the first time recorded T1 relaxation curves from FNDs internalized by live macrophages. During the T1 acquisition, the cells were exposed to the iNOS inhibitor, L-NAME. We then assessed the dynamic changes of T1 relaxation of the NV centers, for the first time observing the lengthening of T1 constant of FNDs internalized by the cells, as the NO production in the system was abolished. The changes in intracellular NO levels were confirmed with the conventional fluorescent assay (DAF-2 DA) by the means of microplate reader and confocal microscopy.

Our study shows the potential of nanodiamond-based nanoMRI for the direct optical monitoring of free radical production on a single-cell level with nanoscale sensitivity and a resolution in the second range.

References:

SESSION S.NM01.09: Nanodiamonds for Bio-Applications
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM01

5:00 AM S.NM01.09.01
Nanodiamonds in Biological Environment—From Selective Cell Targeting to Control of Cell Signalling Petr Cigler;
Institute of Organic Chemistry and Biochemistry of the CAS, Czechia

Nanodiamond is a biocompatible nanomaterial which can accommodate various photoluminescent crystal defects. Nitrogen-vacancy (NV) centers show particularly high photostability and unique electronic sensitivity to magnetic and electric fields. Their spin properties can be read by optical means, which enables construction of various probes based on quantum mechanical interactions. For application in biological environment, a proper interface of the particles is required. Two conceptually different design of nanodiamond surface design will be discussed [1-3]. These includes polymer and biomimetic lipid terminations enabling further modification by chemically reactive groups. Selectivity of cell surface receptors targeting will be discussed.

Furthermore, specific and efficient regulation of the family of extracellular signaling molecules known as fibroblast growth factors (FGFs) using positively charged detonation nanodiamonds without any synthetically installed (bio)organic interface will be presented [4]. The FGF-based regulation of cell signalling using nanodiamonds can be performed in full sera. This nanotherapeutic approach can be potentially applied to mitigation of pathological FGF signaling and neutralization of disease-related activities of FGFs.

References

5:15 AM S.NM01.09.02
Characterization of Lattice Displacement Using In Situ and Operando Bragg Coherent X-Ray Diffractive Imaging Wonsuk Cha¹, F. Joseph P. Heremans²,¹ and Stephan O. Hruszkewycz⁳; ¹Argonne National Laboratory, United States; ²University of Chicago, United States

Because of unique sensitivity to lattice, Bragg coherent x-ray diffractive imaging (BCDI) is a powerful characterization tool to image three-dimensional map of strain and defect distribution inside nano-scaled materials with non-destructive measurements [1]. In-situ and operando imaging became a major driver for BCDI to address scientific questions on metal, metal oxide, and mineral in recent years. In this talk, I will introduce basic concept and current state-of-art of BCDI and recent experimental results on in-situ and operando BCDI. High temperature BCDI reveals unique lattice distortion in ZSM-5 zeolites [2], annealing effect on gold grains on gold thin films [3] and relaxation of strain inside quantum materials such as nanodiamonds and silicon carbides [4, 5]. In addition, some estimates of BCDI in the future will be discussed


5:25 AM S.NM01.09.03
Effects of Nanodiamond Size and Surface Chemistry on the Spin-Lattice Relaxation Times of the NV-Center Thea A. Vedelaar¹,², Sandeep Kumar Padamati¹,², Thamir Hamoli¹,², Felipe Perona¹,² and Romana Schirhagl¹,²; ¹University of Groningen, Netherlands; ²University Medical Center Groningen, Netherlands

The NV-center in nanodiamonds has been applied as a sensor for different applications. They are ideal for this application due to their sensitivity, low cytotoxicity and ability to work at room temperature. However, a limitation of using nanodiamonds to measure a change in the environment, is that one has to use the same nanodiamond. This is due to large variations between nanodiamonds. This study aims to address the differences between nanodiamonds and to develop a method which allows us to understand what contributes to the variation between T1 relaxation times of nanodiamonds. We aim to do this by controlling the size and surface chemistry of the nanodiamonds.

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Previous studies in our group have shown that there is large size variation between nanodiamonds. We assume that the size of the diamonds does not only affect the brightness of the fluorescence, but also the T1 relaxation time of the diamonds. The NV-centers in smaller diamonds are in general closer to the surface than in larger diamonds. Therefore, the NV-centers in smaller diamonds are more sensitive to magnetic noise around the diamond compared to larger diamonds. Hence, larger diamonds have a longer T1 relaxation time compared to smaller diamonds. Magnetic noise closest to the NV-center is noise that originates on the surface. We assume that by controlling the surface chemistry of the nanodiamonds, we can study the effects of the surface chemistry on the NV-centers. We assume that, the T1 relaxation time will vary depending on the properties of chemical compounds on the surface of the nanodiamonds. We assume that the T1 will become longer or shorter depending on the magnetic properties of the chemicals bound to the surface of the nanodiamond.

The T1 relaxation times are measured on dry nanodiamonds. The procedure is to initialize the system by shining a green laser (532nm) onto the nanodiamonds. Afterwards the laser is turned off which allows the system to relax. This sequence is repeated for varying time of the laser being turned off. During this time the red photoluminescence of the nanodiamonds is recorded. The whole procedure is repeated approximately 10000 times to obtain sufficient statistics. To obtain the T1-value, the initial part of each pulse is integrated to obtain a T1-curve which is then fitted by the bi-exponential model.

To account for size, the nanodiamonds are centrifuged to select the average size of the diamonds in the suspension. Afterwards the T1 of the nanodiamonds is measured. The surface chemistry is controlled by applying plasma treatment to the diamonds. The diamonds are treated with different types of plasma (O2, H2, N2 and NH3) for 2, 5 and 10 minutes. Similarly as for size separation, the T1 relaxation times for different plasma treated nanodiamonds have been measured. The T1 curves were recorded for 9 nanodiamonds before plasma treatment and 8 diamonds after 5 minute plasma treatment with NH3. The plasma treated nanodiamonds showed a lower fluorescence than the pre-treatment nanodiamonds. The average T1 value of the bare nanodiamonds is 601(±170) μs and for NH3 treated nanodiamonds is 306(±66) μs.

The observed T1 relaxation times pre- and post-treatment show a clear difference between the T1 relaxation times. However, the proportional error for the plasma treated nanodiamonds only reduces by 6% (28% pre-treatment and 22% post-treatment). This shows that the plasma treatment with NH3 decreases the T1 relaxation time, but does not account for the variation between the nanodiamonds. This experiment was preliminary, therefore we did not account for the size variation between the nanodiamonds yet.

5:35 AM S.NM01.09.04

Clot Imaging Using Photostable Fluorescent Nanodiamonds Marco Torelli1, Nicholas Nunn1, Gowthami Arepally2, Olga A. Shenderova1 and Sam Francis2; 1Adamas Nanotechnologies, Inc., United States; 2Duke University, United States

Thrombosis is the leading cause of morbidity and mortality in the United States. However, there is still a low understanding of its triggers, progression, and response to anticoagulant therapy. Fluorescence microscopy provides targeted, multi-color contrast, which has advanced the study of thrombus formation. However, photodegradation of fluorophores limits the application in processes that occur over longer periods of time (e.g. clot progression and/or dissolution). Fluorescent nanodiamond (FND) is a fluorophore which utilizes the intrinsic fluorescence of color centers located within and protected by the diamond crystalline lattice. Recent developments in diamond processing have allowed for the controlled production of nanodiamond emitting in multiple colors. In this work, FND is used to visualize clots and their degradation, and this imaging capability is compared to commonly used organic fluorophores. The use of FND for thrombus imaging paves the way for longitudinal studies to investigate biomarker expression in acute thrombosis, with the hope to ultimately improve clinical outcomes. These results represent the initial translation of FND research to clinical applications.
A nanocarbon film consisting of nanocrystallites with mixed $sp^2$ and $sp^3$ bonds formed by unbalanced magnetron sputtering was studied with respect to the changes in characteristics caused by surface oxygen concentration. Electrochemical pretreatment (ECP) was conducted to change the surface oxygen concentration of the nanocarbon film. X-ray photoelectron spectroscopy (XPS) measurements revealed that nanocarbon films with different amounts of surface oxygen could be prepared. In addition, we observed no significant increase of surface roughness ($R_a$) at the angstrom level after ECP, owing to stable structure containing 40% of $sp^3$ bonds. Electrode characteristics including potential window, and electrochemical properties for some redox species such as Ru(NH$_3$)$_6^{3+/2+}$, Fe(CN)$_6^{3-/4-}$ and some biomolecules were investigated. The anodic potential limit became wider and $\Delta E_p$ of Fe(CN)$_6^{3-/4-}$ became smaller at the treated nanocarbon film electrode than that of the electrode before the treatment. Based on these results, we realized to measure uridylic acid (UMP) and inosine triphosphate (ITP) with high oxidation potential by direct oxidation, which was difficult to measure at as-deposited nanocarbon film electrode.

**S.NM01.10.03**

**Magnetic Resonance Study of Lightly Boron-Doped Diamond**  
Alexander Panich$^1$, Alexander I. Shames$^1$, Shaul D. Goren$^1$, Natalya Froumin$^2$ and Olga A. Shenderova$^3$;  
$^1$Ben-Gurion Univ of the Negev, Israel; $^2$Ben-Gurion University of the Negev, Israel; $^3$Adamas Nanotechnologies, United States

To study the properties of diamond at the initial stages of boron doping, we conducted XPS, EPR, $^{11}$B and $^{13}$C NMR study of a lightly boron-doped high pressure – high temperature (HPHT) microdiamond with 0.27% of boron. The total content of localized paramagnetic defects is 24 ppm, among them 12 ppm are due to substitutional nitrogen defects (P1). The P1 content is found to be much smaller than that usually observed in conventional HPHT diamonds. $^{11}$B NMR shows two components assigned to boron atoms substituting carbon and those located within the conducting regions, respectively. The latter component demonstrates exceptionally short spin-lattice relaxation time ($T_1 = 2.4$ ms) characteristic of conductive compounds. Increase in the boron concentration would increase the number and size of the conductive clusters and would finally lead to connectivity between them. This will result in conductivity and superconductivity in the heavily B-doped regime.


**S.NM01.10.05**

**Selective Imaging of Diamond Nanoparticles in Complex Matrices Using Magnetically Induced Fluorescence Contrast**  
Zachary Jones$^1$, Nicholas Neimuth$^2$, Margaret Robinson$^1$, Olga A. Shenderova$^3$, Rebecca Klaper$^1$ and Robert J. Hamers$^1$;  
$^1$University of Wisconsin - Madison, United States; $^2$University of Wisconsin–Milwaukee, United States; $^3$Adamas Nanotechnologies, United States

The use of fluorescence microscopy to study fate and transport of nanoparticles in the environment can be limited by the presence of background signals such as autofluorescence and scattered light. Fluorescent diamond nanoparticles offer a solution to these limitations through the unique spin-related luminescence properties of nitrogen vacancy (NV) centers in diamond nanoparticles (NVND). NV centers have spin properties which affect their fluorescence, and which can be altered using applied magnetic or radio-frequency fields. I will present recent studies using magnetic fields to modulate the fluorescence of NVND for background-subtracted imaging of nanoparticles ingested by a model organism, *C. elegans*. By using small magnetic fields from an inexpensive electromagnet, the fluorescence of 40 nm NVND can be modulated by 10% in a widefield imaging configuration. We use differential imaging of magnet-induced changes in NVND fluorescence intensity to image and to isolate the emission arising from nanodiamond within the gut of *C. elegans*. This method represents a promising approach to probing the uptake of nanoparticles by organisms and to assessing the environmental fate and transport of nanoparticles in the environment.

**S.NM01.10.06**

**Oxime-Functionalized Nanodiamonds as a Platform for Treatment of Organophosphate Poisoning**  
Yevgen Karpichev$^1$, Denys Bondar$^1$, Pavel Starkov$^1$, Ivo Heinmaa$^2$, Ondrej Soukup$^1$, Daniel Jun$^3$, Kamil Kuca$^3$ and Vadym Mochalin$^5$;  
$^1$Tallinn University of Technology, Estonia; $^2$National Institute of Chemical Physics and Biophysics, Estonia; $^3$University of Hradec Kralove, Czechia; $^4$University of Defence, Czechia; $^5$Missouri S&T, United States

Nanodiamonds (ND) have emerged since about a decade ago as a key platform for many developments in nanoscience and
nanotechnology due to their outstanding mechanical performance, biocompatibility and unique properties. The NDs bearing biologically active fragments or immobilized on biomolecules are remarkably suitable for biomedical application [1]. Recently, NDs were reported to affect endothelial permeability to deliver anticancer drugs [2, 3].

The main strategy to manage acute poisoning with organophosphorus agents include, either for pre-treatment or for ex-post therapy, administration of oxime AChE reactivator, along with atropine and anticonvulsant drug. The reactivators based on mono- or bis-pyridinium scaffold are not able to diffuse readily into the central nervous system to restore activity of inhibited AcChE. A challenging issue is to design a scaffold providing as high antidotal efficiency towards inhibited AcChE as quaternary oximes along with their ability to come across the blood-brain barrier (BBB).

The NDs with a surface modified with the pyridinium oxime moieties have been synthesized. Using carboxylated NDs (ND-COOH) as starting material, there was elaborated method of attaching 4-oximino pyridinium (4-PAM) fragment via variable linkers. The amino-PEG3-amine linker has been selected for studying counterion effect on the modified ND properties. Using 3-chloropropionyl chloride instead of 2-bromoethyl bromide sufficiently increases yield and purity of the final material. The FTIR, elemental analysis, and solid state NMR (13C MAS and 13C CP-MAS) confirm the structure of the substituents and conversion of ND-COOH.

Following our green chemistry approach applied recently for the synthesis of inherently biodegradable ionic liquid-derived oxime surfactants [4] and antidotes [5], the closed bottle test was adapted to estimate biodegradability of the organic material covalently attached to of the nanoparticle and therefore evaluate potential impact of the transformation products on the environment.

The MDCK assay, an example of the tight junction cell line modelling BBB, has been selected to evaluate the ability of oxime-modified NDs to diffuse from the donor compartment through the MDCK cell membrane into the acceptor compartment. An separate experiment included noncovalent loading of the quaternary oximes on the ND-COOH. Concentrations of HI-6 or 2-PAM in acceptor wells (when the cell monolayer was exposed to NDs) were not elevated in comparison to untreated cell monolayers showing that noncovalent binding is not effective enough to come across the cellular barrier, compared to covalently bound oxime-functionalized NDs.

The AcChE reactivation have been performed against three toxic OP: banned insecticide paraoxon and two CWA – sarin (GD) and VX. Our study demonstrates that, as compared to obidoxime, 800 μg/ml of Ox-ND (bromide salt) demonstrate 25-30% of its activity (taken as 0.1 mM aq. solution). For GD and paraoxon, the reactivation with 800 μg/ml is similar to that in the presence of 400 μg/ml; for VX, obidoxime reveals 3 times higher percentage of reactivation. Switching to chloride remarkably elevates the antidotal potency.

The molecular docking was applied to estimate optimal distance between the oxime moieties attached to the ND and spacer properties (length, hydrophobicity, rigidity) to get the active cite of human AcChE and act as the antidote.

References:
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S.NM01.10.03
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S.NM01.10.05
Selective Imaging of Diamond Nanoparticles in Complex Matrices Using Magnetically Induced Fluorescence Contrast
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S.NM01.10.06
Oxime-Functionalized Nanodiamonds as a Platform for Treatment of Organophosphate Poisoning
Yevgen Karpichev¹, Denys Bondar¹, Pavel Starkov¹, Ivo Heinmaa², Ondrej Soukup³, Daniel Jun⁴, Kamil Kuca³ and Vadym Mochalin⁵; ¹Tallinn University of Technology, Estonia; ²National Institute of Chemical Physics and Biophysics, Estonia; ³University of Hradec Kralove, Czechia; ⁴University of Defence, Czechia; ⁵Missouri S&T, United States

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The molecular docking was applied to estimate optimal distance between the oxime moieties attached to the ND and spacer properties (length, hydrophobicity, rigidity) to get the active cite of human AcChE and act as the antidote.

References:

S.NM05.12.17

Air Driven Electrospinning of CNT Doped Conductive Polymer Fibers for Electronics Emily Kooistra-Manning, Lane G. Huston, Jessica M. Andriolo and Jack L. Skinner, Montana Technological University, United States

Electrospinning (ES) is a rapid and simple manufacturing process for producing polymer materials with high surface-area-to-volume ratios. Traditional ES fabrication involves an electrostatic force that pulls polymer from a grounded spinneret tip to a charged metallic deposition surface held at high voltage. Due to the high voltages and the charged electrodes required for ES fiber creation, ES conductive polymers presents a great challenge. During ES of conductive materials, a circuit is completed from the ES spinneret to the deposition substrate, resulting in electrical arcing and non-predictable deposition. In the work presented here, a handheld ES device that incorporates directed airflow was used for deposition of conductive polymer fiber materials directly onto substrates regardless of dielectric charges. In the portable ES device described, deposition occurs by placing a conductive, ring electrode between a spinneret and a deposition surface. The resulting electrostatic force pulls polymer from the spinneret and toward the ring electrode. Directed airflow then carries the polymer fiber through the center of the ring electrode and onto a non-conductive surface beyond the device. Such a system prevents electrical arcing, thereby improving predictability and allowing for the creation of a fiber mat capable of carrying electrical current ranging from direct to alternating. Electrically conductive polymer fiber mats are desirable due to their mechanical compliance, high surface area, potential for optical transparency, and a variety of electrical, optical, and mechanical applications. These applications include but are not limited to materials for water filtration, photocatalysis, light polarization, light energy harvesting, sensors, actuators, and miniature electrical components.

The portable, electrostatic and air driven (ESTAD) ES device presented includes enclosed electrodes and a fiber propulsion system that provides several additional benefits as compared to other portable ES devices including improved safety for the
Quantum Coupling of Spatially Patterned Guanine Defects in DNA Functionalized Carbon Nanotubes

Youngehee Kim, Yu Zheng, Sergei Bachilo, R. Bruce Weisman, Stephen K. Doorn and Han Htoon; Los Alamos National Laboratory, United States; Rice University, United States

Chemical functionalization of the sidewalls of semiconducting single-wall carbon nanotubes (SWCNTs) has attracted intense attention because of the localization of tightly bound excitons at defect sites on the nanotube surface, allowing single-photon emission (SPE) at room temperature. Such covalently functionalized SWCNTs hold the potentials as single-photon sources (SPSs) for the applications of quantum photonics and quantum information processing. Aryl sp3 defects have been sparsely and covalently implanted to the random positons of SWCNT sidewalls through diazonium chemistry, leading to the trapping of mobile band-edge excitons in the aryl defects and causing spectrally shifted photoluminescence (PL). Single photon has been emitted through the radiative recombination of localized excitons at the defect sites in the altered nanotube with ultrahigh single-photon purity (99%).

Previous reports about chemically functionalized SWCNTs as single-photon emitters are based on sparse and random placement of oxygen atom or aryl group on the nanotube surface. Incorporation of multiple defects with spatial pattern in nanotube sidewalls has not been achieved until recent discovery of covalently functionalizing SWCNTs with single-stranded DNA (ssDNA). The coating agents such as surfactants, polymers, or DNA are required for individualizing nanotube particles. ssDNA oligomers have been found to helically wrap around nanotube surfaces through noncovalent interactions. Recently, a room-temperature chemical reaction in samples of ssDNA-suspended SWCNTs has been found between the guanine nucleotides in the ssDNA coating and the nanotube sidewall in the presence of singlet oxygen (1O2). Therefore, introducing and controlling spatially patterned guanine defects on nanotube surfaces is easily achieved by manipulating ssDNA sequences. Such DNA-templated covalent functionalization allows smooth modulation of SWCNT electronic energy levels along the nanotube axis with customized spatial pattern and depth.

Each reacted guanine nucleotides creates a defect with shallow trapping depth in the nanotubes. The axial separation between guanines in the (GT)n ssDNA coating is estimated to be ~0.4 nm, which is at least 5 times smaller than the exciton size. Therefore, excitons in the DNA-tailored SWCNTs are capable of sensing the cumulative potential of several nearby guanine-introduced defects. On the contrary, the exciton is localized in a defect site with deep trapping depth for SWCNT samples with sparse chemical doping of oxygen atom or aryl group on the nanotube surface. We have found that single photon can be generated from the defect-state emission in DNA-altered SWCNTs. Notably, quantum coupling of multiple defect-states has been achieved, resulting from multiple guanine defects with spatial patterning on the nanotube surface.

Superparamagnetic Properties of Metal-Free Nitrogen Doped Graphene Quantum Dots Synthesized by Pulsed Laser Ablation

Muhammad Shehzad Sultan, Vladimir I. Makarov, Brad R. Weiner and Gerardo Morell; University of Puerto Rico - Rio Piedras, United States

In this study, we developed a novel approach to synthesize high-quality metal-free Nitrogen-doped graphene quantum dots (N-GQDs) with high quantum yield, via irradiation of s-triazene in a solution with benzene by using pulsed laser. The TEM, HRTEM, XPS, XRD, Raman spectroscopy and FTIR were carried out to observe the morphology, size distribution, crystalline structure and to prove successful doping of GQDs with nitrogen atoms. Furthermore, for the first time, to our
knowledge, their magnetic properties were investigated. The results indicate that N-GQDs exhibit superparamagnetic behavior. The specific size, shape and zigzag edge structure of N-GQDs were considered to explain the origin of the observed magnetism. The magnetization dependence led to estimating the N-GQD material magnetic permeability for different ambient temperatures. From the zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements, carried out at 50 Oe magnetic field strength, we estimated the blocking temperature $T_B$ to be around 300 K. Based on the experimental data analysis, the magnetic permeability, number of correlated spins per single N-GQD, and number density of superparamagnetic N-GQD per gram of material were estimated. The excellent superparamagnetic properties together with optical properties manifested by N-GQDs have the potential to lead to high performance biomedical applications.

S.NM05.12.08
Optical Response of Ultrathin Periodically Aligned Single-Wall Carbon Nanotube Films Chandra Adhikari and Igor Bondarev; North Carolina Central University, United States

Finite-thickness films of aligned single-wall carbon nanotubes (SWCNT) are recently demonstrated to have extraordinary optoplasmonic properties including a tunable negative dielectric response in a wide photon energy range[1]. We explain this theoretically using the Maxwell-Garnett (MG) mixing[2] for the dielectric responses of planar periodic arrays of identical SWCNTs. We start with the calculation of the conductivity for an individual SWCNT using the (k*p)-method of band structure calculations[3]. Then we use the low-energy plasmonic response calculation technique earlier proposed by one of us for finite-thickness metallic films with periodic cylindrical anisotropy[4], to derive an analytical expression for the dynamical dielectric response tensor of an ultrathin finite-thickness periodically aligned SWCNT array. The dielectric responses of about a dozen of SWCNT arrays with different chiralities and very close diameters are then mixed using the MG method to obtain the anisotropic optical response of the finite-thickness SWCNT film which explains the experimental ellipsometry measurements reported[1]. We also note that in such SWCNT films the inhomogeneously broadened interband plasmon resonance of individual SWCNTs overlaps with the broadened exciton resonance, thus making the exciton-plasmon coupling and associated photon bandgap formation possible[5] for these and similar cylindrically anisotropic compound systems including double-walled carbon nanotubes.

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S.NM05.12.10
Flexible Configurable Multifunctional Electronics Based on Carbon Nanotube Dual-Material Gate Devices Fan Xia, Li Xiang and Youfan Hu; Peking University, China

Electronic devices with configurability to providing multiple functions are of great interests for their superior adaptability to the ever-changing and multifarious application scenarios. Here, we report flexible integrated circuits possessing configurable functions constructed with dual-material gate (DMG) devices based on carbon nanotube thin films, which can serve as either transistors or diodes, on a 2-μm-thick parylene substrate. When configured as a transistor, the DMG device has great advantages over the normal-gated devices regarding the current on/off ratio , the subthreshold swing and the drain-induced barrier lowering due to the regulated energy band distribution in channel area. When operating as a diode, a typical DMG device demonstrates a sufficient rectification ratio of approximately five orders and a diode-on-current of over 26μA. Scalable manufacturing of DMG devices was also demonstrated with great uniformity both in diode and transistor configurations. Finally, multifunctional integrated circuits, which can dynamically switch their function from rectifier to follower or from OR gate to voltage adder by changing controlling signals, were constructed. The functional-configurability, together with scalable manufacturing and the realization on ultrathin flexible substrates, will open up great opportunity for the future environmentally-adaptive system in the field of flexible electronics.

S.NM05.12.12
Pseudocarbynes—Stabilization of Polynes in Solid-State by Gold Clusters Hyunsun Kim, Pilarisetty Tarakeshwar, Peter Buseck and Scott G. Sayres; Arizona State University, United States
Carbyne, the structure consisting of one-dimensional (1D) chain of sp-hybridized carbons is predicted to have greater tensile strength than graphene, making it a highly sought material. However, the highly reactive sp-hybridized carbon chains convert to the more stable sp$^2$-hybridized phase through cross-linking reactions and ozonolysis by exposure to oxygen. We have developed a new class of molecules/materials, “pseudocarbynes”, that we define as sp-hybridized carbon chains that are stabilized through non-covalent interactions with small metal clusters. Here, I will present our progress in synthesizing pseudocarbynes through two distinct experimental techniques: 1) through direct laser ablation of a gold target submerged in liquid, and 2) through the self-assembly of conjugated carbon chains with a colloidal solution of gold nanoparticles. Pseudocarbynes remain stable in the solid-state (tested for up to several months). We characterize the sp$^2$-hybridized carbon structure by analyzing FT-IR and Raman spectroscopies, as well as X-ray powder diffraction directly in the solid state. By securing stability in the solid state, pseudocarbynes are expected to be a good candidate for a diverse set of optical or electronic applications.

S.NM05.12.13
**Design, Solution Synthesis and Characterization of Graphene Nanoribbons and Heterojunctions** Mamun Sarker and Alexander Sinitskii; University of Nebraska-Lincoln, United States

Graphene nanoribbons (GNRs) are known for their highly tunable physical properties and great promise for a broad spectrum of electronic applications. The current study focuses on the chemical design of novel molecular precursors for the bottom-up solution synthesis of atomically precise GNRs. As semiconducting properties of GNRs are highly dependent on their width, edge geometry, and heteroatom doping, here we report on the design, synthesis, and characterization of three different GNRs, which include C4N- and C8N-GNR heterojunctions derived from the pristine with nitrogen-substituted chevron-based monomers, laterally extended chevron GNRs (LecGNRs) and edge-modulated chevron GNRs (EmcGNRs). The XPS-data for C4N- and C8N-GNR heterojunctions confirms the presence of nitrogens and suggests the random positions of pristine and nitrogen-doped GNR segments. The data on the structural, optical and electronic properties of all three GNRs will be presented. In particular, LecGNRs showed an expected lower optical bandgap than their counterparts, while EmcGNRs demonstrate a higher optical bandgap than the pristine chevron GNRs. While this study has a particular focus on the solution synthesis of nanoribbons, the developed molecular precursors may also be compatible with the established on-surface synthesis approaches for GNRs.

S.NM05.12.03
**Low-Power Carbon Nanotube-Based Flexible Integrated Circuits with Bio-Integration Capabilities** Li Xiang and Youfan Hu; Peking University, China

Carbon nanotubes (CNTs) is one of the most promising candidates for next-generation electronics for its extraordinary intrinsic properties, including high carrier mobility, excellent mechanical flexibility and solution processability, which are desirable in unique application scenarios, from smart sensing to biomedical implants. However, the integrated circuits (ICs) with enough complexity and integration scale for signal processing, which is the core units in modern electronic systems, are still lacking, which is mainly due to the nonuniformity of the devices, low yield manufacturing and large power consumption. This presentation would detail approaches for wafer-scale, high-yield and highly-uniform manufacturing of CNT devices and ICs. Chips using CNTs as semiconducting materials are 100% successfully transferred to water-soluble substrates with average device yield of 96.6%. Great uniformity is also demonstrated with minimum standard deviation of 55 mV in threshold voltage. The ICs could be successfully transferred onto biological surfaces, such as human wrist, biodegradable polymers and plant leaf. Integrated with other sensors, the CNT based flexible ICs could demonstrate system-level environmental monitoring. In addition, to further push forward the CNT based flexible electronic devices, we propose a gate engineering approach to boost the electrical performance of the carbon nanotube transistors, to make them more energy-efficient and fit for the low power consumption requirement in practical biological or environmental applications.

Reference

S.NM05.12.04
**Wearable Two-Dimensional Thermoelectric Imaging Sensor Array Based on Carbon Nanotube** Nabila Fairuz, Fariba Islam and Ahmed Zubair; Bangladesh University of Engineering and Technology, Bangladesh
Thermal imaging has applications in non-destructive imaging, testing, detection, and many more areas. Here, we demonstrate a thermal imaging sensor design made of carbon nanotubes (CNTs) using the thermoelectric effect. We designed the sensor device consisted of an array of p-type CNT fibers that crisscross with another array of n-type CNT fibers. Temperature differences between different p-n fiber knots produce voltage differences. Measuring the voltage differences between p and n terminals of each knot, the temperature of each knot can be determined and the thermal image of the object can be obtained. For a 7×7 sensor array, the p-n terminal voltage difference of ~0.22 mV was attained for a temperature difference of 100 K. As CNT gives flexibility and tunability of the Seebeck coefficient in the device, this thermal sensor device can be made wearable with nanorange thermal imaging with extreme precision.

S.NM05.12.05
Density Control of Vertically Aligned Carbon Nanotubes Grown Directly on Stainless Steel through Nanosphere Lithography and Its Effect on Field Emission Properties Arun Thapa and Wenzhi Li; Florida International University, United States

The direct contact of vertically aligned carbon nanotube (VACNT) based field emitter arrays (VACNT-FEAs) to their growth substrate and their structurally controlled morphology are critical factors for applications in vacuum micro/nano-electronic devices. Here, we propose a method for fabricating a high-performance VACNT-FEAs by controlling the morphology of VACNT micro/nano-pillars synthesized directly on stainless steel substrates without external metal catalyst particles via nanosphere lithography (NSL). Exposure of carbon precursor gas to the limited space, created after the NSL using polystyrene spheres of different sizes, on the surface of the thermally heated bulk catalytic substrate was a key for manipulating the morphology of the VACNT-FEAs. Field emission properties of the as-synthesized VACNT-FEAs were measured and found fascinating field emission properties along with high emission current stability. The correlation between the number of emitters in a pillar structure and their field emission behavior has been investigated. The proposed method may be used to fabricate the cold cathodes for vacuum electronic devices requiring high emission current density along with extended emission current stability.

S.NM05.12.06
High Pressure Raman Spectroscopy of Linear Carbon Chain Encapsulated in Isolated Multiwall Carbon Nanotube Keshav Sharma1, Paulo T. Araujo1, Nathalia L. Costa2 and Alexandre R. Paschoal2; 1The University of Alabama, United States; 2Universidade Federal do Ceará, Brazil

Elusive measurements of the Longitudinal optical (LO) phonon mode frequency of isolated Cn@MWCNT systems (linear carbon chains encapsulated by multi-wall carbon nanotubes) were studied under extreme high pressure via Resonance Raman spectroscopy. The pressure-dependent frequency softening with increasing pressure is discussed in terms of a simple force constant model in which the spring constants present a dependence with pressure. The model allowed us to easily obtain both the Young’s modulus and the Gruneisen parameter associated to such LO mode. In particular, the Gruneisen parameter was found to be much higher than that of Graphene and CNTs. Additionally, the LO phonon lifetime was found to be decrease with increasing stress.

S.NM05.12.01
Hybrid Integration of CNT Logic and Analog RRAM towards Monolithic 3DSoC Yijun Li, Jianshi Tang, Zhenxuan Zhao, Jian Yuan, Bin Gao, He Qian and Huaqiang Wu; Tsinghua University, China

With the fast development of emerging technologies such as artificial intelligence and internet of things, there has been higher and higher demand for future chips in terms of computing power, speed, and energy efficiency. Amid the slowdown of Moore's law, new chip architecture is needed to alleviate or overcome the so-called von Neumann bottleneck. Monolithic three-dimensional (3D) integration of multiple layers of functional components, such as emerging memory, logic and sensors, through high-density interlayer interconnects, provides a promising approach to build highly energy-efficient system-on-chip (SoC). On one hand, carbon nanotube (CNT) has been demonstrated as a superior candidate for high-speed logic technology that can be fabricated with low-temperature process. On the other hand, resistive random-access memory (RRAM) has been extensively studied for energy-efficient computing-in-memory (CIM) by taking advantage of its analog switching characteristics. In this work, we report the monolithic integration of CNT logic circuits and analog RRAM array using back-end-of-line (BEOL) compatible low-temperature fabrication processes. The performance of CNT integrated circuits and analog RRAM devices have been carefully optimized. Hybrid circuits such as ternary content-addressable memory (TCAM) are also fabricated. Our work represents a critical step towards 3DSoC with CIM capability.
The motivation behind this project is to study the structure of complex hetero ion based lamellar materials and their physical properties, including ferroelectricity and ferromagnetism, at the 2D limit. By mechanically exfoliating bulk single crystals of CuInP$_2$S$_6$, CuCrP$_2$S$_6$, and CuCrP$_2$S$_6$, a top down approach is used to obtain flakes that are as thin as possible. By isolating a monolayer of these materials, future studies will be conducted to probe for the existence of subnanometer ferroelectric, ferromagnetic, or magnetoelectric multiferroic responses from each respective material systems. Furthermore, studies on heterostructures formed from stacking different monolayers of material in order to study the coupling between different layers are also considered. In hope of its success, we can formulate a device that can take advantage of its magnetoelectric coupling in applications of spintronics and capacitors for more advanced computing.

Using Atomic Force Microscope (AFM) and Raman Spectroscopy, I developed a system to measure the thickness of flakes and to correlate them to Raman spectra and optical images. Despite its challenges, I have successfully measured a range of flake thickness that correlates to a trend in the intensity of the Raman spectra. This allows us a way to identify thin flakes of materials to pursue future studies on the multiferroic character of these materials systems at the 2D limit.

Among the many chemical and physical processes capable of modifying 2D materials, laser plasma processing provides an attractive suite of unique experimental parameters. Using appropriate laser irradiation conditions of a solid target, the ionization fraction, density, temperature, and kinetic energy of a laser-generated plasma can all be adjusted. These plasmas can be used to modify atomically-thin materials. This approach has been employed in the use of a laser-generated sulfur plume for alloying and creation of lateral heterostructures in transition metal dichalcogenides (TMDs) [1]. Further development in this area may be possible with a quantitative understanding of the formation/expansion process of laser-produced chalcogen plumes. In this work, we report on full-scale fluid dynamic simulations of laser-generated chalcogen ion plasmas from initial light-matter interactions to long-range expansion away from a solid target. Contrary to previous studies, our simulation is carried out to centimeter distances, which is the length scale relevant for materials modification. The simulation makes use of implicit partial differential equation solvers and is implemented in a state-of-the-art, multidimensional adaptive Cartesian mesh (ACM) framework. The ACM approach is essential since the spatial resolution required in the early stage of laser-matter interaction is a fraction of a micron while the entire computational domain is several centimeters. As the plasma begins to expand, the fine resolution at the target surface is no longer required, allowing the grid to be coarsened. A dense mesh is still required at the moving plasma front throughout the entire domain and so the ACM follows the front, and allows a coarse mesh elsewhere. The ACM technique makes the computation fast and enables large scale, multidimensional simulations. We simulate the plasma produced during pulsed nanosecond ablation (e.g., KrF excimer) of elemental tellurium and selenium and calculate the kinetic energy distribution of neutral and ionic species, analyzing in detail the evolution of their spatial dynamics. Compared to other metals like copper, bulk tellurium and selenium have drastically lower melting and boiling points as well as mass density. The result of these physical properties is that plasma absorption of the laser pulse begins earlier in the ablation process, and is sustained for longer times, leading to greater vapor densities and temperatures. For instance, at the surface of a copper target, vapor densities are in the 10$^{23}$ m$^{-3}$ range while a selenium or tellurium target irradiated with the same laser power exhibits vapor densities that are an order of magnitude higher, with a greater number of highly ionized species. Both 1D and 2D-axisymmetric simulations show that singly and doubly ionized species expand outwards with high kinetic energy ahead of the high-density neutral vapor. At high vacuum conditions, reducing the laser irradiance below the plasma absorption threshold minimizes the number of energetic species and the thermal component of the plume is dominant. Simulations such as these provide quantitative understanding of the physical properties of chalcogen ion plasmas and can guide experiments in laser plasma modification of TMDs.

The emergence of two dimensional (2D) materials opened up many potential avenues for novel device applications such as nanoelectronics, topological insulators, field effect transistors, microwave and terahertz photonics and many more. To date there are over 1,000 theoretically predicted 2D materials. Of those theoretical materials, only 55 have been experimentally synthesized. The incorporation of this technology into device applications has been hindered due to the difficulty of the mesoscopic growth mechanisms of 2D materials on various substrates using density functional theory calculations within the atomate framework. These parameters, coupled with the elastic constants for the 2D material are used to fit phase field models to predict the mesoscopic growth of various 2D materials.

Various 2D materials are placed epitaxially on substrate surfaces which possess hexagonal symmetry. The 2D materials are pre-screened to ensure that each 2D material will not possess a strain that is more than 10%. For all substrate-2D systems the binding and formation energy is computed using a high-throughput approach to density functional theory performed within the atomate framework. These parameters, coupled with the elastic constants for the 2D material are used to fit phase field models to predict the mesoscopic growth of various 2D materials.

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From last decade, the interest of graphene is rising spanning almost all research areas due to its outstanding electrical, optical, mechanical, etc. properties inherited by its 2D structure [1]. Due to this remarkable discovery, the material graphene oxide (GO) became famous as a precursor for graphene synthesis, even though it was discovered about 150 years ago [2]. The GO is oxygenated form of graphene with many oxygen-containing groups (O-groups) and lattice defects. Hence, to fabricate graphene from GO, removal of these O-groups and repairing of the lattice defects is vital. This process is known as reduction [3]. However, to obtain pristine graphene from GO is the most challenging task due to the difficulty in complete removal of O-groups and repairing of lattice defects by conventional reduction method.

It has been reported that, reduction of GO by high temperature annealing (>1500 °C) is an effective reduction method, particularly in producing conducting RGO films [4]. However, high temperature annealing transforms into high-energy consumption. Further, high temperatures cannot be used on all types of substrates in making graphene films. Therefore, the road to make pristine graphene like material by reducing GO still poses obstacles. As an alternative strategy, thermal annealing of GO in the presence of a carbon source (C-source) such as, ethanol, methane, ethylene, and acetylene via chemical vapour deposition (CVD) has been reported (<1000 °C) [5,6]. In our previously published work, fabrication of conducting RGO films by the restoration of graphitic structure via ethanol-CVD was reported [7]. As a continuation of this work, here we report, with the objective to understand the restoration behaviour of lattice defects, thermal annealing of GO in the presence of various organic solvents such as ethanol, methanol, isopropanol, tert-butanol, ethylene glycol, and toluene.

To mention the methodology in brief, first a dispersion of GO was spin-coated on SiO2/Si substrates and thermal annealing was done in the presence of the above solvents using a CVD device. Characterization of the synthesized samples was done by Raman spectroscopy, atomic force microscopy (AFM) along with Kelvin probe force microscopy (KPFM), and X-ray photoelectron spectroscopy (XPS). Preliminary results showed that there is a significant effect on restoration of lattice defects depending on the organic solvent used. Particularly, the Raman spectroscopic results show the evolution of the G’-peak, which is an indication of restoration of lattice defects, and depending on the C-source the spectral properties change (intensity of G’-peak increases with more carbon atoms). The AFM results showed that the thickness of a single GO sheet has reduced from 1 nm to 0.4 nm due to removal of O-groups upon thermal treatment. Further, conductivity measurements of the synthesized RGO films will be carried out to clarify the solvent dependence on the restoration of lattice defects.

References
S.NM06.10.09
Symmetry Dependent Kinetics of 2D Materials’ Growth and Etching
Jichen Dong¹ and Feng Ding¹,²; ¹Center for Multidimensional Carbon Materials, Institute for Basic Science, Korea (the Republic of); ²Ulsan National Institute of Science and Technology, Korea (the Republic of)

The unique structures of 2D materials make them to show many excellent electronic, chemical and thermal properties that are absent from their 3D counterparts. To date, tremendous efforts have been devoted to the synthesis of large-area high-quality 2D materials. Moreover, studies have shown that etching, which has been one of the key techniques in the semiconductor society, can be used to create various structures in 2D materials, which can not be obtained by direct growth (PNAS 110 20386 (2013)). Therefore, A deep understanding on the growth and etching behaviors of 2D materials is crucial for their controllable fabrication. Here, we propose a general model for the growth and etching of two dimensional (2-D) crystals. In this model, low index edges are treated as the basis, while high index ones are described to be composed of terraces along the basis directions and kinks that connect the terraces. Considering the high formation energy penalty of forming a 1D nucleus on a terrace and the easy addition or removal of atoms to or from the kink sites, symmetry dependent edge growth and etching rate profiles of 2D crystals are constructed. By applying the kinetic Wulff construction (KWC) for growth and our modified KWC for etching, we simulated the shape evolutions of 2-, 3-, 4- and 6-fold symmetric 2D crystals during their growth and etching processes, which are well consistent with many experimental observations. This proposed model is expected to be a standard model for the growth and etching of 2D crystals.

S.NM06.10.11
Robustness of Atomic Scale Phosphorous Delta Layers—Toward Room Temperature Operation
David A. Scrymgeour, Connor Halsey, Daniel Ward, DeAnna Campbell, Evan Anderson, Scott W. Schmucker, Jeffrey A. Ivie, Ezra Bussmann, Suzey Gao, Tzu-Ming Lu and Shashank Misra; Sandia National Labs, United States

Atomic precision phosphorus doping of silicon by scanning tunneling microscope (STM) based hydrogen resist lithography is a promising fabrication platform for creating advanced silicon based electrical and quantum structures. In this process, termed atomic precision advanced manufacturing (APAM), the doping is accomplished by selective depassivation of bound hydrogen with the STM tip, incorporation of phosphine molecules, and capping with epitaxial silicon. APAM devices could provide a platform to learn about the device physics relevant to future transistor technologies. Moreover, these structures can carry a surprising 2 mA/μm of current, potentially enough to integrate APAM structures and devices with modern CMOS transistors. However, these devices have limited applicability because they only operate at cryogenic temperatures, and their ability to withstand the operational environments of CMOS is an open question. In this work, we report on our attempts to demonstrate room temperature devices realized in silicon-on-insulator devices and delta layer analogs, and the discuss the robustness and failure mechanisms at elevated temperature and current densities. These results show utility and challenges of this material platform for future discovery platforms.

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S.NM06.10.15
Fabrication and Characterization of DNA Origami-Based Metal-Semiconductor Junctions
Basu R. Aryal, Dulashani R. Ranasinghe, Tyler R. Westover, Robert C. Davis, John N. Harb and Adam T. Woolley; Brigham Young University, United States

DNA-assisted bottom-up nanofabrication has demonstrated promise in creating both metal and non-metal nanostructures with diverse applications. To date, different-shaped and electrically connected metal nanostructures have been created and
electrically characterized. However, the self-assembly and electrical measurement of semiconducting materials on DNA at the nanoscale have not been demonstrated. We have examined the fabrication yield and electrical properties of various Au nanowire structures created on DNA origami tiles by site-specific attachment of Au nanorods to molecularly programmed sites. We are now working with metals and semiconductors on these DNA nanostructures. We have attached Au and Te nanorods to designed locations on individual DNA origami templates and connected the nanorods via electroless Au deposition technique to create metal-semiconductor junctions. In addition, two-point probe electrical measurements were performed to verify the electrical continuity of the junctions, and non-linear current vs voltage curves were obtained. This work is a step toward self-assembling metals and semiconductors at the nanoscale using DNA origami structures, with potential future nanoelectronics applications.

Reference
Modern medical applications require the design of multifunctional polymers. These substances shall fulfill several roles while implanted in the human body, for example as mechanically supporting devices that can release a drug, followed by a full, non-toxic degradation. A concept for implanting multiple functions is molecular integration through well-defined polymer architectures. Here, structure parameters, which can be varied include composition and ratio of different molecular building blocks as well as the branching type. Moreover, the aqueous biological environment can influence polymer behavior, like hydrogel swelling in water that may trigger both drug release and subsequent degradation.

Material design therefore implies knowledge on structure-function relationships that enable rapid prediction of material properties under specific conditions and external stimuli over sufficiently long time scales. Especially, polymer degradation has major impact on material physicochemical properties and requires thorough understanding of the molecular processes [1]. Importantly, degradation at the polymer surface links to medical applications. For example, medical drugs are delivered in the human body without functional loss if they are encapsulated in a polymer matrix which degrades at the surface without effecting its bulk composition. Recent experimental studies have shown that defined two-dimensional thin film polymer layers are highly suitable to quantitatively study degradation kinetics with Langmuir techniques [2]. In this work we now apply computational simulations to provide an all-atomistic description of the polymer degradation process at the two dimensional interface. A molecular modeling approach is used to show how a molecular monolayer polymer surface film at the water interface behaves at different stages of the degradation process. The models are validated by exploring chemically established commercially available implant materials such as PLGAs (poly(lactide-co-glycolide)) and PCL (poly(ε-caprolactone)). The validation takes random chains as well as end-chain cutting as degradation mechanisms into consideration.

Finally, the model will be used as a predictive tool for digitally assembled copolyesters comprising the same repeating units, but aligned in sequence structure, which in part are challenging to synthesize such as strictly alternating structures. The gained knowledge will form the basis for the design of the next generation of degradable implant materials.

S.NM06.10.27
Exploring the Role of Dimensional Variation in Molybdenum Disulphide (MoS2) by Relating the Structural, Morphological and Optical Characteristics
Margi Jani, Dhyey Raval, Abhijit Ray and Indrajit Mukhopadhyay; Pandit Deendayal Petroleum University, India

Molybdenum disulphide (MoS2) as a transition metal dichalcogenides (TMDCs) sketching a wide research interests with unique optical and electronic properties then a bulk. Bandgap engineering technique is a potential way for tuning to its optimization. MoS2 owing to band gap tailoring from 1.3 to 1.9 eV for bulk (indirect) and single-layered (direct) structures makes it a promising material in the field of energy applications. The present article deals with variation in the properties along with dimensional (1-3D) change in molybdenum disulphide nanostructure. Syntheses, structural, morphological, optical properties of bulk to few layers of nanostructures are investigated. The exfoliation of MoS2 Flake like nanostructure has been studied for its unique properties. Uniform 3D flower like nanostructures has been prepared by one-pot hydrothermal method. Nanostructure flakes by a solution based exfoliation method are compared with a bulk MoS2. Structural, morphological and optical properties were investigated by XRD, FESEM, EDAX, UV–Visible for the bulk and nanostructures properties.
Enhanced Intracellular Uptake of Quantum Dots and Gold Nanocrystals Promoted by an Antimicrobial Peptide

Hedi M. Mattoussi; Florida State Univ, United States

There has been much interest in developing multimodal imaging platforms, using colloidal nanocrystals made of luminescent quantum dots and plasmonic nanomaterials. Such approach is highly promising. However, the lack of adequate and effective strategies to deliver these nanocrystals into the cytoplasm of live cells has been a major challenge. We have designed a set of high affinity hydrophilic polymer ligands and tested them for the stabilization of various inorganic nanocrystals (e.g., luminescent quantum dots and Au nano-colloids) in biological media. Furthermore, introducing additional reactive groups facilitates easy coupling of the polymer-coated nanocrystals to specific cell targeting peptides or/and NMR-active labels.

Here, we report on the ability of an anti-microbial peptide to promote the uptake of three types of nanomaterials (QDs, AuNPs and AuNRs) into mammalian cells. Using fluorescence microscopy experiments, we found that incubation with these conjugates yielded nanocrystal staining throughout the cell volumes. Additional experiments showed that uptake persisted under endocytosis inhibition conditions, such as incubation at low temperature and in the presence of hypertonic sucrose solution. These findings were complemented with flow cytometry measurements and confocal microscopy imaging. Overall, the imaging data support the hypothesis of physical translocation of these conjugates through the membrane rather than endocytosis.

Intracellular Transport of TiO₂ Nanoparticles—Single Particle Tracking and Modeling of Stochasticity

Keisha Cook¹, Nathan T. Rayens², Scott A. McKinley¹ and Christine K. Payne²; ¹Tulane University, United States; ²Duke University, United States

Titanium dioxide nanoparticles (TiO₂ NPs) are indispensable in consumer products due to their function as pigments and photocatalysts. For example, TiO₂ NPs are included in food products and cosmetics to brighten white colors and in sunscreen to block UV rays from reaching the skin. Previous work has shown that the effects of TiO₂ NP exposure on human cells through food consumption and skin contact are negligible, but the effects of TiO₂ NP inhalation are unknown. Using fluorescence microscopy and transmission electron microscopy, we have found that TiO₂ NPs are internalized by human lung cells (A549). In these cells, TiO₂ NPs accumulate in lysosomes, membrane-bound organelles responsible for the transport and degradation of cell cargo. Enlargement of these organelles can have significant effects on cell health. We have found that TiO₂ NP-containing lysosomes are 1.85 times larger on average than lysosomes in untreated cells when compared through representative distributions of size.

We used single particle tracking fluorescence microscopy to follow the motion of TiO₂ NP-containing lysosomes in living cells. Lysosomes were fluorescently labeled with fluorescent proteins and by the absorption of fluorescently-labeled proteins on the TiO₂ NPs. In both of these cases, and for any single particle tracking experiment, observation time is limited by photobleaching, cell viability, and microscope stability. As such, a stochastic model of lysosome motion is warranted to extrapolate beyond trajectory limitations and establish confidence in data validity.

Our goal was to determine the trajectory length necessary to establish confidence in the validity of the observed velocity and diffusivity of lysosome motion. Using Bayesian methods, we estimated unknown information given a set of single particle trajectories. With this information from lysosome trajectories, we could then assign a likelihood that each lysosome was in a specific state of motion (e.g., active transport or diffusion) during a given time interval. This provides insights on the mobility distribution of lysosomes in the cell as a function of TiO₂ NP transport. Based on the inferred relative frequencies of the various states of motion, we then built a forward simulation to explore what the long-term distributions of enlarged lysosomes might be compared to normal lysosomes. Our stochastic model, in combination with experimental data, verifies the validity of our observed trajectories and predicts lysosome transport modes for both untreated control and TiO₂ NP-
containing cells. This confidence in the stochastic modeling of particle tracking is useful not only for TiO₂ NP-containing lysosomes, but also broad questions of cellular transport studied with single particle tracking.

SESSION S.NM04.02: Nanosafety—Safety and Risk Assessment
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday
Morning, November 21, 2020
S-NM04

5:00 AM *S.NM04.02.02
Application of Combined Computational and Machine Learning Based Cheminformatics Approaches towards Nanomaterials Toxicity Assessment Bakhtiyor Rasulev; North Dakota State University, United States

For the last two decades, breakthrough research has been going on in all aspects of materials science, including nanotechnology at an accelerated pace. New nanomaterials of unprecedented functionality and performance are being developed and characterized. However, environmental exposure to nanomaterials is inevitable as nanomaterials become part of our daily life, and as a result, nanotoxicity assessment is getting increasingly important. Here we show the adaptation and application of various computational and cheminformatics methods in nanomaterials toxicity prediction. Since nanomaterials are complex entities from a chemical point of view and the study of these kind of materials requires an interdisciplinary approach, involving multiple aspects ranging from physics and chemistry to biology, informatics and medicine. We show how the combination of computational chemistry, available experimental data, machine learning and cheminformatics approaches can help in nanomaterials toxicological risk assessment. We discuss here a few case studies where data-driven models developed help to decode the relationships between the toxicity of nanomaterials and their physicochemical characteristics, by application quantum chemical, protein-ligand docking, developed nanodescriptors and cheminformatics approaches, including a quantitative multi-nano-read-across approach that combines interspecies correlation analysis.

SESSION S.NM04.03: Poster Session: Nanosafety
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday
Morning, November 21, 2020
5:00 AM - 8:00 AM
S-NM04

S.NM04.03.02
Flame-Based Fabrication of Superhydrophobic Surfaces from Silicones Souvik Banerjee¹, Xinchun Tian¹, Deyny L. Mendivelso-Perez¹, Kara Lind², Santosh Shaw³, Emily Smith¹ and Ludovico Cademartiri¹;¹Iowa State University, United States;²Ochsner LSU Health Shreveport, United States;³Intel Corporation, United States

Outdoor applications of superhydrophobic coatings require synthetic approaches that allow their simple, fast, scalable, and environmentally benign deployment on large, heterogeneous surfaces and their rapid regeneration in situ. We show that the thermal degradation of silicones by flames fulfills these characteristics by spontaneously structuring silicone surfaces into a hierarchical, textured structure that provides wear-resistant, healable superhydrophobicity. We will elucidate how flame processing is a simple, rapid, and out-of-equilibrium process that is counterintuitively reliable and robust in producing such a complex structure. A comprehensive study of the effect of the processing speed and flame temperature on the chemical and physical properties of the coatings yielded three surprising results. (i) Three thermal degradation mechanisms drive the surface texturing: depolymerization (in the O₂-rich conditions of the surface), decomposition (in the O₂-poor conditions found a few micrometers from the surface), and pyrolysis at excessive temperatures. (ii) The operational condition is delimited by the onset of the depolymerization at low temperatures and the onset of pyrolysis at high temperatures. (iii) The remarkably wide operational conditions and robustness of this approach result from self-limiting growth and oxidation of the silicone particles that are responsible for the surface texturing and in the extent of their deposition. As a result of this analysis, we show that superhydrophobic surfaces can be produced or regenerated with this approach at a speed of 15 cm s⁻¹ (i.e., the length of an airport runway in ~4.5 h).
A Highly Selective Sensor Based on Fluorescent Fe2O3-CdSe Nanocomposite for Detection and Removal of Picric Acid

Vishal Kumar and Soumitra Satapathi; Indian Institute of Technology Roorkee, India

Detection of the nitro-fragrant compound at trace level is critical in combating terrorism, for keeping up national security and for providing environmental and clinical safety. Among various nitroaromatics compounds (NACs), the importance of picric acid (PA) owes to its extensive usage in the manufacture of rocket fuels, fireworks, deadly explosives, leather processing and sensitizers in photographic emulsions.[1] As of now, many fluorescence chemosensors/probes have been effectively applied for the detection of PA with functional specificity based on its characteristic properties, particularly resonance energy transfer and electron-deficient nature of the nitro group (-NO2), yet only a few appeared closer to the practical applications. Late reports on CdSe nanoparticles and expedient to surface modification showed its fate in the detection of NACs. Quantum dots have a clear advantage over molecule-based emitters; however, these multi-model sensors are inconvenient for the removal of the target species, which might cause secondary contamination. Towards this end, the incorporation of a fluorescent and magnetic functionality in a single nanocomposite particle would be a promising alternative.[2]

Here, we present a methodology and promising novel hybrid nano-structure that comprises of magnetic core encapsulated inside a thin silica shell (Fe2O3@SiO2 NPs), electrostatically adsorbed through the free anionic carboxyl group with a positively charged spacer arm of florescent Cysteamine-capped CdSe quantum dot (QD) (particle size ≈ 12.7 nm). This multimodal nanosensor provides an efficient sensitive and selectivity detection of PA over a number of other explosive (NACs) in DMSO, (LOD ≈ 2.2 µM) (Quenching constant KPA ≈ 4.3×104 M^{-1}) in solution via photo-induced electron transfer mechanism. The sensing mechanism is probed via UV-Vis spectroscopy, steady-state and time-resolved fluorescence spectroscopy which was found to be a mixture of immediate dynamic and static quenching as the lifetime of nanosensor (0.98 ns) is reduced to 0.63 in presence of PA. In addition to solution-phase sensing, this magneto-fluorescent nanosensor also showed an excellent ability for the removal of detected PA molecules with the use of an external magnet, staging as a possibility for the potential application of low-cost and stand-off sensor. In summary, this elegant architecture results in an ultra-small magneto-fluorescent nanoparticle offering a novel platform for the development of a field-based PA sensor.

References

Effects of Polyethylene Particles from 0.2 μm - 0.9 μm in Size on Synechococcus sp. PCC 7002

Mary Machado¹, Gina Vimbela¹, Tania Silva de Oliveira², Arijit Bose² and Anubhav Tripathi¹; ¹Brown University, United States; ²University of Rhode Island, United States

Microplastics or plastic particles less than 5 mm in size are a common and damaging pollutant in the marine ecosystem. However, the full adverse impacts of these particles on marine microorganisms are just starting to be understood. Polyethylene is one of the most abundant microplastics found within the marine environment, but few studies have been performed on microorganisms exposed to these particles. Additionally, little work has been done to identify the cytotoxic, genetic, enzymatic and morphological effects that nanoplastics and microplastics have on marine microorganisms. This study used molecular techniques such as High-Resolution Automated Electrophoresis and RT-PCR to quantitatively analyze expression changes in characteristic marine organism (Synechococcus sp. PCC 7002) exposed to polyethylene nanoparticles and polyethylene microparticles. Novel visualization techniques such as scanning electron cryomicroscopy (CryoSEM) were also used by this investigation to measure morphological changes in bacterial colonization on these particles. Results of this study showed significant differences between nanoparticle, microparticle and control samples. A viability analysis using neutral red showed decreases in the number of viable cells after 5 days of exposure to polyethylene nanoparticles that were not seen in microparticle or control samples. RT-PCR analyses showed differences in the expression of esterase and hydrolase genes. For samples exposed to polyethylene nanoparticles, increases in expression occurred at 5 days of exposure. In samples exposed to polyethylene microparticles, however, expression increased more substantially at 10 days of exposure. A plate based enzymatic assay showed increased esterase activity at the 5 day time point in the nanoparticle exposed samples. Cryo-scanning electron microscopy results identified changes in exopolymer formation in all samples exposed to polyethylene particles. These results illustrate that exposure to polyethylene microparticles and nanoparticles results in genetic, enzymatic and morphological changes in Synechococcus sp. PCC 7002 and argue for further molecular study of the effects of anthropogenic stressors on marine microorganisms.
SYMPOSIUM S.NM05

1D Carbon Electronics—From Synthesis to Applications
November 21 - November 29, 2020

Symposium Organizers
Michael Arnold, University of Wisconsin Madison
Roman Fasel, EMPA
Youfan Hu, Peking University
Jianshi Tang, Tsinghua University

* Invited Paper

SESSION S.NM05.13: Live Keynote I: Graphene Nanoribbon
Session Chairs: Roman Fasel and Pascal Ruffieux
Saturday Afternoon, November 28, 2020
S.NM05

2:45 PM *S.NM05.05.08
Atomically Precise Graphene Nanoribbons—From Synthesis to Electronic Applications Alexander Sinitskii; University of Nebraska - Lincoln, United States

Atomically precise graphene nanoribbons (GNRs) are at the forefront of nanocarbon research and hold great promise for electronic and optoelectronic applications. Theoretical studies have shown that narrow GNRs possess interesting electronic and magnetic properties that strongly depend on the nanoribbon’s width and edge structure. GNRs with different structures can be synthesized with atomic precision and fine-tuned properties by coupling properly designed molecular precursors and planarization of the resulting polymers.

In this talk, I will discuss our recent results on solution and on-surface synthesis and characterization of atomically precise GNRs. The solution approach is based on Yamamoto coupling of pre-synthesized molecular precursors followed by cyclodehydrogenation using Scholl reaction. This approach can be applied to the synthesis of a variety of GNRs, including pristine and nitrogen-doped GNRs with the chevron structure. The on-surface approach is based on the coupling of halogenated molecular precursors on metal substrates and subsequent cyclodehydrogenation of the resulting polymers at elevated temperatures.

Both solution and on-surface approaches were used to synthesize laterally extended chevron GNRs (eGNRs). The ribbons grown on Au(111) were used for extensive scanning tunneling microscopy (STM), noncontact atomic force microscopy (nc-AFM) and scanning tunneling spectroscopy (STS) characterization. They were found to exhibit a bandgap of about 2.2 eV, which is considerably smaller than the values reported for chevron GNRs in similar studies. The solution-synthesized eGNRs were processed into uniform thin films that exhibited improved electrical conductivity compared to similar films of regular chevron GNRs. The eGNR films were employed in gas sensors that showed very high responsivity to low molecular weight alcohols compared to similar sensors based on benchmark graphitic materials, such as graphene and graphene oxide. Finally, we demonstrated the first electronic nose system based on atomically precise GNRs that could reliably recognize analytes of nearly the same chemical nature, such as methanol and ethanol. Overall, this work demonstrates the entire path from designing new atomically precise GNRs with improved properties to their bottom-up synthesis, characterization, processing and implementation in electronic devices.

3:05 PM *S.NM05.08.01
High Performance Graphene Nanoribbon Transistors Jeffrey Bokor1, Zafer Mutlu1, Juan Pablo Llinás1, Gabriela Borin Barin2, Peter Jacobse1, Ilya Piskun1, Raymond Blackwell1, Andrew Fairbrother1, Xinliang Feng2, Klaus Müllen2, Felix R. Fischer1, Pascal Ruffieux2, Michael Crommie1 and Roman Fasel1; 1University of California, United States; 2Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; 3National Institute of Standards and Technology,
Recent advances in on-surface organic synthesis have led to the development of bottom-up graphene nanoribbon (GNR) growth with atomic precision. Bottom-up synthesized GNRs have promising electronic properties for high performance field effect transistors (FETs) and ultra-low power devices such as tunneling FETs. However, the short length, wide band gap, and random spatial orientation of GNRs have impeded the fabrication of devices with the expected performance and switching behavior. Here, recent progress in integrating bottom-up synthesized GNRs into devices will be presented. High on-current and high on-off ratio FETs with a nine-atom wide GNRs as the channel material were successfully fabricated.

Strategies to further improve FET device yield and performance with the parallel arrays of GNRs transferred from single crystal Au (788) will be discussed. Finally, a new approach for the transfer-free fabrication of GNR devices has been developed.

References

**Electronic and Vibrational Properties of 1D Carbon Nanostructures from First-Principles** Vincent Meunier1, Colin Daniels1 and Liangbo Liang2; 1Rensselaer Polytechnic Institute, United States; 2Oak Ridge National Laboratory, United States

I will provide an overview of the recent progress made in my group on the understanding of the electronic and vibrational properties of 1D carbon nanostructures based on a combination of theoretical and computational methods. In the first part of the presentation, I will first focus on providing a model to account for the significant screening caused by the presence of a substrate on the electronic properties of graphene nanoribbons. In the second part of the talk, I will present a broad and detailed overview of the intrinsic vibrational properties of 1D carbon nanostructures with a variety of edge configurations, sizes, and shapes. These results will be systematically compared to experiment (notably, Scanning Tunneling Spectroscopy and Raman Spectroscopy). While theory and experiment are found to usually be in excellent agreement, I will also discuss a number of unresolved issues and will suggest a roadmap to tackle them.

**Forging Symmetry Protected Topological States into Metallic Graphene Nanoribbons** Felix R. Fischer1,2,3, Michael Crommie1,2,3 and Steven G. Louie1,2; 1University of California, Riverside, United States; 2Lawrence Berkeley National Laboratory, United States; 3Kavli Energy NanoScience Institute, United States

We have recently demonstrated the rational design and experimental realization of a graphene nanoribbon (GNR) superlattices that hosts a 1D array of symmetry-protected topological states, thus generating otherwise inaccessible electronic structure. This new class of materials can be thought of as an extended form of poly-acetylene wherein highly localized half-filled topological states replace the familiar single occupied p-orbitals along a conjugated p-system. Experimental results and first-principles calculations reveal that the frontier band structure of these GNR superlattices is defined purely by the coupling between adjacent topological interface states and can be tuned all the way from a semiconductor to a metal. This novel manifestation of 1D topological phases presents an entirely new route to band engineering in 1D materials based on precise control of their electronic topology, and is a promising new platform for future studies of 1D quantum spin physics.

**Emergence of Spin States in Graphene Nanostructures** José Ignacio Pascual; CIC nanoGUNE, Spain

Graphene can spontaneously develop intrinsic paramagnetism. Crucial examples are the magnetization of zig-zag edges in graphene, or the emergence of paramagnetism in open shell graphene nanostructures. I will show that graphene nanoribbons (GNRs), fabricated with atomic precision on a metal surface exhibit fingerprints of π-paramagnetism on a metal surface, which can be detected and spatially localized using low temperature scanning tunneling [1]. Single electron spins emerge localized at certain zigzag sites of the carbon backbone. Their presence could be detected and mapped by spatially resolving the zero-energy resonance due to the Kondo effect. We found that near-by spins are coupled into a singlet ground state and quantify their exchange interaction via singlet-triplet inelastic electron excitations. Theoretical
simulations picture how electron correlations result in spin-polarized radical states with the experimentally observed spatial distributions. Extra hydrogen atoms bound to radical sites quench their magnetic moment and switch the spin of the nanostructure in half-integer amounts.

I will also review other methods for activating magnetic ground states in graphene. For example, spin states can be created on a ribbon simply by substitutional doping or by incorporating magnetic species into a ribbon using on-surface synthesis routes (see included image of a Fe porphyrin contacted to chiral nanoribbons). In this last case, we proved that the molecular spin survives in the ribbon by using spin-excitation inelastic spectroscopy [2]. By proper selecting the position of the halogen functionalization, we fabricated linear GNR-FeTPP-GNR structures and performed electronic transport measurements [3], detecting spin-excitation fingerprints in transport mode.


4:25 PM *S.NM05.05.04

Bottom-Up Solution Synthesis of Structurally Well-Defined Graphene Nanoribbons—Modulation of the Width and Edge Functionalization

Akimitsu Narita1,2; 1Okinawa Institute of Science and Technology Graduate University, Japan; 2Max Planck Institute for Polymer Research, Germany

In contrast to zero-bandgap graphene, structurally confined graphene nanoribbons (GNRs) features open bandgaps due to the quantum confinement effect, which render them highly promising for nanoelectronic and optoelectronic applications.[1] The properties of the GNRs are determined by their chemical structures, in particular the width and the edge configuration, which makes their precise structural control essential. Whereas such precision cannot be achieved by “top-down” fabrication methods such as “cutting” of graphene, bottom-up chemical synthesis can afford atomically precise GNRs with various structures.[1,2] The synthesis is carried out through polymerization of a tailor-made monomer leading to a polymer precursor, which can be “planarized” and “graphitized” into GNRs by oxidative cyclodehydrogenation. While it is challenging to obtain very long GNRs through transition-metal-catalyzed or metal-surface-assisted polymerization, we have demonstrated solution synthesis of GNRs with average lengths larger than ~600 nm through AB-type Diels-Alder polymerization.[2,3] Solubilizing alkyl chains can be attached on the GNR edges through the solution synthesis, making them dispersible in organic solvents and thus allowing for the liquid-phase processing for the device integration.[3,4] By modifying the monomer structure, laterally extended GNRs with the width of up to ~2 nm could be obtained, revealing the lowering of the optical bandgap down to ~1.2 eV.[2,3] We have also achieved edge functionalization of the GNRs by introducing a bromo group on the monomer. For example, introduction of perylene monoimide units led modulation of the self-assembly behavior, providing intriguing “rectangular” networks of GNRs.[6] Moreover, introduction of spin-bearing organic radicals on the GNR edges allowed for spin injection to the aromatic core, inducing a delocalized magnetic state, which might have potential for application in the quantum computers.[7] These results form a fundamental basis for applications of such GNRs in the future nanotechnology.

References
5:00 PM *S.NM05.03.01
**Controlling Carbon Nanotubes by DNA—From Separation to Integration** Ming Zheng; National Institute of Standards and Technology, United States

A unique feature of single-wall carbon nanotube (SWCNT) material is its structure diversity: within the same rolled-up graphene sheet structure framework one finds SWCNTs of different electronic bandgaps: metals with zero bandgap, quasi-metals with meV bandgap and semiconductors with ~ 1 eV bandgap. However, making use of SWCNT structure diversity requires a method to obtain SWCNTs of defined structures. In this contribution, we present our current state of DNA-based sorting of SWCNTs. In particular, we show our ability to put any DNA sequence on any SWCNT species, enabling DNA-based assembly of high-density SWCNT devices. In the end, we discuss the design of a device we call Photon Perceptron Array (PPA). PPA is an array of micron-sized spectrometer units that can measure the spectrum of incoming photon in the wavelength range of 200 nm to 2000 nm (and possibly going all the way to THz), with a spatial resolution comparable to the size of a single spectrometer unit. Each spectrometer unit is composed of a set of distinct photodetectors made of SWCNTs of defined atomic structures, placed in parallel with tube-to-tube separations controlled at nanometer precision by DNA origami technology. A high-density array of identical spectrometers can be constructed by placing DNA origami/carbon nanotube complexes in photolithographically-defined locations. PPA may be used in spectral imaging in many fields of science and technology.

5:20 PM *S.NM05.02.01
**Flexible, Wearable and High-Temperature Devices Based on Aligned Carbon Nanotubes** Junichiro Kono; Rice University, United States

The remarkable flexibility, stable chemical structure, and extraordinary thermal, electrical, and optical properties of carbon nanotubes (CNTs) are promising for a variety of applications in flexible and/or high-temperature electronics, optoelectronics, and thermoelectrics, including wearables, refractory photonics, and waste heat harvesting. However, the long-standing problem in the preparation of CNT ensembles is to maintain the extraordinary properties of individual CNTs on a macroscopic scale; the polydispersity and randomness remain two main challenges. Here, we will discuss three ways of creating wafer-scale aligned CNTs: direct growth of aligned CNTs by chemical vapor deposition, production of ultrahigh-conductivity CNT fibers through solution spinning and coating, and spontaneous formation of wafer-scale aligned CNT films via controlled vacuum filtration. We will then describe flexible and high-temperature applications of these materials, such as flexible CNT broadband detectors, spectrally selective thermal emitters, and thermoelectric devices.

5:40 PM *S.NM05.02.02
**Self-Assembly of Carbon Nanotubes into Tunable Hyperbolic Metamaterials** Abram Falk; IBM T.J. Watson Research Center, United States

Plasmon resonance in carbon nanotubes is an exciting resource for confining light to the nanometer scale [1]. In this talk, I will discuss how dense films of carbon nanotubes have emergent optical properties related to these resonances. We assemble our films with a simple vacuum filtration technique and find that optimal assembly leads to the nanotubes crystallizing into monolithic, two-dimensionally ordered films. Using Mueller-matrix ellipsometry, we then characterize the films’ optical properties and find a broadband, electrostatically tunable hyperbolic region in the mid-infrared [2]. Another fascinating property of dense nanotube films is that excitons in the nanotubes can couple to the nanotubes’ own plasmon resonances – that is, cavity quantum electrodynamics (cQED) without an external cavity [3]. In fact, this coupling strength can reach the ultrastrong light-matter interaction regime. Technologically, crystallized nanotube films could provide a materials-driven pathway from fundamental concepts in cQED to advanced telecommunications hardware, including tunable thermal emitters.
super-resolution imaging systems, and active, nonlinear optical devices like modulators and nanolasers.


6:00 PM *S.NM05.07.02
Transforming Ideas to Reality—Emerging Nanotechnologies from the “Lab” to the “Fab” Max Shulaker and Christian Lau; Massachusetts Institute of Technology, United States

At this exact moment when future applications are demanding massive improvements in computing performance, conventional approaches to improving computing are becoming increasingly challenging. Nanosystems – leveraging unique properties of emerging nanotechnologies to realize new systems and architectures – promise to enable the next wave of computing gains for next-generation applications as well as provide the means for developing rich new functionalities that lie beyond the scope of traditional computing today. Yet despite this promise, imperfections and variations inherent in beyond-silicon emerging nanotechnologies have made realizing large-scale integrated systems infeasible. In this talk, I describe how by combining advances across the entire stack – from nanomaterial synthesis to new processing techniques, circuit design methodologies, and architectures – these challenges can be overcome to realize the first large-scale and complex electronic systems leveraging beyond-silicon emerging nanotechnologies. As a case-study, I will describe the journey of transforming carbon nanotubes from an interesting scientific nanomaterial into the foundation for realizing the first beyond-silicon microprocessor built entirely from carbon nanotube transistors – RV16X-NANO, a 16-bit microprocessor based on the RISC-V instruction set. I will conclude by describing how emerging nanotechnologies are beginning to be transferred from the “lab” to the “fab,” promising a new and exciting age for nanoelectronics and computing.

6:20 PM *S.NM05.07.01
Carbon Nanotube Based High Performance CMOS and Optoelectronic Devices Lian-mao Peng¹,² and Yang Liu¹; ¹Peking University, China; ²Columbia University, United States

Carbon nanotube (CNT)-based electronics has been considered one of the most promising candidates to extend Si complementary metal-oxide-semiconductor (CMOS) technology. In particular CNTs have been investigated for various electronic and optoelectronic device applications, such as sub-10nm CMOS devices which outperform that of state-of-the-art Si based CMOS devices in both speed and power consumption [1-5], as well as idea material for monolithic optoelectronic integration with complementary MOS-compatible signal processing circuit [6-8].

Prototype device studies on individual CNTs revealed that CNT based devices have the potential to outperform Si CMOS technology in both performance and power consumption. With a well-designed device structure and in combination with graphene, we showed that high-performance top-gated CNT FETs with a gate length of 5 nm can be fabricated. Significant progress has also been made in fabricating carbon nanotube low-power devices. An efficient way to reduce the power is to lower the supply voltage VDD, but this voltage is restricted by the 60 millivolts per decade thermionic limit of subthreshold swing (SS) in FETs. A Dirac source (DS) with a much narrower electron density distribution around the Fermi level than that of conventional FETs was recently proposed and demonstrated using CNT to reduce SS [2].

References
Nanomaterials for Printable Electronics Patrick R. Malenfant; National Research Council Canada, Canada

The National Research Council (NRC) is Canada’s premier organization for research and technology development. NRC’s Printable Electronics (PE) program develops materials and inks for additive manufacturing in order to enable a sustainable PE sector in Canada. Progress has been made over the last 15 years, yet many challenges remain at the materials, fabrication and integration level, limiting performance and commercialization. This presentation covers our progress in high purity semiconducting single-walled carbon nanotube (sc-SWCNT) enrichment and transistor fabrication via solution based processes as well as conductive molecular ink development\[1-11\]. I will highlight our recent progress in understanding sc-SWCNT enrichment using conjugated polymers, with special consideration given to the effects of solvent parameters and doping on the mechanism and yield/purity of the final product\[2-4\]. Removal of the wrapping polymer using a dry process on-wafer will also be described\[5\]. Developments in conductive molecular inks and progress towards the commercialization of new applications will be described such as in-mold electronics\[6-8\]. Challenges and advances associated with using polymer-based dielectrics and encapsulants will be discussed as well\[9-10\]. Such transistor packages have enabled the realization of fully inkjet-printed transistors as a result of the excellent electrical properties of sc-SWCNTs\[2,11\]. A demonstration of a fully additive process to make TFT backplanes via R2R printing will also be highlighted. The development of new functional nanomaterials and their successful integration into devices will enable additive manufacturing of TFT arrays and in-mold electronics.

\[4\] Z. Li et al. ACS Omega 3, 3413 (2018).
\[11\] C. Homenick et al. ACS Appl. Mater. Interfaces 8, 27900, (2016)
considered to be the main reason for obtaining the excellent field emission performance.

SESSION S.NM05.02: Carbon Nanotube Assembly
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday
Morning, November 21, 2020
S-NM05

5:00 AM *S.NM05.02.01
Flexible, Wearable and High-Temperature Devices Based on Aligned Carbon Nanotubes Junichiro Kono; Rice University, United States

The remarkable flexibility, stable chemical structure, and extraordinary thermal, electrical, and optical properties of carbon nanotubes (CNTs) are promising for a variety of applications in flexible and/or high-temperature electronics, optoelectronics, and thermoelectrics, including wearables, refractory photonics, and waste heat harvesting. However, the long-standing problem in the preparation of CNT ensembles is to maintain the extraordinary properties of individual CNTs on a macroscopic scale; the polydispersity and randomness remain two main challenges. Here, we will discuss three ways of creating wafer-scale aligned CNTs: direct growth of aligned CNTs by chemical vapor deposition, production of ultrahigh-conductivity CNT fibers through solution spinning and coating, and spontaneous formation of wafer-scale aligned CNT films via controlled vacuum filtration. We will then describe flexible and high-temperature applications of these materials, such as flexible CNT broadband detectors, spectrally selective thermal emitters, and thermoelectric devices.

5:15 AM *S.NM05.02.02
Self-Assembly of Carbon Nanotubes into Tunable Hyperbolic Metamaterials Abram Falk; IBM T.J. Watson Research Center, United States

Plasmon resonance in carbon nanotubes is an exciting resource for confining light to the nanometer scale [1]. In this talk, I will discuss how dense films of carbon nanotubes have emergent optical properties related to these resonances. We assemble our films with a simple vacuum filtration technique and find that optimal assembly leads to the nanotubes crystallizing into monolithic, two-dimensionally ordered films. Using Mueller-matrix ellipsometry, we then characterize the films’ optical properties and find a broadband, electrostatically tunable hyperbolic region in the mid-infrared [2]. Another fascinating property of dense nanotube films is that excitons in the nanotubes can couple to the nanotubes’ own plasmon resonances – that is, cavity quantum electrodynamics (cQED) without an external cavity [3]. In fact, this coupling strength can reach the ultrastrong light-matter interaction regime. Technologically, crystallized nanotube films could provide a materials-driven pathway from fundamental concepts in cQED to advanced telecommunications hardware, including tunable thermal emitters, super-resolution imaging systems, and active, nonlinear optical devices like modulators and nanolasers.


5:30 AM S.NM05.02.03
Uniform Alignment of Carbon Nanotubes via Interfacial Assembly Katherine R. Jinkins, Vivek Saraswat, Robert M. Jacobberger, Padma Gopalan, Arganthaël Berson and Michael Arnold; University of Wisconsin-Madison, United States

In order to achieve a sufficiently high on-current, carbon nanotube based electronic devices must be comprised of highly aligned, densely packed arrays of nanotubes. One technique that has demonstrated immense promise for aligning nanotubes at optimal packing densities across technologically relevant substrates is floating evaporative self-assembly (FESA). The FESA process is a fluid-based method to align carbon nanotubes from solution post-synthesis and electronic sorting.\(^\text{1,3}\) FESA aligned carbon nanotube films exhibit exceptional local alignment and packing density, which has enabled the fabrication of field-effect transistors (FETs) with current densities exceeding that of GaAs and Si.\(^\text{4}\) However, globally, FESA carbon nanotube films are highly non-uniform, as the films are comprised of alternating stripes of aligned and unaligned nanotubes.
In the work presented here, we demonstrate a new technique in order to overcome the shortcomings of the FESA method and produce uniform films of aligned carbon nanotubes at desired packing densities, in a scalable technique.

In our technique, nanotubes are continuously deposited onto planar surfaces by sweeping a nanotube ink/water interface over a target substrate. The ink/water interface serves to collect and confine the carbon nanotubes, which aids in their alignment across the substrate during deposition. By translating the substrate vertically through the flowing nanotube ink/water interface, we fabricate uniform films of highly aligned (within ± 5.7°) carbon nanotubes on the wafer-scale. Carbon nanotube ink concentration is varied from 0.1 to 100 µg mL⁻¹ to control the film packing density from 0.3 to 50 µm⁻¹, near those required for electronics. Using optimized conditions, we align carbon nanotubes 60 mm laterally across a 100 mm wide wafer, with no limit on the deposition in the vertical/lift direction. The high uniformity of nanotube alignment leads to excellent FET characteristics—high on-state current density averaging 520 µA µm⁻¹ at -0.6 V and FET to FET variation of only 19%. In contrast, FETs fabricated across FESA films demonstrate variation of 52%, due to the stripes of aligned and unaligned nanotubes.


5:40 AM S.NM05.02.04
Aligned and Spatially Localized Semiconducting Single-Walled Carbon Nanotube Arrays Jonathan H. Dwyer, Zhizhang Shen, Katherine R. Jinkins, Michael Arnold, Reid Van Lehn and Padma Gopalan; University of Wisconsin–Madison, United States

Conjugated polymers have been extensively utilized to isolate semiconducting single-walled carbon nanotubes (s-CNTs) to greater than 99.9% purity in organic solvents creating a high-purity s-CNT “ink”. Solution deposition of s-CNTs from these inks onto target substrates has been widely studied in the literature for fabricating field-effect transistors (FETs). However, s-CNT-based FETs have so far underperformed compared to conventional silicon- and gallium arsenide-based FETs. One limiting factor is the difficulty in fabricating ideal s-CNT arrays using scalable methods. The ideal morphology of s-CNTs in array FET consists of perfectly aligned s-CNTs (i.e. 0° orientation difference between all s-CNTs in the array) with a pitch of 5-10 nm between nanotubes. Even with the plethora of alignment and spatially localized s-CNT deposition methods designed to control s-CNT deposition, fundamental understanding of the driving forces for s-CNT deposition is still lacking. The individual roles of the polymer wrapper, solvent, target substrate composition, and the s-CNT itself are not completely understood because it is difficult to decouple the deposition parameters.

In order to understand and control s-CNT deposition onto substrates, we present our studies to understand the multitude of factors driving polymer wrapped s-CNT deposition onto substrates. Chemical modification of the substrate with self-assembled monolayers (SAMs) presents an ideal platform to explore these parameters. We use poly[(9,9-dioctylfluorenyl-2,7-diyi)-alt-co-(6,6'-{2,2'-bipyridine})] (PFO-BPy) wrapped s-CNTs and study their interactions with chemically modified substrates. Experimentally, we characterize number density of s-CNT deposition on different chemically modified surfaces from toluene and chloroform. To gain a molecular level understanding we use atomistic molecular dynamics simulations to examine the driving forces for s-CNT adsorption. Multiple parameters are considered including substrate surface energy, substrate chemistry, solvent type, and the interactions that arise from the polymer wrapper PFO-BPy. We find that the global free-energy minimum associated with favorable s-CNT adsorption occurs for a configuration in which the minimum of the solvent density around the s-CNT coincides with the minimum of the solvent density above a SAM-grafted surface. This configuration indicates that solvent structure near a SAM-grafted surface determines the adsorption free-energy landscape driving s-CNT deposition.

Knowledge gained from these simulations and experiments guides substrate surface pattern designs for spatially localized s-CNT deposition. We use scalable s-CNT alignment techniques in combination with surface patterned substrates to fabricate aligned and spatially localized s-CNT arrays for integrated device structures. These s-CNTs arrays are characterized by s-CNT alignment degree for use in s-CNT-based FETs.
Controlled Surface Grafting of 3D Carbon Nanotube Structure—Nanomanipulation for Hydrophobic to Hydrophilic Tunability

Mostakima M. Lubna, Jakub Sciora and Philip Bradford; North Carolina State University, United States

Three-dimensional (3D) assemblies of super porous carbon nanotube (CNT) structure is the recent focus of nano-carbon research for the unique properties offered by the interconnected conductive network in multifunctional applications like flexible sensors, energy storage, ultra-low-density electromagnetic interference (EMI) shielding, and selective organic compound absorption. In a 3D macroscopic assembly not only the purity, size and diameter of the CNTs are major variables also the orientation, alignment, and stability of the CNT-CNT junctions play a crucial role in the final structural performance. We developed a 3D free-standing CNT sponge from high purity, similar-sized (length 1mm, diameter ~ 23 ±4 nm) spinnable CNTs with complete control over the CNT network alignment technique. And the CNT-CNT junctions within the 3D sponge were secured by conformal coating with atomic layer by layer infiltration of amorphous pyrolytic carbon (PyC) inside the CVD furnace at 800 °C. The density (as low as 6 mg cm⁻³) and porosity (as high as 99.8 %) of the CNT/PyC sponge can be tuned by varying the PyC coating time and regulated consolidation of aligned CNTs. The CNT sponges are super compressible with quick recovery of the structure even after as high as 80 % compressive strain and showed negative poison ratio auxetic compression behavior. Further, nanomanipulation of the superhydrophobic surface of the CNT sponge is done by controlled pulse corona treatment, which allows initiating certain hydrophilic polymer grafting on the surface. The surface modification changes the water contact angle from 153 ° to 0° and enables us to directly incorporate different polymers (polyvinyl chloride, polycarbonate, polydimethylsiloxane) into CNT sponge to fabricate CNT/PyC-polymer sponges without interrupting the stable alignment of the CNTs. The conformal polymer wrapping around the CNT/PyC can be easily controlled from a very few nanometres to hundreds of nanometres. All the CNT/PyC and CNT/PyC-polymer sponges were fully characterized using SEM, TEM, FTIR, Raman, and TGA. The polymer coating on the CNT/PyC sponges not only help to prevent the nano-release into the environment during dynamic use also showed very promising sensing and EMI shielding capabilities. This tunable nanomanipulation of the CNT/PyC sponge surface chemistry open-up a platform for easier multi-material hybrid structure construction in bulk without disrupting the pre-formed super aligned nano conductive network.
Supramolecular polymer sorting is a promising approach to separating single-walled carbon nanotubes (CNTs) by electronic type. Unlike conjugated polymers, they can be easily removed from the CNTs after sorting by breaking the supramolecular bonds, allowing for isolation of electronically pristine CNTs as well as facile recycling of the sorting polymer. However, little is understood about how supramolecular polymer properties affect CNT sorting. Herein we use chain stoppers to engineer the conformation of a supramolecular sorting polymer. Through NMR and UV-vis spectroscopy, SAXS, and thermodynamic modeling, we show that this supramolecular polymer exhibits ring-chain equilibrium, and that this equilibrium can be skewed towards chains by the addition of chain stoppers. We also demonstrate that by controlling the stopper-monomer ratio, we can double the sorting yield without compromising the purity or properties of sorted CNTs.

5:25 AM  S.NM05.03.04
Temperature Dependent Thermoelectric Transport in Polymer-Sorted Semiconducting Carbon Nanotube Networks with Different Diameter Distributions Martin Statz¹, Severin Schneider², Felix Berger³, Lianglun Lai¹, William A. Wood¹, Jana Zaumseil³ and Henning Sirringhaus³; ¹University of Cambridge, United Kingdom; ²Heidelberg University, Germany

In the past decade tuning the chirality distribution of single-walled carbon nanotube (SWCNT) networks has led to rapid advances of their optoelectronic, electronic and thermoelectric applications. Nevertheless, the full potential of this design freedom in those networks is yet to be explored, both in terms of the processes governing charge transport as well as their performance in applications. Here we report on charge carrier density and temperature dependent field-effect mobility and on-chip Seebeck coefficient measurements of polymer-sorted small diameter (6,5) SWCNT (0.76 nm) networks, 1,2,4,5-tetrakis(tetramethylguanidino)benzene (ttmgb) treated (6,5) networks as well as large diameter plasma torch SWCNT (1.17-1.55 nm) networks with different network densities to provide insights into their charge transport mechanisms and potential for thermoelectric applications. The Seebeck coefficient offers insights into transport energetics, potential contributions from electron-electron and electron-phonon interactions and the relative contributions of inter- versus intra-CNT transport.¹ Contrary to previous studies we conclude that a pure percolation theory and variable-range hopping description of transport is insufficient to explain the charge density and temperature dependence of both transport coefficients. Instead intrananotube transport that depends on the chirality of the CNTs composing the network needs to be considered as well. All untreated networks show remarkable ambipolar behaviour in both the mobility and the Seebeck coefficient, emphasizing the purity of our samples suitable to study their intrinsic transport mechanisms. Interestingly, in the high network density regime, the network density influences neither electric nor thermoelectric transport strongly, indicating both are dominated by the tubes rather than the tube-tube junctions. Furthermore, we emphasize the importance of density of states (DoS) engineering via chirality selection for thermoelectric generators. Despite their generally lower mobilities (6,5) SWCNTs show comparable power factors to large diameter, small bandgap networks with a broad chirality distribution. These findings provide design guidelines towards narrow DoS distribution, large diameter SWCNT networks for both electronic and thermoelectric applications.²


SESSION S.NM05.04: Carbon Nanotube Flexible Electronics
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM05

5:00 AM *S.NM05.04.01
Flexible Sensor Sheets Using Carbon Nanotube-Based Composite Materials Kuni Takei¹,²; ¹Osaka Prefecture University, Japan; ²JST PRESTO, Japan

Flexible and stretchable electronics are now widely studied for a next class of electric devices replaced from the silicon-based conventional inflexible devices. In particular, multi-functional sensor sheets can contribute to a variety of applications for Internet of Things (IoT) including wearable healthcare. For this flexible device concepts, one of the potential materials is nanocarbons including carbon nanotube and graphene due to their unique electrical and mechanical properties. Furthermore, material handling to pattern these on a macroscale flexible film is readily conducted which is an important factor for practical flexible electronics. By utilizing the advantages of nanocarbon, in this study, macroscale, multi-functional flexible sensor sheets fabricated by mainly printing methods of nanocarbon composite materials are introduced for healthcare and IoT.
applications. Firstly, fundamental characteristics of strain, tactile pressure, temperature, and humidity sensors are discussed, followed by the device demonstrations. Healthcare, wind flow mapping, and soft-robotic applications are mainly discussed in this talk. Finally, to move forward to building the platform of flexible electronics, stability and reliability of sensors in terms of sensitivity and long-time measurements will be briefly introduced. Although a lot of researches and developments are still required for practical application, these studies may help to open a door for the next step of flexible electronics.

5:15 AM *S.NM05.04.02
Energy Harvesting Technologies Based on Low-Dimensional Materials for Self-Powered Sensing Devices
Yutaka Ohno; Nagoya University, Japan

There is a movement to realize a more efficient and energy-saving society by utilizing a vast amount of data obtained by a huge number of sensors installed in various places of our society. In order to construct such a sensor network, it is essential to realize self-powered sensor devices that do not require wirings. Energy harvesting technology is expected as one of the power sources. The energy harvesting technology gains a power source for driving sensors from small energy existing in the environment. Recently, researches to realize energy harvesters using graphene and carbon nanotubes has extensively being conducted. The nanocarbon materials is a highly conductive film with excellent flexibility and transparency so as to have installation flexibility. In this presentation, we introduce our research on flexible energy harvesting technologies and ultra-low power sensing circuit technologies.

5:30 AM S.NM05.04.03
Ultra-Thin Flexible Tactile Pressure Sensor Network by Integrating Large-Area Carbon Nanotube Active Matrix with Highly Sensitive Piezoresistive Thin Film
Zhenxuan Zhao1, Jianshi Tang1,2, Jian Yuan1, Xiao Li3, Ning Suo3, Huaping Liu1, Yuan Dai2, Yijun Li1, Bin Gao1,2, He Qian1,2 and Huaqiang Wu1,2; 1Tsinghua University, China; 2Beijing National Research Center for Information Science and Technology (BNRist), Tsinghua University, China; 3Institute of Physics, Chinese Academy of Sciences, China; 4Robotics X lab, Tencent, China

The rapid development in smart robotics and prosthetic solutions calls for large-area and low-cost tactile sensor networks with high performance in both electrical and mechanical properties. Tremendous progress has been made recently on the research of flexible pressure sensors using various nanomaterials including organic and oxide semiconductors, carbon nanotube (CNT), semiconductor nanowire, etc. However, several key challenges remain, such as the fabrication of high-performance flexible transistor arrays with high density as well as the synthesis of ultra-thin piezoresistive film with high sensitivity. In this work, we report the integration of large-area CNT active matrix and highly sensitive piezoresistive thin film into a functional flexible tactile pressure sensor network. The 16×16 CNT active matrix was fabricated using highly purified (99.9%) semiconducting single-walled CNT solution, achieving a high density of 7 pixels per inch (ppi) over 4-inch area. A novel piezoresistive thin film was made with low-temperature processed multi-walled CNT composite, showing excellent pressure sensitivity with tunable thickness and flat surface. The highly integrated flexible tactile pressure sensor network was built on ultra-smooth polyimide with a surface roughness less than 1 nm, and it can be easily delaminated from the silicon substrate while maintaining the integrity and performance of the integrated system fabricated on top. The thickness of the entire flexible tactile sensor system can be controlled around 50 μm, leading to excellent flexibility. The demonstration in this work paves the road to build large-area electronic skins with high integration density and superior performance for future applications in smart robotics.

SESSION S.NM05.05: Graphene Nanoribbon Synthesis
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

5:00 AM *S.NM05.05.01
Synthetic Electronics
Chagaan Baatar; Office of Naval Research, United States

Building electronic circuitry with atomic precision is beyond the capability of current, and in the foreseeable future, top-down lithographic techniques. In recent years, the US Office of Naval Research (ONR) has championed several research initiatives that sought to address this key challenge. One of the most exciting development and initial success that resulted
from these initiatives is a bottom-up chemical synthesis technique that has proven highly effective at assembling two-dimensional (2D) graphene nanostructures with spatial precision control down to single atom and single bond level. In this presentation, I will briefly review the current status of this exciting new research field, and also the challenges that still remain. I will share some personal perspectives and speculate on possible future directions. The motivation behind the discussion is to socialize the basic ideas and capabilities with, and get feedback from, the relevant research communities, in order to further refine and improve future research agenda.

5:15 AM *S.NM05.05.02
Engineering Electronic Properties in Graphene Nanoribbons Pascal Ruffieux; Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland

On-surfaces synthesis has become a versatile tool for the fabrication of atomically precise graphene nanostructures. Recent studies have successfully focused on the controlled synthesis of graphene nanoribbons (GNRs) (1), which offer a wide range of physical properties depending on edge structure and width. For instance, width-control in armchair GNRs gives access to band gap tuning in a wide range and allows, owing to the deterministic selection of a single width, for the preparation of an electronically homogenous material. For the case of nine atom wide armchair GNRs (9-AGNRs), the band gap is of 1.4 eV and allows, together with the development of suitable GNR transfer procedures, for the realization of field effect transistors with high on-currents (~1 µA) and high on/off current ratios (10^6) (2).

Some particularly appealing properties of graphene nanostructures are achieved when the sublattice symmetry is broken. For zigzag GNRs this gives rise to spin-polarized edge states and opens new opportunities for spintronic applications. For the case of six atom wide zigzag GNRs (6-ZGNRs), we have recently identified suitable molecular building blocks and have confirmed the existence of edge-localized states for electronically decoupled 6-ZGNRs (3).

Such localized states also emerge from short zigzag segments embedded in armchair GNRs. By periodically positioning these zigzag segments along the GNR axis, this can be used to design one-dimensional lattices of coupled states yielding electronic bands in the band gap of the hosting armchair GNR (4). These bands are fully described by the Su-Schrieffer-Heeger (SSH) model, from which all relevant electronic properties can be derived by considering two coupling constants. Depending on the relative strength of these coupling constants, topologically trivial and non-trivial electronic quantum phases can be realized and give rise to characteristic topological boundary states in heterostructures consisting of topologically trivial and non-trivial segments. Tuning of the coupling constants of the SSH model also allows for the design of low-bandgap GNRs. In this limit, charge carrier properties can be approximated by the dispersion of massive Dirac fermions. The experimental realization of such a system together with its electronic characterization will be presented.

Finally, recent achievements in the on-surface synthesis of magnetic nanographenes will be discussed. Using inelastic scanning tunneling spectroscopy, the unambiguous identification of robust antiferromagnetic order in specific nanographenes is achieved and opens new opportunities for carbon-based magnetism.


5:30 AM S.NM05.05.03
Bottom-Up Synthesis of Edge-Functionalized Graphene Nanoribbons Manabu Ohtomo, Hironobu Hayashi, Hideyuki Jippo, Junichi Yamaguchi, Kenjiro Hayashi, Juanjuan Zhu, Ryunosuke Hayashi, Xiaogi Pang, Tong Wang, Mari Ohfuchi, Richiro Saito, Hiroko Yamada and Shintaro Sato; 1Fujitsu Labs Ltd. and Fujitsu Ltd., Japan; 2Nara Institute of Science and Technology, Japan; 3Tohoku University, Japan

Bottom-up synthesis of graphene nanoribbons (GNR) enables us to obtain atomically-precise GNRs with well-defined edges [1]. The GNR heterojunction is one of the key elements required for realizing promising electronic devices, such as tunneling field-effect transistors and backward diodes. One of the promising applications of extremely narrow GNRs is a detector diode, which rectifies THz-waves into a direct-current (DC) output voltage [2]. Due to its small junction capacitance of sub-nm wide GNR p-n junction, it was predicted that the backward diode with GNR heterojunction can outperform the state-of-the-art diodes made from III-V compound semiconductors [2]. Among various techniques of manipulating electronic states of GNRs, we focus on the edge-functionalization of GNRs in this study. While a couple of edge-functionalized GNRs have been reported to date [3, 4], the edge-functionalization is still challenging mainly due to protonation of edges during cyclo-dehydrogenation [5, 6]. In this research, we report on some of our recent attempts for realizing edge-functionalized GNRs.
First, we refer to the effect of edge-functionalization on the on-surface polymerization. It was found that the on-surface reaction of newly-developed precursor named 5-bromo-11(10-bromoanthracene-9-yI)anthra[2,3-b:7,6-b']dithiophene (BABAT) with isomers, which has a similar structure as 10,10'-Dibromo-9,9'-bianthryl (DBBA) with one anthracene substituted with anthradithiophene, ends in intramolecular cyclodehydrogenation [7]. Unlike DBBA, which is widely known to form anthracene polymers and armchair-edge graphene nanoribbons on Au(111), BABAT was found to make planar nanographene with intramolecular C-C bonding after annealing at 200°C on Au(111). The mechanism was investigated using first-principle density functional theory, which revealed that on-surface polymerization is not kinetically preferred in the case of BABAT. The intramolecular C-C bonding in DBBA biradicals, on the other hand, does not take place because of a faster reverse reaction. By referring to the electron density of BABAT biradicals, it was concluded that thiophene functionalization modifies the distribution of electron density in BABAT biradicals and facilitates electrophilic addition, leading to intramolecular C-C bonding after 200°C annealing. These results indicate that the design of radical moiety is particularly important in the on-surface Ullmann-type coupling.

The second part of our presentation is dedicated to the bottom-up synthesis of GNRs with edges functionalized by methylenedioxy functional groups. Unlike BABAT, it was confirmed by STM measurement that GNRs functionalized by methylenedioxy were obtained from anthracene trimer precursor functionalized by methylenedioxy. Unlike fluoride, which was detached during cyclodehydrogenation [5], methylenedioxy groups seem to be robust and survive cyclodehydrogenation process, while co-existence of hydroxyl groups was also confirmed by XPS. The GNR formation process was studied using the nudged elastic band (NEB) method within the density functional theory (DFT). One of the important findings is that methylenedioxy substitution opens an alternative path for dehydrogenation, which protects methylenedioxy groups from protonation. Due to electron-donating nature of methylenedioxy groups, it was also confirmed, by first-principles simulations, that the ionization potential and electron affinity of Medioxy-7AGNR differ from those of pristine 7AGNR, which may lead to the formation of a Type II heterojunction of GNRs.

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References

5:40 AM *S.NM05.05.04
Bottom-Up Solution Synthesis of Structurally Well-Defined Graphene Nanoribbons—Modulation of the Width and Edge Functionalization Akimusu Narita1,2; 1Okinawa Institute of Science and Technology Graduate University, Japan; 2Max Planck Institute for Polymer Research, Germany

In contrast to zero-bandgap graphene, structurally confined graphene nanoribbons (GNRs) features open bandgaps due to the quantum confinement effect, which render them highly promising for nanoelectronic and optoelectronic applications.[1] The properties of the GNRs are determined by their chemical structures, in particular the width and the edge configuration, which makes their precise structural control essential. Whereas such precision cannot be achieved by “top-down” fabrication methods such as “cutting” of graphene, bottom-up chemical synthesis can afford atomically precise GNRs with various structures.[1,2] The synthesis is carried out through polymerization of a tailor-made monomer leading to a polymer precursor, which can be “planarized” and “graphitized” into GNRs by oxidative cyclodehydrogenation. While it is challenging to obtain very long GNRs through transition-metal-catalyzed or metal-surface-assisted polymerization, we have demonstrated solution synthesis of GNRs with average lengths larger than ~600 nm through AB-type Diels-Alder polymerization.[2,3] Solubilizing alkyl chains can be attached on the GNR edges through the solution synthesis, making them dispersible in organic solvents and thus allowing for the liquid-phase processing for the device integration.[3,4] By modifying the monomer structure, laterally extended GNRs with the width of up to ~2 nm could be obtained, revealing the lowering of the optical bandgap down to ~1.2 eV.[2,3] We have also achieved edge functionalization of the GNRs by introducing a bromo group on the monomer. For example, introduction of perylene monoimide units led modulation of the self-assembly behavior, providing intriguing “rectangular” networks of GNRs.[6] Moreover, introduction of spin-bearing organic radicals on the GNR edges allowed for spin injection to the aromatic core, inducing a delocalized magnetic state, which might have potential for application in the quantum computers.[7] These results form a fundamental basis for applications of such GNRs in the future nanotechnology.
Hierarchical Graphene Nanoarchitectonics Aran Garcia-Lekue1,2 and Aitor Mugarza1,3; 1Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Spain; 2Ikerbasque, Basque Foundation for Science, Spain; 3Institució Catalana de Recerca i Estudis Avançats (ICREA), Spain

On-surface synthesis has emerged as an efficient strategy for the synthesis of 1D and 2D covalent nanostructures (1). The vast variety of graphene nanoribbons (GNR) that have been synthesized during the last decade represent the most successful case of this bottom-up approach. GNRs have indeed been synthesized with atomic scale control over the edge structure, width, or chemical composition (3). However, extending dimensionality to 2D nanostructures has revealed itself as a paramount challenge for on-surface chemistry. In this talk, I will report on some novel 2D graphene nanostructures obtained by a hierarchical onsurface method. The method relies on the stepwise synthesis of polymeric chains that turn into arrays of aligned graphene nanoribbons that then couple into nanoporous graphene (NPG), which combines 1nm size ribbons and pores (4). As demonstrated by combining scanning tunneling (STM) and density functional theory (DFT), the peculiar topology of the NPG imprints a band-gap, novel electronic pore states and high electronic in-plane anisotropy. Our calculations have also predicted that the anisotropic electron propagation within the mesh gives rise to Talbot interference effects (5), analogous to photons in coupled waveguides. Moreover, as I will show with particular examples, all these unique properties of NPG can be tuned by controlling the geometry and/or composition of the pores.


Longitudinal Vibrational Modes in Atomically Precise Graphene Nanoribbons Jan Overbeck1, Gabriela Borin Barin1, Colin Daniels2, Perrin L. Mickael1, Oliver Braun1, Pascal Ruffieux1, Vincent Meunier2, Roman Fasel1 and Michel Calame1; 1Empa, Switzerland; 2Rensselaer Polytechnic Institute, United States

Graphene nanoribbons (GNRs) exhibit an electronic bandgap due to the lateral confinement of charge carriers and edge effects. They can be fabricated by bottom-up on-surface synthesis from molecular precursors resulting in atomically precise structures [1]. This approach promises tunable optical and electronic properties [2]. Their integration into functional devices will require an in-depth understanding of their structural properties, in particular after transfer from their metallic growth substrates to the target device substrate. We use Raman spectroscopy to characterize GNRs with a large area Raman mapping approach on optimized substrates exhibiting interference enhancement [3]. This allows the investigation of low-intensity geometry dependent Raman modes. We show that a longitudinal compressive mode (LCM) is particularly suited to investigate the length of bottom-up synthesized GNR, probe the effects of device processing as well as their interaction with different types of substrates [4].

Graphene nanoribbons (GNRs) are narrow strips of graphene, with exciting properties deriving from electron confinement and related band gap tunability[1]. The ability to tune GNRs’ electronic and magnetic properties by structural design at the single atom level makes them an ideal platform for a wide range of device applications, from classical transistors to spintronics. Despite their exceptional properties, significant challenges remain for GNR fabrication, processing and characterization. This contribution addresses some of the critical challenges in the further development of GNR technologies in particular on GNR fabrication, transfer, and characterization.

Bottom-up synthesis of graphene nanoribbons is most commonly performed under ultra-high-vacuum conditions, which is one of the bottlenecks in the further technological advancement of this material. Additionally, little is known about the stability of ultra-narrow GNRs under ambient conditions or during device processing. In this work we focused on 9- and 5-atom wide armchair GNRs (9-AGNR and 5-AGNR, respectively) grown under ultra-high vacuum conditions on Au(111) and on vicinal gold surfaces Au(788), which promotes GNR's unidirectional growth on the narrow (111) terraces along the step edges. We first investigate the role of halogen functionalization of the precursor monomer in the final GNR length. Using different precursor monomers and synthesis protocols we show an increase in the average length for the 9-AGNR from 15 nm to 45 nm[2] and for the 5-AGNRs from 8 nm to 20 nm. GNRs grown on Au(111) substrates are transferred using a polymer-free method[3]. Raman spectra indicate no significant degradation of GNRs' quality, reveal their homogeneous distribution on the target surface and also show that GNRs have remarkably stability under ambient conditions tracked over a 2-year period[3]. GNRs grown on Au(788) are transferred via electrochemical delamination method[4], and Polarized Raman of the G mode show that GNRs retain their orientation after transfer with maximum Raman intensity along the ribbon axis and minimum intensity perpendicular to it.

These process steps allowed us to integrate both 9- and 5-AGNR into short channel field-effect transistors (FETs). Using the 9-AGNRs as channel material we demonstrate FETs with high on-current $I_{on}>1\ \mu A$ at $V_d = -1\ \text{V}$, high $I_{on}/I_{off}$ ratios of $\sim10^5$ and 10% device yield[5]. In a next step, aligned 9-AGNR-FET devices are produced using graphene electrodes, and a performance of $I_{on}>6\ \mu A$ at $V_d = 0.1\ \text{V}$ and high $I_{on}/I_{off}$ ratios of $\sim10^4$ is observed along with an increase of device yield to 80-100%, due to the GNRs' orientation along the source-drain axis of the devices. GNR-FET devices using short 5-AGNRs (2-10 nm) as channel material and graphene as electrodes show linear I-V curves (metal-like behavior) at room temperature, while long 5-AGNRs (>20 nm) integrated into FETs with Pd as contacts behave as a semiconductor. The role of GNRs' surface coverage and length on the transfer efficiency and electronic/transport properties will be discussed.

References:
[2] M. Di Giovannantonio et al., ACS Nano, 12, 74-81, 2018
elevated temperatures. Both solution and on-surface approaches were used to synthesize laterally extended chevron GNRs (eGNRs). The ribbons grown on Au(111) were used for extensive scanning tunneling microscopy (STM), noncontact atomic force microscopy (nc-AFM) and scanning tunneling spectroscopy (STS) characterization. They were found to exhibit a bandgap of about 2.2 eV, which is considerably smaller than the values reported for chevron GNRs in similar studies. The solution-synthesized eGNRs were processed into uniform thin films that exhibited improved electrical conductivity compared to similar films of regular chevron GNRs. The eGNR films were employed in gas sensors that showed very high responsivity to low molecular weight alcohols compared to similar sensors based on benchmark graphitic materials, such as graphene and graphene oxide. Finally, we demonstrated the first electronic nose system based on atomically precise GNRs that could reliably recognize analytes of nearly the same chemical nature, such as methanol and ethanol. Overall, this work demonstrates the entire path from designing new atomically precise GNRs with improved properties to their bottom-up synthesis, characterization, processing and implementation in electronic devices.

Chemical Vapor Deposition of Semiconducting Armchair Graphene Nanoribbons

Robert M. Jacobberger, Austin J. Way, Vivek Saraswat and Michael Arnold; Univ of Wisconsin-Madison, United States

Graphene nanoribbons with sub-10 nm widths and ultra-smooth armchair edges are exciting candidates for next-generation semiconductor electronics because of their potential to exhibit exceptional charge and thermal transport properties. However, widespread integration of nanoribbons into commercial applications has been limited by challenges in producing nanoribbons with a high degree of structural precision and assembling the nanoribbons into large-area arrays on technologically-relevant substrates.

Here, we present a promising scalable approach for producing nanoribbons with sub-10 nm widths, smooth armchair edges, and excellent charge transport properties directly on conventional semiconductor wafer platforms via chemical vapor deposition (CVD). We have discovered that by exploiting highly anisotropic crystal growth of graphene from hydrocarbon precursors on Ge(001), narrow nanoribbons with high-aspect ratios can be synthesized. Due to the bottom-up, self-defining nature of growth, the nanoribbons have nearly atomically smooth armchair edges. The nanoribbon width can be continuously tuned to virtually zero by controlling the growth time and growth rate, which depends on the precursor flux and substrate temperature, and nanoribbons with sub-10 nm widths can be hundreds of nanometers in length. Breaking the symmetry of the Ge(001) surface by introducing a miscut results in wafer-scale unidirectional nanoribbon alignment. Control over both the alignment as well as the placement of individual nanoribbons is realized by initiating growth from lithographically-defined nanoscale seeds, enabling large-area hierarchical nanoribbon arrays. This nanoribbon synthesis is also adapted onto Si(001) wafers by utilizing epitaxial Ge interlayers.

Nanoribbons grown on Ge(001) via CVD have sizeable bandgaps and display high-performance charge transport properties at room temperature. For example, field-effect transistors with nanoribbon channels can simultaneously exhibit on/off conductance ratio of 2×10^4 and on-state conductance of 5 µS. Therefore, this bottom-up nanoribbon synthesis may provide a high-throughput route for realizing future state-of-the-art technologies based on semiconducting graphene.


Towards Chirality Control of Graphene Nanoribbons Embedded in Hexagonal Boron Nitride

Haomin Wang, Lingxiu Chen, Huishan Wang, chen chen and Chengxin Jiang; Shanghai Institute of Microsystem and Information Technology Chinese Academy of Sciences, China

Ideal graphene nanoribbons (GNRs) have been shown to exhibit extreme chirality dependence as metals or semiconductors.
Therefore, the capability to precisely produce GNRs with defined chirality at the atomic level is required in order to engineer their band gap and electrical properties. It is obvious that earlier approaches have fundamental limitations for further electronic investigation. Electronics always require scalable transfer-free approaches for growing GNRs and conducting band gap engineering. Controlled fabrication of oriented GNRs embedded on hexagonal boron nitride (h-BN) has the capability to overcome the above difficulties. With proper control, the band gap and magnetic properties can be precisely engineered. Most desired features for GNRs can be automatically attained using this approach.

Here we developed a two-step growth method and successfully achieved sub-5 nm zigzag and armchair GNRs embedded in h-BN, respectively. Further transport measurements reveal that the sub-7 nm zigzag GNRs exhibit openings of the bandgap inversely proportional to their width, while narrow armchair GNRs exhibit some fluctuation in the bandgap-width relationship. Transistors made of these GNRs with large bandgaps (>0.4 eV) exhibit excellent electronic performance even at room temperature (e.g. conductance on-off ratio more than 10E5 and carrier mobility more than 0.15m2 per volt per second ). An obvious conductance peak is observed in the transfer curve of 8-10 nm-wide zigzag GNRs while it is absent in most of armchair GNRs of similar width. Magneto-transport experiments show that zigzag GNRs exhibit relatively small magneto-conductance (MC) while armchair GNRs have much higher MC than zigzag GNRs. This integrated lateral growth of edge-specific GNRs in h-BN brings more robust and orientation-controlled edges than previously demonstrated, and will enable exciting future investigations into the physics and applications of edge-specific GNRs.

5:10 AM *S.NM05.06.04
Electronic and Vibrational Properties of 1D Carbon Nanostructures from First-Principles Vincent Meunier1, Colin Daniels1 and Liangbo Liang2; 1Rensselaer Polytechnic Institute, United States; 2Oak Ridge National Laboratory, United States

I will provide an overview of the recent progress made in my group on the understanding of the electronic and vibrational properties of 1D carbon nanostructures based on a combination of theoretical and computational methods. In the first part of the presentation, I will first focus on providing a model to account for the significant screening caused by the presence of a substrate on the electronic properties of graphene nanoribbons. In the second part of the talk, I will present a broad and detailed overview of the intrinsic vibrational properties of 1D carbon nanostructures with a variety of edge configurations, sizes, and shapes. These results will be systematically compared to experiment (notably, Scanning Tunneling Spectroscopy and Raman Spectroscopy). While theory and experiment are found to usually be in excellent agreement, I will also discuss a number of unresolved issues and will suggest a roadmap to tackle them.

5:25 AM S.NM05.06.05
Progress in Extending the Pseudocarbyne Library Hyunsub Kim, Pilarisetty Tarakeshwar, Peter Buseck and Scott G. Sayres; Arizona State University, United States

Using the high energy environment of laser ablation, we have synthesized several new materials composed of 1D carbon chains stabilized through interaction with small metal clusters, that we have named “Pseudocarbynes”. These new materials are expected to approach the unprecedented strength, elastic modulus, and stiffness of carbyne, which has defied isolation and characterization for over a century. Our spectroscopic characterization suggests that pseudocarbynes self-assemble from colloidal solutions into new mesomaterials that bridge the molecular and materials realms. These measurements are supported by density functional theory (DFT) calculations that highlight a strong tendency of small metal clusters to interact with the sides of the -C≡C- chains. X-ray powder diffraction and high-resolution electron microscopy demonstrate the long-range material crystallinity. I will discuss our recent experimental results aimed at extending the pseudocarbyne library to include a variety of transition metals, cluster sizes, and lengths of carbon chain. Our results suggest that pseudocarbynes have potential to become a platform for developing an array of materials with tunable electronic properties.

5:35 AM S.NM05.06.06
Tunable, Bottom-up Synthesis of Semiconducting Graphene Nanoribbons on Germanium Virtual Substrates Vivek Saraswat1, Nathan Guisinger2, Yuji Yamamoto3, Robert M. Jacobberger1, Austin J. Way1 and Michael S. Arnold1; 1University of Wisconsin-Madison, United States; 2Argonne National Laboratory, United States; 3IHP GmbH, Germany

Graphene nanoribbons (GNRs) are quasi-1D strips of graphene that are tunable semiconductors and can exhibit excellent electronic, thermal and mechanical properties.1 Field effect transistors (FETs) made of sub-10 nm wide GNRs with smooth, armchair edges can outperform silicon-FETs in drive current and suppress short channel effects due to ultra-thin geometry.2, 3 However, in order to become a viable contender to silicon based high volume manufacturing, compatibility with existing
CMOS processes is of paramount importance. Although, the synthesis of GNRs has been demonstrated on Ge(001),\textsuperscript{4,5} owing to the lack of availability of 300 mm Ge wafers and relatively higher cost, a promising alternative is to synthesize graphene nanoribbons on Ge virtual substrates, which can be epitaxially grown on 300 mm Si wafers. Here we explore the concept of transfer-free growth of armchair graphene nanoribbons on a Si(001) platform by conducting the GNR synthesis on germanium virtual substrates by CVD.\textsuperscript{6} By tuning the thickness of the Ge epilayer, growth temperature, methane flow rate and the synthesis duration, we are able to achieve sub-10 nm wide GNRs that possess a semiconducting bandstructure and are several hundred nanometers long. Scanning tunneling microscopy reveals that these GNRs possess smooth armchair edges, which is critical to achieving high on/off ratios and drive currents. We also find that GNR growth kinetics on Ge virtual substrates is identical to Ge(001) and that Si diffusion from the bulk can be suppressed for as long as 9 h, preventing SiC formation on the surface. Furthermore, the threading dislocations, which are inevitably present in heteropitaxially mismatched systems as Ge-Si are also not found to influence GNR nucleation and/or growth. These results indicate that all previous advances of GNR growth on Ge(001) (e.g. seeding initiated synthesis)\textsuperscript{7,8} can be readily scaled to Ge virtual substrates, overcoming a substantial barrier for adoption of GNRs in novel semiconductor technologies. This demonstration also opens up the possibility of achieving nanoribbons directly on a Si surface via selective vapor phase etching of Ge.\textsuperscript{9}

References


SESSION S.NM05: Carbon Nanotube Electronics
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM05

5:00 AM *S.NM05.07.01
Carbon Nanotube Based High Performance CMOS and Optoelectronic Devices Lian-mao Peng\textsuperscript{1,2} and Yang Liu\textsuperscript{2}; \textsuperscript{1}Peking University, China; \textsuperscript{2}Columbia University, United States

Carbon nanotube (CNT)-based electronics has been considered one of the most promising candidates to extend Si complementary metal-oxide-semiconductor (CMOS) technology. In particular CNTs have been investigated for various electronic and optoelectric device applications, such as sub-10nm CMOS devices which outperform that of state-of-the-art Si based CMOS devices in both speed and power consumption [1-5], as well as idea material for monolithic optoelectronic integration with complementary MOS-compatible signal processing circuit [6-8]. Prototype device studies on individual CNTs revealed that CNT based devices have the potential to outperform Si CMOS technology in both performance and power consumption. With a well-designed device structure and in combination with graphene, we showed that high-performance top-gated CNT FETs with a gate length of 5 nm can be fabricated. Significant progress has also been made in fabricating carbon nanotube low-power devices. An efficient way to reduce the power is to
lower the supply voltage VDD, but this voltage is restricted by the 60 millivolts per decade thermi-onic limit of subthreshold swing (SS) in FETs. A Dirac source (DS) with a much narrower electron density distribution around the Fermi level than that of conventional FETs was recently proposed and demonstrated using CNT to reduce SS [2].

References
Developing an Advanced Integration Technology for Condition Monitoring with Pre-Strained Carbon Nanotubes Simon Böttger1, Eric Pankenin1, Martin Hartmann1,2 and Sascha Hermann1,2,3; 1Chemnitz University of Technology, Germany; 2Center for Advancing Electronics Dresden CFAED, Germany; 3Fraunhofer Institute for Electronic Nano Systems ENAS, Germany

Giant piezoresistivity of Carbon Nanotubes (CNTs) is a unique feature promoting further miniaturization of strain sensors. In the context of condition monitoring for safety relevant applications, Industry 4.0, or robotics, especially integrated scalable solutions are overdue. CNT-based electro-mechanical transducers were already shown in proof-of-principle studies [1, 2] and recently also scalable technologies were applied [3]. However, there are still remaining challenges hindering reproducible device fabrication. To emphasize, on the material side a lack of control over chirality and length distribution of single-walled CNTs leads to a distribution of sensor properties. On the other side, an undefined initial CNT-strain condition makes reliable and controlled operation of sensors very challenging.

Here, we have addressed several in-depth studies along a reproducible CNT integration technology, such as length separation, role of CNT/metal contacts, pre-straining CNTs, and their impact on CNT device performance. This integration technology was consequently utilized on wafer-level in order to enable a scalable fabrication of CNT-based piezoresistive sensors in the perspective of forthcoming heterogeneous system-integration in e.g. safety-relevant ASICs. We found significant improvements on the CNT-FET performance by integrating pre-sorted long CNTs which is mainly correlated to reduced network effects, since less amount of CNT to CNT intersections are formed in the transistor channel [4]. In particular, we statistically revealed improvements in terms of fabrication yield, charge carrier mobility and subthreshold controllability. Moreover, we identified tunneling-related contact effects in CNT-based piezoresistive sensors to enhance the intrinsic gauge factor up to 165% [5]. The gauge factor can further be controlled by the input drain-source and gate-source voltage.

In addition, we realized pre-straining of integrated CNTs, which was verified by a significant blue-shift of the CNT-specific phonon mode G+ of up to 6.2 cm⁻¹, with respect to un-strained CNTs. Based on previous literature [6], we assessed the built-in strain ranging from 0.4% up to 0.8%.

In conclusion, we emphasize several technological aspects of the process value-chain and their relevance for a successful manufacturing of miniaturized CNT-based piezoresistive sensors for condition monitoring of forthcoming smart systems.

References

Carbon Nanotube Transistors for Highly Energy-Efficient Digital Systems Carlo Gilardi1, Gage Hills2, Qing Lin1, Rebecca Park1, Gregory Pitner1, H.S. Philip Wong3 and Subhasish Mitra4; 1Stanford University, United States; 2Massachusetts Institute of Technology, United States

Carbon nanotube field-effect transistors (CNFETs) are a promising candidate for implementing highly energy-efficient future digital systems. This is due to the superior transport properties of carbon nanotubes (CNTs) together with small body
thickness. Furthermore, low-temperature (< 200°C) fabrication of CNFETs enables new monolithic three-dimensional (3D) architectures with computation immersed in memory, enabling up to 1,000-fold system-level energy-delay-product benefits for abundant-data applications (such as deep learning). In this talk, we will present ways in which many challenges traditionally associated with CNFETs have been overcome in the recent years. At the device-level, hysteresis in CNFET electrical characteristics is reduced to < 0.5% of the $V_{GS}$ sweep range by studying charge impurities around CNTs. CNT PFET with low contact resistance of 6.5 kΩ (10 nm contact length) has been successfully demonstrated. At the circuit-level, a combination of fabrication and design techniques (the imperfection-immune paradigm) overcomes substantial inherent imperfections and variations traditionally associated with CNTs. The imperfection-immune paradigm has been key to the demonstration of CNFET digital VLSI circuits, as well as monolithic 3D NanoSystems that will also be highlighted in this talk.

SESSION S.NM05.08: Graphene Nanoribbon Device
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM05

5:00 AM *S.NM05.08.01
High Performance Graphene Nanoribbon Transistors Jeffrey Bokor¹, Zafer Mutlu¹, Juan Pablo Llinás¹, Gabriela Borin Barin², Peter Jacobs¹, Ilya Piskun¹, Raymond Blackwell¹, Andrew Fairbrother¹, Xinliang Feng¹, Klaus Müllen¹, Felix R. Fischer¹, Pascal Ruffieux², Michael Crommie¹ and Roman Fasel²; ¹University of California, United States; ²Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; ³National Institute of Standards and Technology, United States; ⁴Technische Universität Dresden, Germany; ⁵Max Planck Institute for Polymer Research, Germany

Recent advances in on-surface organic synthesis have led to the development of bottom-up graphene nanoribbon (GNR) growth with atomic precision¹. Bottom-up synthesized GNRs have promising electronic properties for high performance field effect transistors (FETs) and ultra-low power devices such as tunneling FETs². However, the short length, wide band gap, and random spatial orientation of GNRs have impeded the fabrication of devices with the expected performance and switching behavior³. Here, recent progress in integrating bottom-up synthesized GNRs into devices will be presented. High on-current and high on-off ratio FETs with a nine-atom wide GNRs as the channel material were successfully fabricated⁴. Strategies to further improve FET device yield and performance with the parallel arrays of GNRs transferred from single crystal Au (788) will be discussed. Finally, a new approach for the transfer-free fabrication of GNR devices has been developed.

References

5:15 AM *S.NM05.08.02
Integrated Synthesis of Millions of Suspended Graphene Nanoribbons and Its Non-Volatile Memory Applications Toshiaki Kato¹,² and Toshiro Kaneko¹; ¹Tohoku University, Japan; ²JST-PRESTO, Japan

We have developed a new, simple, scalable method based on novel plasma catalytic reaction [1-3] for directly fabricating narrow graphene nanoribbons (GNRs) devices on an insulating substrate [4]. Since the establishment of our novel GNRs fabrication method, direct conversion of a Ni nanobar to a suspended GNR is now possible. Indeed, GNRs can be grown at any desired position on an insulating substrate without any post-growth treatment, and the wafer-scale synthesis of suspended GNRs arrays with a very high yield (over 98%) is realized [5]. The growth dynamics of suspended GNRs is also investigated through the systematic experimental study combined with molecular dynamics simulation and theoretical calculations for phase diagram analysis. Unique optoelectrical property, known as persistent photoconductivity (PPC), is also observed in our suspended GNRs devices. By using the PPC, GNRs-based non-volatile memory operation is demonstrated [6]. High thermoelectric performance is also shown in our as-grown suspended GNRs [7]. We believe that our results can contribute to pushing the study of atomically thin layered materials from basic science into a new stage related to the optoelectrical applications [8-11] in industrial scale.
Graphene nanoribbons (GNRs) have attracted a strong interest from researchers worldwide, as they constitute an emerging class of quantum-designed materials [1-4]. Some of the major challenges towards their exploitation in electronic applications are their reliable contacting due to their small size (< 50 nm), as well as the preservation of their physical properties upon device integration.

In this combined experimental and theoretical study, we report on the first demonstration of quantum dot (QD) transport in atomically precise GNRs [5]. The devices consist of a film of aligned 5-atoms wide GNRs (5-AGNRs) transferred onto graphene electrodes with a sub 5-nm nanogap [6-8]. We demonstrate that the narrow-bandgap 5-AGNRs exhibit metal-like behavior resulting in linear IV curves for low bias voltages at room temperature and single-electron transistor behavior at 13 K. By performing spectroscopy of the molecular levels, we obtain addition energies in the range of 200-300 meV. DFT calculations predict comparable addition energies, and reveal that, due to the finite length of the 5-AGNRs, two states at the termini of the 5-AGNRs are formed within the bandgap of the infinite ribbons. The properties of the obtained QD reflect the band-structure and therefore demonstrate the preservation of the GNR properties upon device integration, a critical step in the realisation of more exotic GNR-based nano-electronic devices.

References:
SESSION S.NM05.09: Graphene Nanoribbon Magnetism

On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM05

5:00 AM *S.NM05.09.01
Probing the Magnetism of Topological End-States in Armchair Graphene Nanoribbons Dimas de Oteyza\textsuperscript{1,2,3}; 1Donostia International Physics Center, Spain; \textsuperscript{2}Centro de Física de Materiales (CFM-MPC), CSIC-UPV/EHU, Spain; \textsuperscript{3}Ikerbasque, Basque Foundation for Science, Spain

Materials purely made up of non-magnetic atoms can display magnetic properties. One such example are aromatic hydrocarbon structures. Following Lieb’s theorem, if the number of atoms in each carbon sublattice is different, the molecular structure will hold a net spin. However, even in the absence of net spin, polyradicals can be generated on graphitic structures subject to particular edge topologies. In addition to the edge topologies, also the structure’s size determines the presence or absence of such radical states, whose corresponding spin, if present, is furthermore predicted to display a specific relative alignment. These interesting predictions are hard to verify because of the difficulty in the synthesis of appropriate nanographitic structures with atomic precision. In this respect, on-surface synthesis under vacuum conditions has appeared as an extremely promising approach. Making use of it, we have synthesized a variety of nanosized aromatic hydrocarbon structures with well-determined shapes and sizes, including graphene nanoribbons with different edge morphologies, widths and lengths. For the particular case of 5 atoms wide armchair graphene nanoribbons we describe, based on scanning tunneling microscopy and spectroscopy, and combined with theoretical calculations, their electronic properties and the magnetism associated to its topologic end-states.

5:15 AM *S.NM05.09.02
Emergence of Spin States in Graphene Nanostructures José Ignacio Pascual; CIC nanoGUNE, Spain

Graphene can spontaneously develop intrinsic paramagnetism. Crucial examples are the magnetization of zig-zag edges in graphene, or the emergence of paramagnetism in open shell graphene nanostructures. I will show that graphene nanoribbons (GNR), fabricated with atomic precision on a metal surface exhibit fingerprints of π-paramagnetism on a metal surface, which can be detected and spatially localized using low temperature scanning tunneling microscopy and spectroscopy, and combined with theoretical calculations, their electronic properties and the magnetism associated to its topologic end-states.

5:30 AM S.NM05.09.03
Magnetotransport Spectroscopy of Graphene Nanoribbon Devices Simen Sopp\textsuperscript{1}, Alessandro Lodi\textsuperscript{1}, Tian Pei\textsuperscript{1}, Akimitsu
A long-standing challenge in nanoscience has been to fabricate devices of only a few nanometers with single-atom accuracy. The necessary structural control can be provided by bottom-up fabricated molecular graphene nanoribbons with atomically precise edges. Only such control of the graphene nanoribbons should allow derived field-effect transistors that exhibit magnetic and topological effects. Here we report the observation of magnetic, topological, and electronic effects on the quantum transport of hitherto unexplored molecular graphene nanoribbons. This includes magnetic shifting of molecular energy levels, topology and time-reversal symmetry breaking in a universality-class transition, negative differential conductance, and quantum transport effects up to near-room temperature.


Forging Symmetry Protected Topological States into Metallic Graphene Nanoribbons

Felix R. Fischer¹²³, Michael Crommie¹²³ and Steven G. Louie¹²; ¹University of California, Riverside, United States; ²Lawrence Berkeley National Laboratory, United States; ³Kavli Energy NanoScience Institute, United States

We have recently demonstrated the rational design and experimental realization of a graphene nanoribbon (GNR) superlattices that hosts a 1D array of symmetry-protected topological states, thus generating otherwise inaccessible electronic structure. This new class of materials can be thought of as an extended form of poly-acetylene wherein highly localized half-filled topological states replace the familiar single occupied p-orbitals along a conjugated p-system. Experimental results and first-principles calculations reveal that the frontier band structure of these GNR superlattices is defined purely by the coupling between adjacent topological interface states and can be tuned all the way from a semiconductor to a metal. This novel manifestation of 1D topological phases presents an entirely new route to band engineering in 1D materials based on precise control of their electronic topology, and is a promising new platform for future studies of 1D quantum spin physics.

Quantum Interference Engineering of Nanoporous Graphene for Carbon Nanocircuitry

Isaac Alcon¹², Gaetano Calogero³, Nick Papior², Antti-Pekka Jauho² and Mads Brandbyge²; ¹Freie Universitat Berlin, Germany; ²Technical University of Denmark, Denmark; ³Università degli Studi di Pisa, Italy

Bottom-up prepared carbon nanostructures appear as promising platforms for future carbon-based nanoelectronics due to their atomically precise and versatile structure.[1] An important breakthrough is the recent preparation of nanoporous graphene (NPG) as an ordered covalent array of graphene nanoribbons (GNRs).[2] Within NPG, the GNRs may be thought of as 1D electronic nanochannels through which electrons preferentially move, highlighting NPG’s potential for carbon nanocircuitry. However, the π-conjugated bonds bridging the GNRs give rise to electronic crosstalk between the individual 1D channels, leading to spatially dispersing electronic currents.[3] In this talk, we propose a chemical design of the bridges resulting in destructive quantum interference, which blocks the crosstalk between GNRs in NPG, electronically isolating them. Our multiscale calculations reveal that injected currents can remain confined within a single, 0.7 nm wide, GNR channel for distances as long as 100 nm.[4] The concepts developed in this work thus provide an important ingredient for the quantum design of future carbon nanocircuitry. In addition, our latest results demonstrating an external control of these characteristics will also be presented.

SESSION S.NM05.11: Carbon Nanotube Transport
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM05

5:00 AM S.NM05.11.02
Asymmetric CNT Transistors for Enhanced High Frequency Performance
Martin Hartmann1,2, Simon Böttger1, Georg Heldt3, Martin Claus2, Michael Schröter3 and Sascha Hermann1,2,3; 1Chemnitz University of Technology, Germany; 2Center for Advancing Electronics Dresden (cfaed), Germany; 3Fraunhofer Institute for Electronic Nano Systems, Germany; 4University of Technology Dresden, Germany

A strong driving force for future communication systems is the improvement of transceiver electronics efficiency. Carbon nanotube-based field effect transistors (CNTFETs) are promising electronic components, since high intrinsic speed and linearity due to their high charge carrier mobility, current carrying capability and one-dimensional charge transport are prospected. We report on design rules for the high frequency (HF) CNTFETs device architecture with improved operating speed. Therefore, the spacer between the gate and the source electrode (S-spacer) and gate to drain electrode (D-spacer) was investigated with respect to the HF performance. It will be discussed to which extent the spacer variation is balancing the device electrostatics in the CNT-metal contact area which influences the charge carrier injection and reflection by the Schottky barriers (SBs) that form between the metal covered CNT ends and the uncovered CNT channel region. Theoretically the dependence of the S-spacer and D-spacer on speed and linearity has been shown by simulations but was not yet investigated in an experimental study. Mothes et al. point out that especially within the S-spacer the fringing fields are needed to modulate the SBs, which is essential to gain highest speed and linearity. Therefore a small finite SB is essential to reduce the impact of charge carrier back-scattering from the source electrode. In contrast to FET geometry variations reported in literature, where additional gate electrodes or asymmetrical gate oxide trenches were introduced and investigated with respect to their DC performance, we report on the impact of S-spacer and D-spacer variations on the HF performance of CNTFETs. In terms of HF performance, inspiring results were obtained with symmetrical gate arrangements, using a self-aligned T-shape top gate electrode where Cao et al. realized CNTFETs with a transit frequency $f_T$ as well as maximum frequency of oscillation $f_{\text{max}}$ of up to 70 GHz at 100 nm channel length. In contrast, a buried gate helps minimizing parasitic capacitances and thus improving the HF performance further. We present HF CNTFETs with a buried gate fabricated by an additional lithography step enabling to realize devices with asymmetrical S-spacer and D-spacer. Thereby we followed scalable device fabrication procedures based on a wafer-level prototyping platform allowing to fabricate sufficiently large device counts for systematic and conclusive studies. The studies exposed a speed increase, measured by the external $f_T$ and $f_{\text{max}}$, of up to 20% for a specific asymmetrical gate electrode position in the channel. The fabricated devices show transit frequencies up to 16 GHz for 280 nm long channels with randomly oriented CNTs and a tube density of up to 30 CNTs/µm.

SESSION S.NM05.12: Poster Session: Carbon Nanotube
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday
Morning, November 21, 2020
5:00 AM - 8:00 AM
S-NM05

S.NM05.12.01
Hybrid Integration of CNT Logic and Analog RRAM towards Monolithic 3DSoC
Yijun Li, Jianshi Tang, Zhenxuan Zhao, Jian Yuan, Bin Gao, He Qian and Huaqiang Wu; Tsinghua University, China

With the fast development of emerging technologies such as artificial intelligence and internet of things, there has been higher and higher demand for future chips in terms of computing power, speed, and energy efficiency. Amid the slowdown of Moore's law, new chip architecture is needed to alleviate or overcome the so-called von Neumann bottleneck. Monolithic three-dimensional (3D) integration of multiple layers of functional components, such as emerging memory, logic and sensors, through high-density interlayer interconnects, provides a promising approach to build highly energy-efficient system-on-chip (SoC). On one hand, carbon nanotube (CNT) has been demonstrated as a superior candidate for high-speed logic technology that can be fabricated with low-temperature process. On the other hand, resistive random-access memory (RRAM) has been extensively studied for energy-efficient computing-in-memory (CIM) by taking advantage of its analog switching characteristics. In this work, we report the monolithic integration of CNT logic circuits and analog RRAM array using back-end-of-line (BEOL) compatible low-temperature fabrication processes. The performance of CNT integrated circuits and analog RRAM devices have been carefully optimized. Hybrid circuits such as ternary content-addressable memory (TCAM) are also fabricated. Our work represents a critical step towards 3DSoC with CIM capability.

S.NM05.12.03
Low-Power Carbon Nanotube-Based Flexible Integrated Circuits with Bio-Integration Capabilities
Li Xiang and Youfan Hu; Peking University, China

Carbon nanotubes (CNTs) is one of the most promising candidates for next-generation electronics for its extraordinary intrinsic properties, including high carrier mobility, excellent mechanical flexibility and solution processability, which are desirable in unique application scenarios, from smart sensing to biomedical implants. However, the integrated circuits (ICs) with enough complexity and integration scale for signal processing, which is the core units in modern electronic systems, are still lacking, which is mainly due to the nonuniformity of the devices, low yield manufacturing and large power consumption. This presentation would detail approaches for wafer-scale, high-yield and highly-uniform manufacturing of CNT devices and ICs. Chips using CNTs as semiconducting materials are 100% successfully transferred to water-soluble substrates with average device yield of 96.6%. Great uniformity is also demonstrated with minimum standard deviation of 55 mV in threshold voltage. The ICs could be successfully transferred onto biological surfaces, such as human wrist, biodegradable polymers and plant leaf. Integrated with other sensors, the CNT based flexible ICs could demonstrate system-level environmental monitoring. In addition, to further push forward the CNT based flexible electronic devices, we propose a gate engineering approach to boost the electrical performance of the carbon nanotube transistors, to make them more energy-efficient and fit for the low power consumption requirement in practical biological or environmental applications.

Reference

S.NM05.12.04
Wearable Two-Dimensional Thermoelectric Imaging Sensor Array Based on Carbon Nanotube
Nabila Fairuz, Fariba Islam and Ahmed Zubair; Bangladesh University of Engineering and Technology, Bangladesh

Thermal imaging has applications in non-destructive imaging, testing, detection, and many more areas. Here, we demonstrate a thermal imaging sensor design made of carbon nanotubes (CNTs) using the thermoelectric effect. We designed the sensor device consisted of an array of p-type CNT fibers that crisscross with another array of n-type CNT fibers. Temperature differences between different p-n fiber knots produce voltage differences. Measuring the voltage differences between p and n
terminals of each knot, the temperature of each knot can be determined and the thermal image of the object can be obtained. For a 7×7 sensor array, the p-n terminal voltage difference of ∼0.22 mV was attained for a temperature difference of 100 K. As CNT gives flexibility and tunability of the Seebeck coefficient in the device, this thermal sensor device can be made wearable with nanorange thermal imaging with extreme precision.

S.NM05.12.05
Density Control of Vertically Aligned Carbon Nanotubes Grown Directly on Stainless Steel through Nanosphere Lithography and Its Effect on Field Emission Properties Arun Thapa and Wenzhi Li; Florida International University, United States

The direct contact of vertically aligned carbon nanotube (VACNT) based field emitter arrays (VACNT-FEAs) to their growth substrate and their structurally controlled morphology are critical factors for applications in vacuum micro/nano-electronic devices. Here, we propose a method for fabricating a high-performance VACNT-FEAs by controlling the morphology of VACNT micro/nano-pillars synthesized directly on stainless steel substrates without external metal catalyst particles via nanosphere lithography (NSL). Exposure of carbon precursor gas to the limited space, created after the NSL using polystyrene spheres of different sizes, on the surface of the thermally heated bulk catalytic substrate was a key for manipulating the morphology of the VACNT-FEAs. Field emission properties of the as-synthesized VACNT-FEAs were measured and found fascinating field emission properties along with high emission current stability. The correlation between the number of emitters in a pillar structure and their field emission behavior has been investigated. The proposed method may be used to fabricate the cold cathodes for vacuum electronic devices requiring high emission current density along with extended emission current stability.

S.NM05.12.06
High Pressure Raman Spectroscopy of Linear Carbon Chain Encapsulated in Isolated Multiwall Carbon Nanotube Keshav Sharma1, Paulo T. Araujo1, Nathalia L. Costa2 and Alexandre R. Paschoal2; 1The University of Alabama, United States; 2Univsridade Federal do Ceará, Brazil

Elusive measurements of the Longitudinal optical (LO) phonon mode frequency of isolated Cn@MWCNT systems (linear carbon chains encapsulated by multi-wall carbon nanotubes) were studied under extreme high pressure via Resonance Raman spectroscopy. The pressure-dependent frequency softening with increasing pressure is discussed in terms of a simple force constant model in which the spring constants present a dependence with pressure. The model allowed us to easily obtain both the Young’s modulus and the Gruneisen parameter associated to such LO mode. In particular, the Gruneisen parameter was found to be much higher than that of Graphene and CNTs. Additionally, the LO phonon lifetime was found to be decrease with increasing stress.

S.NM05.12.08
Optical Response of Ultrathin Periodically Aligned Single-Wall Carbon Nanotube Films Chandra Adhikari and Igor Bondarev; North Carolina Central University, United States

Finite-thickness films of aligned single-wall carbon nanotubes (SWCNT) are recently demonstrated to have extraordinary optoplasmnic properties including a tunable negative dielectric response in a wide photon energy range[1]. We explain this theoretically using the Maxwell-Garnett (MG) mixing[2] for the dielectric responses of planar periodic arrays of identical SWCNTs. We start with the calculation of the conductivity for an individual SWCNT using the (k*p)-method of band structure calculations[3]. Then we use the low-energy plasmonic response calculation technique earlier proposed by one of us for finite-thickness metallic films with periodic cylindrical anisotropy[4], to derive an analytical expression for the dynamical dielectric response tensor of an ultrathin finite-thickness periodically aligned SWCNT array. The dielectric responses of about a dozen of SWCNT arrays with different chiralities and very close diameters are then mixed using the MG method to obtain the anisotropic optical response of the finite-thickness SWCNT film which explains the experimental ellipsometry measurements reported[1]. We also note that in such SWCNT films the inhomogeneously broadened interband plasmon resonance of individual SWCNTs overlaps with the broadened exciton resonance, thus making the exciton-plasmon coupling and associated photon bandgap formation possible[5] for these and similar cylindrically anisotropic compound systems including double-walled carbon nanotubes.

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References:
Flexible Configurable Multifunctional Electronics Based on Carbon Nanotube Dual-Material Gate Devices

Fan Xia, Li Xiang and Youfan Hu; Peking University, China

Electronic devices with configurability to providing multiple functions are of great interests for their superior adaptability to the ever-changing and multifarious application scenarios. Here, we report flexible integrated circuits possessing configurable functions constructed with dual-material gate (DMG) devices based on carbon nanotube thin films, which can serve as either transistors or diodes, on a 2-μm-thick parylene substrate. When configured as a transistor, the DMG device has great advantages over the normal-gated devices regarding the current on/off ratio, the subthreshold swing and the drain-induced barrier lowering due to the regulated energy band distribution in channel area. When operating as a diode, a typical DMG device demonstrates a sufficient rectification ratio of approximately five orders and a diode-on-current of over 26μA. Scalable manufacturing of DMG devices was also demonstrated with great uniformity both in diode and transistor configurations. Finally, multifunctional integrated circuits, which can dynamically switch their function from rectifier to follower or from OR gate to voltage adder by changing controlling signals, were constructed. The functional-configurability, together with scalable manufacturing and the realization on ultrathin flexible substrates, will open up great opportunity for the future environmentally-adaptive system in the field of flexible electronics.

Pseudocarbynes—Stabilization of Polynes in Solid-State by Gold Clusters

Hyunsub Kim, Pilarisetty Tarakeshwar, Peter Buseck and Scott G. Sayres; Arizona State University, United States

Carbyne, the structure consisting of one-dimensional (1D) chain of \( sp \)-hybridized carbons is predicted to have greater tensile strength than graphene, making it a highly sought material. However, the highly reactive \( sp \)-hybridized carbon chains convert to the more stable \( sp^2 \)-hybridized phase through cross-linking reactions and ozonolysis by exposure to oxygen. We have developed a new class of molecules/materials, “pseudocarbynes”, that we define as \( sp \)-hybridized carbon chains that are stabilized through non-covalent interactions with small metal clusters. Here, I will present our progress in synthesizing pseudocarbynes through two distinct experimental techniques: 1) through direct laser ablation of a gold target submerged in liquid, and 2) through the self-assembly of conjugated carbon chains with a colloidal solution of gold nanoparticles. Pseudocarbynes remain stable in the solid-state (tested for up to several months). We characterize the \( sp \)-hybridized carbon structure by analyzing FT-IR and Raman spectroscopies, as well as X-ray powder diffraction directly in the solid state. By securing stability in the solid state, pseudocarbynes are expected to be a good candidate for a diverse set of optical or electronic applications.

Design, Solution Synthesis and Characterization of Graphene Nanoribbons and Heterojunctions

Mamun Sarker and Alexander Sinitskii; University of Nebraska-Lincoln, United States

Graphene nanoribbons (GNRs) are known for their highly tunable physical properties and great promise for a broad spectrum of electronic applications. The current study focuses on the chemical design of novel molecular precursors for the bottom-up solution synthesis of atomically precise GNRs. As semiconducting properties of GNRs are highly dependent on their width, edge geometry, and heteroatom doping, here we report on the design, synthesis, and characterization of three different GNRs, which include C4N- and C8N-GNR heterojunctions derived from the pristine with nitrogen-substituted chevron-based monomers, laterally extended chevron GNRs (LecGNRs) and edge-modulated chevron GNRs (EmcGNRs). The XPS-data for C4N- and C8N-GNR heterojunctions confirms the presence of nitrogens and suggests the random positions of pristine and nitrogen-doped GNR segments. The data on the structural, optical and electronic properties of all three GNRs will be presented. In particular, LecGNRs showed an expected lower optical bandgap than their counterparts, while EmcGNRs demonstrate a higher optical bandgap than the pristine chevron GNRs. While this study has a particular focus on the solution synthesis of nanoribbons, the developed molecular precursors may also be compatible with the established on-surface synthesis approaches for GNRs.
Electrospinning (ES) is a rapid and simple manufacturing process for producing polymer materials with high surface-area-to-volume ratios. Traditional ES fabrication involves an electrostatic force that pulls polymer from a grounded spinneret tip to a charged metallic deposition surface held at high voltage. Due to the high voltages and the charged electrodes required for ES fiber creation, ES conductive polymers presents a great challenge. During ES of conductive materials, a circuit is completed from the ES spinneret to the deposition substrate, resulting in electrical arcing and non-predictable deposition. In the work presented here, a handheld ES device that incorporates directed airflow was used for deposition of conductive polymer fiber materials directly onto substrates regardless of dielectric charges. In the portable ES device described, deposition occurs by placing a conductive, ring electrode between a spinneret and a deposition surface. The resulting electrostatic force pulls polymer from the spinneret and toward the ring electrode. Directed airflow then carries the polymer fiber through the center of the ring electrode and onto a non-conductive surface beyond the device. Such a system prevents electrical arcing, thereby improving predictability and allowing for the creation of a fiber mat capable of carrying electrical current ranging from direct current to alternating. Electrically conductive polymer fiber mats are desirable due to their mechanical compliance, high surface area, potential for optical transparency, and a variety of electrical, optical, and mechanical applications. These applications include but are not limited to materials for water filtration, photocatalysis, light polarization, light energy harvesting, sensors, actuators, and miniature electrical components.

The portable, electrostatic and air driven (EstAD) ES device presented includes enclosed electrodes and a fiber propulsion system that provides several additional benefits as compared to other portable ES devices including improved safety for the user and predictable deposition with controllable directionality. A highly desirable and novel application of the EstAD device is that it can be used to electrospin conductive materials onto non-conductive substrates without the drawbacks of traditional ES. In the proposed work, the EstAD device will be used to deposit conductive sensors onto non-conductive substrates. Carbon nanotube (CNT) polymer composites will consist of multi-walled CNTs (MWCNTs) treated with amphiphilic surfactants or untreated single and double-walled CNTs dispersed in the neat polymer. Previously, amphiphilic surfactants were used to create homogeneously dispersed MWCNT in an aligned nanofiber network with improved conductivity. The feasibility of using untreated single and double-walled CNTs will also be investigated for sensor creation on non-conductive substrates. The preparation process will include a solution-based purification process (ultracentrifugation) in order to inexpensively achieve high purity, metallic CNTs that have been used in high-performing electronic devices. High-purity metallic CNTs are more suitable for superior optical transparency because poorly conducting, strongly absorbing impurities, and semiconducting CNTs will be eliminated through the purification process. Both amorphous nanofiber mats and aligned fiber arrays will be created for subsequent testing. A four-point probe will be used to measure conductivity across the composite CNT nanofiber mats or arrays. The electronic response of nanofiber sensors to analytes (e.g. water vapor and ammonia) will be characterized through current-voltage (I-V) measurements. Morphological surface characterization will be performed through scanning electron microscope (SEM) imaging and analysis, and CNT dispersion within the composite matrix will be analyzed through transmission electron microscope (TEM) imaging and analysis.

S.NM05.12.18
Quantum Coupling of Spatially Patterned Guanine Defects in DNA Functionalized Carbon Nanotubes Younghee Kim1, Yu Zheng1, Sergei Bachilo2, R. Bruce Weisman2, Stephen K. Doorn1 and Han Htoon1; 1Los Alamos National Laboratory, United States; 2Rice University, United States

Chemical functionalization of the sidewalls of semiconducting single-wall carbon nanotubes (SWCNTs) has attracted intense attention because of the localization of tightly bound excitons at defect sites on the nanotube surface, allowing single-photon emission (SPE) at room temperature. Such covalently functionalized SWCNTs hold the potentials as single-photon sources (SPSs) for the applications of quantum photonics and quantum information processing. Aryl sp3 defects has been sparsely and covalently implanted to the random positons of SWCNT sidewalls through diazonium chemistry, leading to the trapping of mobile band-edge excitons in the aryl defects and causing spectrally shifted photoluminescence (PL). Single photon has been emitted through the radiative recombination of localized excitons at the defect sites in the altered nanotube with ultrahigh single-photon purity (99%).

Previous reports about chemically functionalized SWCNTs as single-photon emitters are based on sparse and random placement of oxygen atom or aryl group on the nanotube surface. Incorporation of multiple defects with spatial pattern in nanotube sidewalls has not been achieved until recent discovery of covalently functionalizing SWCNTs with single-stranded DNA (ssDNA). The coating agents such as surfactants, polymers, or DNA are required for individualizing nanotube particles. ssDNA oligomers have been found to helically wrap around nanotube surfaces trough noncovalent interactions. Recently, a room-temperature chemical reaction in samples of ssDNA-suspended SWCNTs has been found between the guanine
nucleotides in the ssDNA coating and the nanotube sidewall in the presence of singlet oxygen (1^O_2). Therefore, introducing and controlling spatially patterned guanine defects on nanotube surfaces is easily achieved by manipulating ssDNA sequences. Such DNA-templated covalent functionalization allows smooth modulation of SWCNT electronic energy levels along the nanotube axis with customized spatial pattern and depth.

Each reacted guanine nucleotides creates a defect with shallow trapping depth in the nanotubes. The axial separation between guanines in the (GT)_n ssDNA coating is estimated to be ~0.4 nm, which is at least 5 times smaller than the exciton size. Therefore, excitons in the DNA-tailored SWCNTs are capable of sensing the cumulative potential of several nearby guanine-introduced defects. On the contrary, the exciton is localized in a defect site with deep trapping depth for SWCNT samples with sparse chemical doping of oxygen atom or aryl group on the nanotube surface. We have found that single photon can be generated from the defect-state emission in DNA-altered SWCNTs. Notably, quantum coupling of multiple defect-states has been achieved, resulting from multiple guanine defects with spatial patterning on the nanotube surface.

S.NM05.12.20
Superparamagnetic Properties of Metal-Free Nitrogen Doped Graphene Quantum Dots Synthesized by Pulsed Laser Ablation Muhammad Shehzad Sultan, Vladimir I. Makarov, Brad R. Weiner and Gerardo Morell; University of Puerto Rico - Rio Piedras, United States

In this study, we developed a novel approach to synthesize high-quality metal-free Nitrogen-doped graphene quantum dots (N-GQDs) with high quantum yield, via irradiation of s-triazene in a solution with benzene by using pulsed laser. The TEM, HRTEM, XPS, XRD, Raman spectroscopy and FTIR were carried out to observe the morphology, size distribution, crystalline structure and to prove successful doping of GQDs with nitrogen atoms. Furthermore, for the first time, to our knowledge, their magnetic properties were investigated. The results indicate that N-GQDs exhibit superparamagnetic behavior. The specific size, shape and zigzag edge structure of N-GQDs were considered to explain the origin of the observed magnetism. The magnetization dependence led to estimating the N-GQD material magnetic permeability for different ambient temperatures. From the zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements, carried out at 50 Oe magnetic field strength, we estimated the blocking temperature $T_B$ to be around 300 K. Based on the experimental data analysis, the magnetic permeability, number of correlated spins per single N-GQD, and number density of superparamagnetic N-GQD per gram of material were estimated. The excellent superparamagnetic properties together with optical properties manifested by N-GQDs have the potential to lead to high performance biomedical applications.
8:00 AM INTRODUCTION

8:05 AM S.NM06.01.02
Atomic Electrostatic Maps of Defect Structures in 2D TMDs Yi Wen1, Colin Ophus2, Christopher S. Allen1,3, Shiang Fang1,4, Efthimios Kaxiras4,4, Angus I. Kirkland1,3 and Jamie Warner1; 1University of Oxford, United Kingdom; 2National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Laboratory, United States; 3Electron Physical Sciences Imaging Center, Diamond Light Source Ltd., United Kingdom; 4Harvard University, United States

The atomic scale studies on the pristine lattice of TMDs have been carried out with aid from aberration-corrected (scanning) transmission electron microscope (AC-(S)TEM), enabling detailed studies on the evolution of atomic scale defect structures, but their perturbation on local electronic properties, which is essential for understanding their functionality in electronic and optoelectronic devices, are not readily available from direct imaging. Here, we reported the detailed analysis on adatoms, vacancies, line defects, nanopores, nanowires and edge structures in MoS2 and WS2 using 4D STEM, which record not only the scattering information, but also the direct beam, and this allows us to extract phase shift, atomic electric field and charge density map based on the shift of center of mass of direct beam.1 We showed that the electric field map and phase reconstructed imaging are sensitive in detection of abnormal 1D states2 and low atomic number atoms,3 and together provide a comprehensive anatomy on the electronic properties of these defect structures, which is of great importance for the theoretical study of 2D electronic devices.

References

8:15 AM S.NM06.01.05
Study of Atomic and Electronic Structures of Black Arsenic Using Analytical Scanning Transmission Electron Microscopy Hwanhui Yun, Supriya Ghosh, Prafful Golani, Steven Koester and K. Andre Mkhoyan; University of Minnesota, United States

Black arsenic (bAs) is a two-dimensional layered material with similar atomic structures to black phosphorus (bP), and it is expected to exhibit attractive properties for future applications such as high carrier mobility, high anisotropy, tunable band structures by varying the number of layers, etc. [1]. Despite the theoretical predictions, it has only recently gained attention due to difficulties in synthesis of high-quality bAs [2]. Recent experimental reports have shown intriguing nature of bAs including high anisotropy [1,3]. Here, we explore the atomic and electronic structures of exfoliated high-quality bAs using high-angle annular dark-field (HAADF)-scanning transmission electron microscopy (STEM) imaging and spectroscopy and demonstrate changes in optical properties in few-layered bAs. Additionally, a stability study on bAs is conducted to gain insight on the key parameters affecting bAs at ambient conditions.

STEM experiments were carried out using an FEI Titan G2 60-300 (S)TEM at 200 keV equipped with energy dispersive X-ray (EDX) and monochromated electron energy-loss spectroscopy (EELS). HAADF-STEM image simulation was carried out using the TEMSIM code based on the Multislice approach [4,5].

Atomic resolution HAADF-STEM images of bulk bAs were obtained from five different orientations including three major crystallographic directions - armchair direction (x-axis), zigzag direction (y-axis), and plan-view direction (z-axis) - confirming anisotropic atomic structures of bAs. Plan-view images were also obtained from few-layered bAs and compared with simulated images that are computed as a function of the number of layers, by which the thickness of the examined layers was measured precisely. The electronic structure of bAs was investigated by using EELS. Low-loss EELS reveals bulk and surface plasma excitation energies and interband transitions, and characteristics of core-loss EELS are described. Low-loss EELS spectra are then acquired as a function of the number of bAs layers and evidence the changes in optical properties in few-layered bAs from bulk bAs. Lastly, degradation of bAs accompanying structure change is analyzed using HAADF-STEM, EDX, and diffraction pattern of specimens. The effect of air, i.e. O2, and water on the degradation is further investigated and discussed.

Acknowledgment
P.G. and S.J.K. were supported by the NSF under Award No. ECCS-1708769.
Two-dimensional (2D) materials and heterostructures are promising systems for soft robotics, deformable electronics, and nanoelectromechanical systems because they combine the high charge carrier mobilities of hard materials with the pliability of soft materials. Understanding their bending properties is crucial for the development of these next-generation devices. However, experimental measurements of bending stiffness in 2D materials have been widely divergent; for example, the reported bending stiffnesses of bilayer and trilayer graphene range from 3.4-160 eV and 7-690 eV, respectively [1-3]. Even less is known about the bending stiffness of 2D heterostructures. Here, we show that electron microscopy can provide a powerful platform for measuring the bending properties of 2D materials. We use aberration-corrected scanning transmission electron microscopy (STEM) to image graphene and 2D heterostructures draped over a series of atomically sharp hexagonal boron nitride steps. This approach enables atomic-resolution studies of their bending conformation, producing insight into both the bending stiffness and mechanisms of bending. In combination with density functional theory (DFT) and continuum mechanics modeling, we derive a unifying model for bending in 2D materials and their heterostructures.

First, we investigated the bending stiffness of single and few-layer graphene [4]. We derive mechanical models that relate the bending stiffness to geometric parameters—such as the radius of curvature, bending angle, and step height—measured directly from STEM images. For monolayer graphene, we obtain bending stiffness values of 1.2-1.7 eV, consistent with DFT predictions [5] and the experimental value of 1.2 eV derived from graphite phonon modes [6]. In multilayer graphene, we find that the bending stiffness varies strongly as a function of bending angle, tuning by almost 400% for trilayer graphene. For ten-layer graphene, we show that the bending stiffness can be as low as 18 eV, three orders of magnitude lower than the bending stiffness predicted by conventional thin-film mechanics. This unusual behavior results from the atomic-scale bending mechanism in 2D multilayers, which is dominated by interlayer shear and slip.

Our findings have profound implications on 2D heterostructures, where we demonstrate that the bending stiffness can be controlled by tailoring the interfacial interactions between vertical homo- and heterointerfaces. We investigated heterostructures and showed that, by simply changing their stacking order, we can dramatically tune their bending stiffnesses. Using a combination of DFT and classical simulations, we produce a model to predict the bending stiffness of arbitrary 2D heterostructures. Together, our results provide a new lower limit of bending stiffness for the fabrication of ultrasoft, high mobility electronics and demonstrate new methods to fabricate 2D heterostructures with tailored bending stiffnesses.

References:
9:00 AM INTRODUCTION

9:05 AM *S.NM06.07.03
Molecule Functionalization and Intercalation in 2D Materials Judy Cha; Yale University, United States

Owing to the large surface area and layered nature, the electrical and catalytic properties of 2D materials can be tuned greatly by surface functionalization with tailored molecules with specific redox potentials and intercalation of various intercalants. The utility of surface functionalization and intercalation has been amply demonstrated in 2D transition metal dichalcogenides (TMDCs), including the modulation of carrier densities in monolayer MoS2 field-effect transistors (FETs) and the enhancement of catalytic activities of hydrogen evolution reaction in Li+-intercalated WS2. However, fundamental mechanistic understandings that govern molecule-TMDC interactions or intercalation-induced structural and electrical phase transformations remain basic.

In this talk, I will present our approach to elucidate the underlying mechanisms that govern surface functionalization and intercalation in 2D TMDCs, using MoS2 as a material choice. For surface functionalization, we compare doping powers of a family of organic electron donors (OEDs) on MoS2 to understand the OED-MoS2 interactions. This requires accurate knowledge of surface coverage of OEDs, change in the carrier density after functionalization, and the nature of the OED bonding to MoS2. For intercalation, we electrochemically intercalate Li+ ions into individual monolayer or heterostructure FETs and follow the change in crystal structure and electrical properties of the host 2D systems as a function of intercalation. We uncover a host of interesting phenomena, such as the role of a hBN/MoS2 interface on intercalation kinetics and physics, phase transformation in WSe2 by intercalation, and competition between intercalation kinetics and thermodynamics in MoS2/graphene heterostructures. A central theme of our approach to understanding surface functionalization and intercalation is the integration of device physics with electrochemistry.

SESSION S.NM06.13: Live Lightning/Flash II: Theory and Characterization of 2D Materials—Bridging Atomic Structure and Device Performance

9:30 AM *S.NM06.07.09
Ambient Stable Phosphorenes and Covalently Linked Phosphorene-MoX2 (X = S or Se) Nanocomposites with Enhanced H2 Evolution Activity Pratap Vishnoi1,2 and C. N. R. Rao1; 1Jawaharlal Nehru Centre for Advanced Scientific Research, India; 2University of California Santa Barbara, United States

The phosphorene is a 2D puckered sheet composed of sp3 phosphorus with each P atom is covalently bonded to three P atoms in the plane. The phosphorus atoms contain lone-pair electrons. It exhibits high charge carrier mobility as well as a thickness tuneable band-gap in the 0.3-2.0 eV range. The conduction band minimum of phosphorene is appropriately positioned to effectively catalyze the H2 evolution reaction by water splitting. Besides, phosphorus is an earth-abundant and environmentally benign non-metal element. Therefore, it is of great interest to exploit the potential of phosphorene as a metal-free photocatalyst for H2 evolution. However, pristine phosphorene is ambient instable and it produces trace amounts of H2 by water splitting.

The advantage of the lone-pair electrons is that they can be utilized for chemical functionalization of phosphorene without significantly affecting its intrinsic properties. In this work, we present synthesis of ambient stable η–ν adducts of phosphorene, covalently cross-linked phosphorene-MoX2 (X = S or Se) nanocomposites, and their HER activity. The
phosphorenes functionalized with InCl$_3$ and B(C$_6$F$_5$)$_3$ as well as ylide with a benzyl group are ambient stable and disperse well in aqueous medium.\[3\] Their photocatalytic HER activity is enhanced significantly exhibiting H$_2$ yields of 6.6 mmol h$^{-1}$g$^{-1}$ in the case of phosphorene-B(C$_6$F$_5$)$_3$ (hydrogen yields for pristine phosphorene is 0.6 mmol h$^{-1}$g$^{-1}$). Phosphorene-MoS$_2$ nanocomposites are synthesized by forming amide as the cross-linkages.\[4\] Due to improved charge-transfer and suppressed charge recombination rate, phosphorene-MoS$_2$ exhibits excellent photochemical HER activity with H$_2$ yields of 26.8 mmol h$^{-1}$g$^{-1}$, while only a negligible amount is produced by their physical mixture. The phosphorene-MoS$_2$ composite shows high electrochemical HER activity with an onset overpotential of 110 mV, closer to that of Pt/C catalyst. The onset overpotential of a 1:1 physical mixture of phosphorene and MoS$_2$ is 450 mV. The enhanced HER activity of phosphorene-MoS$_2$ nanocomposite can be attributed to the ordered cross-linking of the 2D sheets, leading to increased interfacial area as well as the charge-transfer interaction between phosphorene and MoS$_2$ layers.


9:40 AM S.NM06.07.02
Accurate Molecular Models for MoS$_2$ and Battery Oxides (NMC) to Predict Interfacial Properties up to the Large Nanometer Scale
Juan Liu and Hendrik Heinz; University of Colorado Boulder, United States

We introduce reliable force fields and applications to electrolyte and organic interfaces for molybdenum sulfide and battery oxides, including lithium cobalt oxide as well as nickel and manganese substituted lithium cobalt oxides. Such models, except for MoS$_2$, have not been available and are necessary to understand the dynamics and charge transport properties up to the large nanometer scale. Specifically, the parameters for MoS$_2$ reliably account for structural, interfacial, and mechanical properties and are compatible with many force fields for molecular simulations (Interface force field, CVFF, PCFF, CHARMM, AMBER, OPLS-AA, TEAM). We reproduce chemical bonding, X-ray structure, cleavage energy, infrared spectrum, bulk modulus, Young’s modulus, and interfacial properties with polar and nonpolar solvents within 0.1% to 5% deviation from measurements. Compared to prior models, structural and mechanical instabilities of the nanoscale layers were eliminated, and large deviations in computed interfacial properties (>50%) were reduced to quantitative agreement with experiment (<5%). Computed contact angles of water and diiodomethane agree within ±2° with experimental measurements on freshly cleaved MoS$_2$ surfaces. Similarly, new force field parameters for lithium cobalt oxide as well as Co-Ni-Mn mixed oxide phases are shared that reproduce lattice constants, surface energies, contact angles, and mechanical properties in excellent agreement with experiment. The models can be used as part of multiple force fields (IFF, CHARMM, AMBER, OPLS-AA, PCFF, TEAM) for accurate predictions of fully dynamic, large scale interfacial properties and local analysis by quantum mechanics.

The parameters rely on quantitative representation of chemical bonding using atomic charges, using methods that reach much higher accuracy than DFT calculations, bonded parameters from experimental data, and a consistent interpretation of Lennard-Jones parameters that lead to wide compatibility for multiphase materials. All parameters are supported by a physical chemical interpretation. As an example, we discuss the binding mechanism and adsorption energies of peptides on the MoS$_2$ basal plane using strongly binding and weakly binding sequences derived from phage display. Adsorption is driven by direct surface contact and replacement of surface-bound water molecules, with very widely tunable adsorption energies between -86 and -6 kcal/mol. Weak electrostatic interactions of backbone and side chains with the surface, hydrogen bonds between electrolyte-facing side groups and water, and contributions by hydrophobic groups play a key role to tune the interaction strength.

The models can be applied to any biomaterials and nanomaterials including these 2D compounds, including embedding in electrolytes, polymer matrices, understanding of charge transport, local defects and changes in stoichiometry. The accuracy is comparable to DFT methods at millionfold larger time and length scales, and extensions are feasible for reactive simulations (IFF-R). The models for battery oxides can help overcome problems in designing materials with a higher storage capacity.
SESSION S.NM06.14: Live Keynote II: Theory and Characterization of 2D Materials—Bridging Atomic Structure and Device Performance  
Session Chairs: Yuanyue Liu and Alessandro Molle  
Monday Afternoon, November 30, 2020  
S.NM06

5:15 PM INTRODUCTION

5:20 PM *S.NM06.05.01  
Keynote: Interfacial Engineering of Chemically Reactive Two-Dimensional Materials Mark C. Hersam; Northwestern University, United States

Following the success of ambient-stable two-dimensional (2D) materials such as graphene, hexagonal boron nitride, and transition metal dichalcogenides, new classes of chemically reactive layered solids are being explored since their unique properties hold promise for improved device performance [1] and quantum phenomena [2]. For example, chemically reactive 2D semiconductors (e.g., black phosphorus (BP) and indium selenide (InSe)) have shown enhanced field-effect mobilities and optoelectronic properties under controlled conditions that minimize ambient degradation [3,4]. In addition, 2D boron (i.e., borophene) is an anisotropic metal with a diverse range of theoretically predicted phenomena including confined plasmons, charge density waves, and superconductivity [5], although its high chemical reactivity has limited experimental studies to inert ultrahigh vacuum conditions [6-9]. Therefore, to fully study and exploit the vast majority of 2D materials, methods for mitigating or exploiting their relatively high chemical reactivity are required [10]. In particular, covalent organic functionalization of BP minimizes ambient degradation, provides charge transfer doping, and enhances field-effect mobility [11], while noncovalent organic functionalization of borophene leads to the spontaneous formation of electronically abrupt lateral borophene-organic heterostructures [12]. On the other hand, sequential deposition of atomic carbon and boron on silver substrates results in rotationally commensurate vertical borophene-graphene heterostructures where the graphene adlayer provides robust encapsulation for the underlying borophene [13]. By combining organic and inorganic encapsulation strategies, even highly chemically reactive 2D materials (e.g., InSe and CrI3) can be studied and utilized in ambient conditions [14].


SESSION S.NM06.15: Live Lightning/Flash III: Theory and Characterization of 2D Materials—Bridging Atomic Structure and Device Performance  
Session Chairs: Yuanyue Liu and Alessandro Molle  
Monday Afternoon, November 30, 2020  
S.NM06

5:45 PM S.NM06.08.08  
Exploring Strain-Stabilization of the Conducting 1T Phase in Pulsed Laser Deposited MoS2 Thin Film on Different Single Crystal Substrates Swati Parmar1,2, Suresh Gosavi1 and Satishchandra Ogale2; 1Savitribai Phule Pune University,
The metallic 1T phase of MoS2 has excellent electrical conductivity but it is thermodynamically unstable. Hence there is great interest in realization and stabilization of this phase in different forms such as nanomaterials and thin films for various device applications. The thin film platform affords the element of substrate-induced strain as a tunable parameter that can control the phase equilibria. In the work reported here, we therefore examine the possibility of stabilizing the desirable 1T phase of MoS2 in the case of thin films grown by pulsed laser deposition (PLD) on different crystalline substrates, namely c-Al2O3 (0001), LaAlO3 (001), SrLaAlO4 (001), SrTiO3 (001) and MgO (001). The percent (%) lattice parameter mismatch between the most favorable growth planes of MoS2 and these different substrates varies from 5% to 16%. c-Al2O3, LaAlO3, SrLaAlO4 are noted to induce tensile strain whereas SrTiO3 and MgO cause compressive strain in MoS2 thin film. Interestingly, Raman and X-ray Photoelectron spectroscopy reveal much enhanced and stable 1T phase contribution in MoS2 thin films grown on SrTiO3 and SrLaAlO4 substrates. The X-ray diffraction, X-ray reflectivity, and atomic force microscopy data reveal high crystalline quality of MoS2 thin films. The most enhanced 1T phase film of MoS2 is noted in the case of the film grown on SrLaAlO4, which also shows a reduction in room temperature resistivity and semi-metal behavior. The valence band spectroscopy (VBS) data for this case are also consistent with the expected metal-like nature of the 1T phase MoS2 thin film. Furthermore, while increasing the thickness, structural transition from mixed 1T/2H phase to pure 2H hexagonal phase is observed; a consequence of strain relaxation, which clearly establishes the role of substrate-induced strain in 1T phase stabilization via octahedral rotation. This study will pave the way for making the vast family of transition-metal chalcogenides tetragonal phase thin films and brings out the potential of 1T phase thin film for unfolding phenomenon and technological applications.

References:

Pulsed Laser Deposition of Two-Dimensional Materials
Denys Miakota1, Huu Phuoc Le1, Yu-Chuan Lin2, Raymond R. Unocic2, Fabian Bertoldo1, Kristian Thygesen1, Alexander Puretzky2, Ilia N Ivanov2, Jorgen Schou1, David B. Geohegan2 and Stela Canulescu1; 1Technical University of Denmark, Denmark; 2Oak Ridge National Laboratory, United States

Two-dimensional of transition metal dichalcogenides (2D-TMDCs) stand out from the class of 2D materials due to their appealing properties, including atomic-scale thickness, direct band gap and strong spin-orbit coupling. The precise control of the atomic layer structure can pave new avenues for the integration of TMDCs in future optoelectronic devices, such as light-emitting diodes and van der Waals photovoltaics. In this paper, we present our recent progress on the growth of 2D-TMDCs including MoS2, WS2, MoSe2 and their alloys, by a bottom-up approach, namely Pulsed Laser Deposition (PLD). PLD is a well-established technique for the growth of functional oxide structures1 and superlattices2. It relies on vapor-phase transfer of a material from a target to substrate3. Furthermore, this catalyst-free approach has recently been used for the growth of layered TMDCs4. Nevertheless, the optoelectronic properties of 2D-TMDCs, particularly photoluminescence (PL) emission, are often poor. A good control of the chalcogenide vacancies at the monolayer limit is important to realize the full potential of 2D materials and their heterostructures in devices. In this paper we will discuss the PLD-synthesis of large area, crystalline 2D-TMDCs on sapphire and SiO2/Si. PLD synthesis at high temperature (~600°C and above) using this one-step approach results in the formation of continuous monolayers with grain boundaries, as compared to the triangular-shaped structures, specific to the chemical vapor deposition process. We profile the vacancy concentration in MoS2 monolayer on an atomic scale using annular-dark-field electron microscopy, with an absolute detection sensitivity of one to two sulfur vacancies. A rich variety of defects, including single and double sulfur vacancies, anti-site defects, as well as grain boundaries with periodic rings 8-4-4- rings defects are revealed. Room temperature PL spectra of MoS2 monolayer exhibit two-distinct exciton peaks that can be used to qualitatively asses the as-grown monolayers. Finally, we will discuss the PLD growth of 2D materials using chalcogen-enriched targets as a path towards defect engineering of 2D materials.

4. Serna, M. I. et al. Large-Area Deposition of MoS2 by Pulsed Laser Deposition with In Situ Thickness Control. - ACS Nano 10, 6054

SESSION S.NM06.16: Live Keynote III: Theory and Characterization of 2D Materials—Bridging Atomic Structure and Device Performance
Session Chairs: Yuanyue Liu and Alessandro Molle
Monday Afternoon, November 30, 2020
S.NM06

6:15 PM INTRODUCTION

6:20 PM *S.NM06.02.01
Spatial and Temporal Imaging of Exciton Transport in Two-Dimensional Heterostructures Libai Huang; Purdue University, United States

Charge-transfer (CT) excitons at hetero-interfaces play a critical role in light to electricity conversion using nanostructured materials. However, how CT excitons migrate at these interfaces is poorly understood. Atomically thin and two-dimensional (2D) nanostructures provide a new platform to create architectures with sharp interfaces for directing interfacial charge transport. Here we investigate the formation and transport of interlayer CT excitons in van der Waals (vdW) heterostructures based on semiconducting transition metal dichalcogenides (TMDCs) employing transient absorption microscopy (TAM) with a temporal resolution of 200 fs and spatial precision of 50 nm.

We have recently imaged the transport of interlayer CT excitons in 2D organic-inorganic vdW heterostructures constructed from WS2 layers and tetracene thin films. To investigate driving force for exciton dissociation, we perform measurements on heterostructures constructed with different WS2 thickness ranging from 1 layer to 7 layers. Photoluminescence (PL) measurements confirm the formation of interlayer excitons with a binding energy of ~ 0.3 eV. Electron and hole transfer processes at the interface between monolayer WS2 and tetracene thin film are very rapid, with time constant of ~ 2 ps and ~ 3 ps, respectively. TAM measurements of exciton transport at these 2D interfaces reveal coexistence of delocalized and localized CT excitons, with diffusion constant of ~ 1 cm²s⁻¹ and ~ 0.04 cm²s⁻¹, respectively. The high mobility of the delocalized CT excitons could be the key factor to overcome large CT exciton binding energy in achieving efficient charge separation.

We have also investigated interlayer exciton dynamics and transport modulated by the moiré potentials in WS2-WSe2 heterobilayers in time, space, and momentum domains using transient absorption microscopy combined with first-principles calculations. Experimental results verified the theoretical prediction of energetically favorable K-Q interlayer excitons and unraveled exciton-population dynamics that was controlled by the twist-angle-dependent energy difference between the K-Q and K-K excitons. Spatially- and temporally-resolved exciton-population imaging directly visualizes exciton localization by twist-angle-dependent moiré potentials of ~100 meV. Exciton transport deviates significantly from normal diffusion due to the interplay between the moiré potentials and strong many-body interactions, leading to exciton-density- and twist-angle-dependent diffusion length. These results have important implications for designing vdW heterostructures for exciton and spin transport as well as for quantum communication applications.

SESSION S.NM06.17: Live Lightning/Flash IV: Theory and Characterization of 2D Materials—Bridging Atomic Structure and Device Performance
Session Chairs: Yuanyue Liu and Alessandro Molle
Monday Afternoon, November 30, 2020
S.NM06

6:45 PM S.NM06.02.04
Stable Long-Range Diffusion of Photocarriers in 2D MoS2 Injected by 0D Charge Sources Ilka Kriegel1,2,3, Michele Ghini1, Nicholas Borys2,4, Kehao Zhang5,6, Adam W. Jansons6, Brandon M. Crockett6, Kristopher W. Koskela6, Edward S.
We present stable long-range diffusion of photocarriers in an innovative 0D-2D heterostructure through contactless all solid state photodoping. We implement 0D indium tin oxide nanocrystals (ITO NCs) as light-driven charge injection sources for localized contactless injection of carriers into the underlying monolayer of molybdenum disulfide (2D MoS2). This technique gives us the opportunity to follow carrier diffusion in the 2D transition metal dichalcogenide without the need of invasive and broad physical contacts. With light beyond the bandgap we locally excite the nanocrystals within a diffraction limited excitation spot, promoting electrons from the valence band to the conduction band of ITO. The photogenerated holes spontaneously transfer to the underlying 2D material with charge injection densities comparable to p-type doping in electronically gated MoS2 samples (in the range of 6x10¹² cm⁻²). We collect hyperspectral maps of the 0D-2D hybrid, before and after light-driven charge injection to spatially resolve variations in the emission of the monolayer MoS2. We observe a blue-shift of more than 35 meV of the photoluminescence peak energy and a significant variation in the relative contribution of excitons and trions to the emission, as a consequence of the annihilation of negatively charged excitons. Remarkably, the injected carriers diffuse tens of microns through the monolayer, covering long distances away from the local micron sized excitation spot. The excited holes accumulate preferably in regions that are initially higher in n-doping and preferentially along edges and grain boundaries, following the initial local electronic landscape of the two-dimensional layer. The comparison between hyperspectral maps collected immediately after the photodoping and after months shows no significant variation in the photoluminescence, indicating that the photodoping process is irreversible and stable up to, at least, 73 days. These works demonstrate a new possibility to remotely and locally dope two-dimensional transition metal dichalcogenides in a contact-less way. The accumulation of carriers in specific regions of the monolayer, as observed by us, might play an important role in unveiling the contributions of structural defects, vacancies and strain to the optical properties of 2D materials and in the same time open novel design principles for future applications in the field of energy storage and contactless light-driven nanoelectronics.

6:55 PM S.NM06.02.08  
Quasiparticle Electronic Structure, Exciton and Optical Absorption of Atomically Thin Blue Phosphorus Ju Zhou, Tian-Yi Cai and Sheng Ju; Soochow University, China

Two-dimensional (2D) van der Waals layered materials have attracted wide interest in condensed matter physics, materials, chemistry and engineering. For allotropes of phosphorus, besides black phosphorus with narrow band gap, a single layered phosphorus with bulked honeycomb structure and wide band gap was studied recently and was called blue phosphorus. Here, by considering many-body effects arising from strong electron-electron and electron-hole interactions in low-dimensional systems, we have studied the electronic and optical properties of 2D blue phosphorus. The intrinsic indirect quasiparticle band gap is 3.76 eV, with a sharp bright and strongly bound exciton located at 2.85 eV, with a binding energy of 0.9 eV. By applying the isotropic strain within 6%, the 1s exciton could be tuned effectively from 2.4 eV to 3.2 eV. In addition, the band topology and widing numbers have been illustrated, explaining the existence of p-like excitons with relatively high oscillator strength. Given recent advances in the successful production of two-dimensional blue phosphorus crystals, we expect them to be profoundly applied in sensor, solar, and lighting technologies.

7:05 PM S.NM06.02.06  
Correlative Mapping of Photonic Properties in 2D Semiconductor-Based Optoelectronics Timothy Ismael¹, Kazi Islam¹, Nathan Grinalds² and Matthew Escarra³; ¹Tulane University, United States; ²High Point University, United States

A variety of techniques have proven to be important in characterizing the optical and electronic properties of atomically thin transition metal dichalcogenides (TMDCs). Among these two-dimensional (2D) materials, molybdenum disulfide (MoS₂) is considered a good candidate for applications in optoelectronics and photovoltaics. However, predicted device performance is significantly affected by localized defects such as grain boundaries and non-uniformity in large-area films, including regions with varying number of atomic layers. Improvement of techniques for spatially localized investigation of these materials will help accelerate device development from these materials. In this work, we demonstrate an optical microscope setup capable of transmittance, photoluminescence (PL), and photocurrent spectroscopy with ~1 μm spatial resolution. This spatial-spectral mapping of 2D materials is shown for the visible and near-infrared part of the spectrum. By correlating each of these measurements over the same material and device region, we can draw connections between material properties and device performance. We do this by studying optoelectronic and photovoltaic (PV) devices fabricated on chemical vapor-deposition (CVD) grown MoS₂ samples. We concurrently...
measure the fundamental properties of various excitons, e.g. transmission at the A, B and C peaks, and identify spatial regions of peak photoreponsivity leading to efficient photocurrent generation in MoS$_2$ photodetectors. Our light source is a supercontinuum laser (Fianium/NKT Photonics) with laser line tunable filter, facilitating wavelength dependent excitation and optical studies of our MoS$_2$. PL mapping of MoS$_2$ flakes and films within the device active area is carried out by exciting single and few-layer thick MoS$_2$ samples with a monochromatic 532 nm excitation; emitted PL is measured using an Ocean Optics QePro spectrometer. Transmittance measurements are carried out with Thorlabs FDS1010-CAL calibrated photodiode mounted 1mm beneath the sample on a transparent stage. Device photocurrent is measured using a Keithley 2450 sourcemeter.

While each technique individually yields insightful information on the uniformity and properties of the 2D material, the integrated setup enables spatial correlation of properties as they relate to the performance of 2D PV, photodetectors, and other optoelectronics. From correlated PL and transmission measurements we extract absorption and photogeneration information that enables mapping localized external radiative efficiency. Transmittance measurements probe wavelength dependent absorption and reflectance and their dependence on local defects, while correlated spatial mapping of absorption and photocurrent vs. wavelength reveals the effects on carrier collection and device performance resulting from material uniformity, contact choice, grain boundaries, surface treatments, and defects. Localized layering of materials is visualized through mapping PL intensity and percentage transmittance. We are using this correlative mapping of photonic properties to better understand, design, model, and prototype advanced optoelectronics from 2D materials.

SESSION S.NM06.18: Live Keynote IV: Theory and Characterization of 2D Materials—Bridging Atomic Structure and Device Performance
Session Chairs: Yuanyue Liu and Alessandro Molle
Tuesday Afternoon, December 1, 2020
S.NM06

1:30 PM INTRODUCTION

1:35 PM *S.NM06.09.04
Emerging Two-Dimensional Materials for Memory and Sensing Applications Han Wang; University of Southern California, United States

In this talk, I will discuss our recent research progress in understanding the electronic, photonic and ferroelectric properties of emerging low-dimensional materials, and in developing them for sensing and memory applications. The first part of the talk will focus on discussing the basic properties of emerging 2D materials such as black phosphorus and our progress in developing the material for mid-infrared optoelectronics application. I will also discuss our work on utilizing 4-dimensional imaging techniques to study carrier dynamics in two-dimensional materials, including a study using the newly developed scanning ultrafast electron microscopy (SUeM) technique to image the photo-carrier transport in black phosphorus. In the second part of the talk, I will discuss our recent research on the ferroelectric monolayer materials for memory device applications. I will conclude with remarks on promising future research directions of low-dimensional material properties and devices, and how the emerging materials may benefit future generations of electronics and photonics technology in sensing and memory.

SESSION S.NM06.19: Live Lightning/Flash V: Theory and Characterization of 2D Materials—Bridging Atomic Structure and Device Performance
Session Chairs: Yuanyue Liu and Alessandro Molle
Tuesday Afternoon, December 1, 2020
S.NM06

2:00 PM S.NM06.09.05
Quasi-1D TiS$_3$ Nanoribbons—Mechanical Exfoliation, Thickness-Dependent Raman Spectroscopy and Device Prospects Michael J. Loes, Alexey Lipatov, Haidong Lu, Jun Dai, Natalia Vorobeva, Xiao Cheng Zeng, Alexei Gruverman, Peter Dowben and Alexander Sinitskii; University of Nebraska - Lincoln, United States
Two-dimensional layered materials have received much interest in recent years due to their ease of miniaturization by mechanical exfoliation along with strong light-matter interactions and tunable electronic properties. Quasi-one-dimensional (Quasi-1D) materials, however, have seen considerably less interest, but can express many of the same desirable properties as conventional layered materials, with an added dimension of anisotropy. A representative example of this Quasi-1D subclass is Titanium Trisulfide (TiS₃). We demonstrate similar ease of mechanical exfoliation of TiS₃ accompanied with theoretical calculations and show that these materials exfoliate into few-atomic-layer nanoribbons with very smooth edges. We emulated macroscopic exfoliation experiments on the nanoscale by applying a local shear force to TiS₃ crystals in different crystallographic directions using a tip of an atomic force microscopy (AFM) probe. In the AFM experiments, it was possible to slide the 2D TiS₃ layers relative to each other as well as to remove selected 1D chains from the layers. Further, their characterization by Raman spectroscopy shows a reliable, internally standardized shift of a few cm⁻¹ from monolayer to bulk demonstrating tunability typical of conventional layered materials. Devices made from this material show promising electronic properties with predicted mobilities in excess of 10,000 cm²V⁻¹s⁻¹ with low edge-scattering, as well as in optoelectronics with strong light-matter interactions, particularly along the crystallographic b-axis (anisotropic). Orientation-dependent properties of this nature show promise as filters and polarizers, while high surface areas associated with 2D materials hint towards gas-sensing and energy storage applications.

2:10 PM S.NM06.09.02
Encapsulation and Transfer Schemes for Epitaxial Xenes Deepyanti Tanja, Gabriele Faraone, Md. Hasibul Alam, Christian Martella, Carlo Grazianetti, Emiliano Bonera, Alessandro Molle and Deji Akinwande: 1The University of Texas at Austin, United States; 2CNR IMM, Unit of Agrate Brianza, Italy; 3Università degli Studi di Milano-Bicocca, Italy

Epitaxial Xenes are an emerging class of two-dimensional crystals made of elements spanning group III to group VI of the periodic table (e.g. borophene, silicene, phosphorene, antimomene, tellurene etc) [1]. These materials are synthesized by epitaxy on various substrates and are subject to degradation in environmental conditions. Our work is centered around Xenes grown on noble metal surfaces that are supported by mica, as they can readily undergo delamination and transfer on other substrates for device related studies. In particular, we focus on silicene-on-silver [2] and epitaxial phosphorene [3] as representative cases to establish a stabilization and transfer scheme. Encapsulation of the unstable Xenes is a critical step for achieving transfer of the Xene layer from its pristine growth substrate to a device or functional substrate. We propose the use of an Al₂O₃ encapsulation as a stabilization strategy that can be universally applied to the whole class of Xenes. The integrity of the Xene layer after encapsulation is validated by means of Raman spectroscopy and X-ray photoelectron spectroscopy. We then propose a few different transfer schemes and present experimental results of film transfer. A technical step in the delamination and transfer process is the time-controlled etching of the metal substrate. We achieve this using an optimized KI/I₂ silver etchant with a controllable etch rate. Finally, we demonstrate the stability of air-exposed multilayer silicene, prepared using our developed methods, via Raman spectroscopy, validating our successive delamination and transfer protocol.

References:

2:20 PM S.NM06.04.07
Improving the Electrical Performance of MoS₂ Transistors Using Tensile Strain Isha Datye, Alwin Daus, Kevin Brenner, Ryan W. Grady and Eric Pop: 1Stanford University, United States; 2Southern Methodist University, United States

Transition metal dichalcogenides (TMDs) such as molybdenum disulfide (MoS₂) have gained much interest for scaled nanoelectronics, but their mobilities and drive currents must be improved in order to compete with existing technologies. Theoretical studies predict that tensile strain can increase the mobility of TMDs due to changes in band structure, leading to reduced intervalley scattering [1]. However, such mobility improvement has not yet been experimentally demonstrated. In this work, we utilize uniaxial tensile strain to improve the electrical performance of monolayer (1L) MoS₂ transistors on flexible substrates. Using a two-point bending apparatus, we apply multiple strain levels between 0% and ~0.7%, which we estimate from the curvature radius of the bent substrates. We confirm these strain levels by Raman spectroscopy, using the known shift of the MoS₂ in-plane E' Raman peak of -2 cm⁻¹ per percent of tensile strain [2]. We fabricate our devices on polyethylene naphthalate (PEN) flexible substrates. First, the gate metal is lithographically patterned, and then we form the gate dielectric with ~20 nm of Al₂O₃ by atomic layer deposition (ALD). Monolayer
MoS$_2$ grown by chemical vapor deposition (CVD) on separate SiO$_2$/Si substrates [3] is then transferred to the flexible substrates using a polymer scaffold [4]. Finally, we pattern source and drain contacts onto the MoS$_2$ films, followed by an O$_2$ plasma etch to define the channels.

We characterize the effects of tensile strain on MoS$_2$ transistors with channel lengths from 1 to 15 $\mu$m, by extracting the field-effect mobility. Relatively long channels are used to limit extrinsic contributions of contact resistance. We obtain a continuous mobility improvement up to ~85% with increasing tensile strain up to ~0.7%, leading to a drain current $I_D$ increase of ~2x at the same carrier density. Furthermore, we find that the effects are fully reversible as the device characteristics return to their initial state after strain release. The mobility increase with tensile strain also indicates that these devices could be used as strain sensors. An $I_D$ change of ~2x at 0.7% strain corresponds to a gauge factor of nearly ~150, which is the highest value reported so far for piezoresistive 1L CVD MoS$_2$ strain sensors [5-6]. These results demonstrate the largest mobility and on-state current improvements to MoS$_2$ transistors using strain to date, revealing that strain engineering is a promising way to tune the electrical performance of TMD-based devices. Furthermore, using MoS$_2$ transistors as strain sensors can facilitate the realization of flexible and transparent sensor systems for strain mapping.


SESSION S.NM06.20: Live Keynote V: Theory and Characterization of 2D Materials—Bridging Atomic Structure and Device Performance
Session Chairs: Yuanyue Liu and Alessandro Molle
Tuesday Afternoon, December 1, 2020

2:30 PM INTRODUCTION

2:35 PM *S.NM06.04.02
Interlayer Slip and 3D Deformation in 2D Material Electromechanical Systems Arend M. van der Zande; University of Illinois at Urbana Champaign, United States

Due to their unparalleled mechanical strength and high electronic mobility two dimensional (2D) materials represent the ultimate limit in size of both mechanical atomic membranes and molecular electronics. Bringing these capabilities together make 2D materials and heterostructures promising for emerging technologies like origami robotics, stretchable electronics and mechanically reconfigurable nanoelectromechanical systems. Additionally, many of the most interesting properties of 2D materials and new functionality arise from the interfaces between layers and in engineering multilayer heterostructures. Building an understanding of the mechanics of the van der Waals interface is critical to these next generation devices. In this presentation, we will examine the role of the van der Waals interface in determining the mechanics of deformation in atomic membranes under bending, stretching, and shear and the impact on the behavior of 2D electromechanical systems. First, we use aberration-corrected scanning transmission electron microscopy to image multilayer graphene and 2D heterostructures draped over a series of atomically sharp hexagonal boron nitride steps and extract. Combining the measurements with atomistic simulations and energy conservation models we extract the bending stiffness over a range of thicknesses and step heights. We find an bending angle and interface orientation dependent bending stiffness. At high bending angles, the bending stiffness to scale linearly with the number of layers due to free slip between layers. At low angles, materials made from commensurate interfaces become stiffer, converging to the cubic scaling with thickness predicted from continuum mechanics. In contrast, heterostructures with an incommensurate interface maintain the linear scaling at all bending angles due to the low interfacial friction. By tailoring the ordering of layers within the heterostructure, we demonstrate tuning of the bending stiffness. These results provide a united description for bending in 2D materials which resolve several years of contradictory measurements and enable the design of bending stiffness in 2D heterostructures with mixed commensurate and incommensurate interfaces.

Next, we engineer electromechanical drumhead resonators from 2D membranes such as twisted bilayer graphene, commensurate bilayer graphene and graphene/MoS$_2$ bimorphs. In the commensurate bilayer graphene, we observe discrete
jumps in frequency which do not appear in monolayer resonators. We find the magnitude of the frequency jumps follows a simple model for changes in stress due to the dynamics of solitons at the interface. Moreover, we find enhanced structural dissipation in twisted 2D interfaces due to the inelastic sliding between layers. Finally, we examine the evolution of buckle and fold instabilities in 2D membranes and heterostructures under compression, and examine the behavior of stretchable electronics made from crumpled 2D heterostructure devices. Taken together, these experiments show that interfacial slip strongly impacts the mechanics of 2D materials and heterostructures and leads to membranes which are orders of magnitude more deformable than conventional 3D materials.

SESSION S.NM06.21: Live Lightning/Flash VI: Theory and Characterization of 2D Materials—Bridging Atomic Structure and Device Performance
Session Chairs: Yuanyue Liu and Alessandro Molle
Tuesday Afternoon, December 1, 2020
S.NM06

3:00 PM S.NM06.04.03
Structural Damping in Superlubric Twisted Bilayer Graphene Resonators Paolo F. Ferrari, SunPhil Kim and Arend M. van der Zande; University of Illinois at Urbana-Champaign, United States

A major drawback in shrinking down mechanical components to the nanoscale is the excessive dissipation coming from friction at contacting surfaces. A physical regime where this could be substantially avoided is structural superlubricity, wherein an atomically flat and incommensurate van der Waals interface will lead to ultra-low coefficients of friction of <0.001, less than 1% of conventional interfaces. Superlubricity has been experimentally observed via scanning probe measurements of 2D material surfaces, as well as in static sliding of twisted bilayer graphene [1,2] and heterostructure interfaces [3,4]. Moreover, many theoretical studies have predicted and proposed superlubricity in a variety of systems. Yet, nearly three decades after being predicted, superlubric behavior has not been demonstrated in a nanoelectromechanical system, nor has the energy dissipation from superlubric friction ever been directly measured.

In this study, we directly probe the dissipation due to incommensurate interfaces by engineering and comparing mechanical drumhead resonators made from twisted (incommensurate) bilayer, Bernal-stacked (commensurate) bilayer, and monolayer graphene. Because of the ultra-low mass of graphene, the total energy in the resonators is orders of magnitude less than in conventional MEMS systems, making their response extraordinarily sensitive to changes in the energy dissipation. We find that the incommensurate bilayer graphene resonators have damping coefficients more than twice than that of the commensurate counterparts. The extra dissipation in the twisted interface is well described by a structural damping model common in macroscale vibrating components arising from small slips at mechanical joints [5,6]. In the twisted bilayer graphene, the damping arises from inelastic sliding between layers during vibration. From this structural damping model, we extract an upper limit for the interlayer friction stress to be 0.86 mN/m, in good agreement with the reported value obtained in static measurements of interlayer sliding [2]. Additionally, by measuring the mechanical quality factor versus temperature, we observe that friction decreases with decreasing temperature, down to a value < 0.1 mN/m, in agreement with theoretical predictions of a phonon limiting mechanism for superlubric friction. These results unveil the important role of the superlubric interface in mechanical dissipation and provides a principle for designing nanoelectromechanical systems with 2D heterostructures.


3:10 PM S.NM06.04.04
Mechanical Behavior of Strain Engineered Transition Metal Dichalcogenides for Phase Change Transistors Shoieb Ahmed Chowdhury, Ahmad Azizimanesh, Stephen Wu and Hesam Askari; University of Rochester, United States
Switching mechanism in transistors based on transformation of transition metal dichalcogenides (TMD) between semiconducting and semi-metallic phases may offer superior performance by eliminating static and dynamic power consumption problems associated with scaling of conventional field effect transistors. It has been shown recently that the transformation between semi-metallic TMD 1T'-MoTe2 and semiconducting MoTe2 using nanoscale strain engineering results in such switching behavior at device scale. Since strain is the key factor in controlling such electrical properties in these multilayer materials, we use a combination of modelling and experimental approaches to examine and quantify the efficiency of strain transfer in multilayer TMDs and how strain is tied to electrical properties. In this study, molecular dynamics (MD) models are used to predict properties of both monolayer and multilayer structured TMDs under different mechanical loading such as uniaxial, biaxial strain, and nanoindentation. Using the reactive empirical bond order (REBO) potential available in literature along with local structural identification methods such as polyhedral template matching, phase transformation behavior is studied under mechanical loading. Additionally, nanoindentation is used for experimental measurement of properties of different structure types of TMDs (2H and 1T') for verifying, as well as developing, interlayer van der Waals interaction parameters for atomistic models. Results from the atomistic model coupled with experimental observations using optical microscopy and Raman spectroscopy reveals the mechanism of strain transfer at device scale and its efficiency in various setups.

3:20 PM OPEN DISCUSSION

SESSION S.NM06.01: Advanced Characterization of 2D Materials
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

5:00 AM S.NM06.01.02
Atomic Electrostatic Maps of Defect Structures in 2D TMDs Yi Wen1, Colin Ophus2, Christopher S. Allen1,3, Shiang Fang1,4, Efthimios Kaxiras4, Angus I. Kirkland1,2 and Jamie Warner1; 1University of Oxford, United Kingdom; 2National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Laboratory, United States; 3Electron Physical Sciences Imaging Center, Diamond Light Source Ltd., United Kingdom; 4Harvard University, United States

The atomic scale studies on the pristine lattice of TMDs have been carried out with aid from aberration-corrected (scanning) transmission electron microscope (AC-(S)TEM), enabling detailed studies on the evolution of atomic scale defect structures, but their perturbation on local electronic properties, which is essential for understanding their functionality in electronic and optoelectronic devices, are not readily available from direct imaging. Here, we reported the detailed analysis on adatoms, vacancies, line defects, nanopores, nanowires and edge structures in MoS2 and WS2 using 4D STEM, which record not only the scattering information, but also the direct beam, and this allows us to extract phase shift, atomic electric field and charge density map based on the shift of center of mass of direct beam.1 We showed that the electric field map and phase reconstructed imaging are sensitive in detection of abnormal 1D states2 and low atomic number atoms,3 and together provide a comprehensive anatomy on the electronic properties of these defect structures, which is of great importance for the theoretical study of 2D electronic devices.

References

5:10 AM S.NM06.01.03
Atomic Structure and Dynamics of Defects and Grain Boundaries in 2D Pd2Se3 Monolayers Jun Chen and Jamie Warner; Department of Materials, University of Oxford, United Kingdom

We report the distinctive defect structures and electron-driven dynamics of a novel 2D monolayer Pd2Se3 at the atomic level, which is controllably produced from restructuring few-layered PdSe2 by thermal stimulation at an in-situ heating stage in scanning transmission electron microscopy (STEM). A rich variety of point vacancies, one-dimensional defects, grain boundaries (GBs) and defect ring complex, which are distinctly different from those in typical transition metal chalcogenides,
are directly observed on monolayer Pd$_2$Se$_3$. The self-healing point vacancies, gradually consumed edges, and the fast-evolved peculiar defect complex and voids suggest the high mobility of the Se vacancies mobility under electron beam. Multiple unique defects without losing atoms are rendered by the behaviours of special covalent Se−Se dumbbells, which can elastically shift in a staggered way to buffer strains, forming the wave-like one-dimensional defects, and can also undergo Stone-Wales bond rotations which constitute the significant defect behaviour in Pd$_2$Se$_3$. The GBs can flexibly form in a meandering pathway and migrate by a sequence of Se−Se bond rotations without vacancies formation, and in the GB-rich corners and tilt GBs, the other highly symmetric vacancy-involved defects also occur to adapt to orientation turning. This report gives insights into the novel defects in new 2D materials featuring high adaptability, rich diversity and dynamics, which opens up more possibilities for exploiting versatile properties of new 2D material systems.

5:20 AM S.NM06.01.04
Structure/Function of MoS$_2$ Thin Films by Atom Probe Tomography and Beyond Manuel A. Ramos$^1$, Oscar Alberto Lópex Galán$^1$, John Nogan$^2$, Carlos Ornelas$^3$, Abel Hurtado-Macias$^4$, Torben Boll$^4$, Jose L. Enríquez Carrejo$^1$ and Martin Heilmann$^1$; 1Universidad Autonoma de Ciudad Juarez, Mexico; 2Center for Integration of Nanotechnologies, United States; 3Centro de Investigaciones en Materiales Avanzados, Mexico; 4Karlsruhe Institute of Technology, Germany

We present experimental evidence of extensive characterization for MoS$_2$ thin films. Our findings include: in-situ oxidation by induced Raman spectroscopy, scanning electron microscopy and grazing incidence x-ray diffraction and atom probe tomography. Results indicate Results confirm that nanowires plated shape with the 110-orientation are aligned perpendicular film substrate principal reflections at (002), (100), (101), (201), and Raman spectroscopy vibrational modes at E$_{1g}^\text{12}$ at 378 cm$^{-1}$ and A$_{1g}$ at 407 cm$^{-1}$ correspond to 2H-MoS$_2$. APT reveals MoS$^{+2}$, MoS$^{+3}$ as predominant evaporated molecular ions on the sample, indicating no significant diffusion/segregation of Mo or S species within the ITO layer in correlation with STEM measurements. Mechanical properties indicate a harness value of 10 GPa and elastic modulus value of 136 GPa. Finally, some density functional theory calculations reveal honey-comb superlattices can posses ultra-rapid transitions from semiconducting to metallic as reported previously.

5:30 AM S.NM06.01.05
Study of Atomic and Electronic Structures of Black Arsenic Using Analytical Scanning Transmission Electron Microscopy Hwanhui Yun, Supriya Ghosh, Prafful Golani, Steven Koester and K. Andre Mkhoyan; University of Minnesota, United States

Black arsenic (bAs) is a two-dimensional layered material with similar atomic structures to black phosphorus (bP), and it is expected to exhibit attractive properties for future applications such as high carrier mobility, high anisotropy, tunable band structures by varying the number of layers, etc. [1]. Despite the theoretical predictions, it has only recently gained attention due to difficulties in synthesis of high-quality bAs [2]. Recent experimental reports have shown intriguing nature of bAs including high anisotropy [1,3]. Here, we explore the atomic and electronic structures of exfoliated high-quality bAs using high-angle annular dark-field (HAADF)-scanning transmission electron microscopy (STEM) imaging and spectroscopy and demonstrate changes in optical properties in few-layered bAs. Additionally, a stability study on bAs is conducted to gain insight on the key parameters affecting bAs at ambient conditions.

STEM experiments were carried out using an FEI Titan G2 60-300 (S)TEM at 200 keV equipped with energy dispersive X-ray (EDX) and monochromated electron energy-loss spectroscopy (EELS). HAADF-STEM image simulation was carried out using the TEMSIM code based on the Multislice approach [4,5]. Atomic resolution HAADF-STEM images of bulk bAs were obtained from five different orientations including three major crystallographic directions - armchair direction (x-axis), zigzag direction (y-axis), and plan-view direction (z-axis) - confirming anisotropic atomic structures of bAs. Plan-view images were also obtained from few-layered bAs and compared with simulated images that are computed as a function of the number of layers, by which the thickness of the examined layers was measured precisely. The electronic structure of bAs was investigated by using EELS. Low-loss EELS reveals bulk and surface plasma excitation energies and interband transitions, and characteristics of core-loss EELS are described. Low-loss EELS spectra are then acquired as a function of the number of bAs layers and evidence the changes in optical properties in few-layered bAs from bulk bAs. Lastly, degradation of bAs accompanying structure change is analyzed using HAADF-STEM, EDX, and diffraction pattern of specimens. The effect of air, i.e. O$_2$, and water on the degradation is further investigated and discussed.

Acknowledgment
P.G. and S.J.K. were supported by the NSF under Award No. ECCS-1708769.

Two-dimensional (2D) materials and heterostructures are promising systems for soft robotics, deformable electronics, and nanomechanics systems because they combine the high charge carrier mobilities of hard materials with the pliability of soft materials. Understanding their bending properties is crucial for the development of these next-generation devices. However, experimental measurements of bending stiffness in 2D materials have been widely divergent; for example, the reported bending stiffnesses of bilayer and trilayer graphene range from 3.4-160 eV and 7-690 eV, respectively [1-3]. Even less is known about the bending stiffness of 2D heterostructures. Here, we show that electron microscopy can provide a powerful platform for measuring the bending properties of 2D materials. We use aberration-corrected scanning transmission electron microscopy (STEM) to image graphene and 2D heterostructures draped over a series of atomically sharp hexagonal boron nitride steps. This approach enables atomic-resolution studies of their bending conformation, producing insight into both the bending stiffness and mechanisms of bending. In combination with density functional theory (DFT) and continuum mechanics modeling, we derive a unifying model for bending in 2D materials and their heterostructures.

First, we investigated the bending stiffness of single and few-layer graphene [4]. We derive mechanical models that relate the bending stiffness to geometric parameters—such as the radius of curvature, bending angle, and step height—measured directly from STEM images. For monolayer graphene, we obtain bending stiffness values of 1.2-1.7 eV, consistent with DFT predictions [5] and the experimental value of 1.2 eV derived from graphite phonon modes [6]. In multilayer graphene, we find that the bending stiffness varies strongly as a function of bending angle, tuning by almost 400% for trilayer graphene. For ten-layer graphene, we show that the bending stiffness can be as low as 18 eV, three orders of magnitude lower than the bending stiffness predicted by conventional thin-film mechanics. This unusual behavior results from the atomic-scale bending mechanism in 2D multilayers, which is dominated by interlayer shear and slip.

Our findings have profound implications on 2D heterostructures, where we demonstrate that the bending stiffness can be controlled by tailoring the interfacial interactions between vertical homo- and heterointerfaces. We investigated heterostructures and showed that, by simply changing their stacking order, we can dramatically tune their bending stiffnesses. Using a combination of DFT and classical simulations, we produce a model to predict the bending stiffness of arbitrary 2D heterostructures. Together, our results provide a new lower limit of bending stiffness for the fabrication of ultrasoft, high mobility electronics and demonstrate new methods to fabricate 2D heterostructures with tailored bending stiffnesses.

References:
to low friction\textsuperscript{1} and low interlayer electrical transport\textsuperscript{2}. Using our recent nanomanipulation technology\textsuperscript{3}, based on atomic force microscopy, we show that combined electro-mechanical characterization can uniquely address open fundamental questions related to the dielectric interlayer interactions and electronic charge transport through stacking faulted structures\textsuperscript{4}. In addition, we studied experimentally and theoretically the interlayer charge transport in twisted bilayer graphene systems separately for edges and bulk parts. We find that interlayer edge currents are several orders of magnitude larger than in the bulk and therefore govern the transport up until very large critical diameters depending on the potential across the adjacent layers.


**6:05 AM **S.NM06.01.09

\textbf{Collective Manipulation of Gold Nanoclusters on Mono- and Multilayer MoS\textsubscript{2}} Enrico Gnecco\textsuperscript{1}, Felix Trillitzsch\textsuperscript{1}, Alper Özoğul\textsuperscript{1}, Arkadiusz Janas\textsuperscript{2}, Roberto Guerra\textsuperscript{4} and Franciszek Krok\textsuperscript{2}; \textsuperscript{1}Friedrich Schiller University Jena, Germany; \textsuperscript{2}Jagiellonian University, Poland; \textsuperscript{3}University of Milan, Italy

Apart from being a powerful imaging technique, atomic force microscopy allows a talented user to forge nanostructures out of tiny objects (e.g. metal clusters) deposited and manipulated on atomically flat surfaces. This is important for fundamental investigations in nanotribology as well as for building up conductive networks with potential applications in molecular electronics. Due to the length scales involved, the control over the morphology of these structures remains, nevertheless, very problematic. Generally speaking, one has to distinguish between nanomanipulations performed by displacing the nano-objects one by one in a time-consuming way or collectively. In this talk we will focus on the second case and discuss "scan-induced-assembly" experiments on Au nanoclusters on mono- and multilayer MoS\textsubscript{2} aimed to (i) understand if the direction of manipulation can be controlled by a proper choice of the scan pattern, and (ii) using the information so obtained for fabricating structures with a desired morphology, such as long but tiny Au stripes \[1,2\]. While the first goal could be reached with the motion of the clusters precisely related to the angle of attack of the tip on both mono- and multilayers, this is not (yet) the case with the second goal. On MoS\textsubscript{2} monolayers the Au could be indeed rearranged in the form of crumpled stripes with a separation depending on the cluster size and concentration, but the clusters within each stripe remain slightly disconnected, which is possibly due to the roughness of the underlying SiO\textsubscript{2} substrate and/or to charge transfer effects. The presentation is supplemented by molecular dynamics simulations reproducing the displacement of single Au clusters on MoS\textsubscript{2}. Differences with collective manipulation experiments on larger and irregularly shaped Sb islands forming incommensurate contacts with MoS\textsubscript{2} \[3\] will be also discussed.

\[3\] P. Nita, S. Casado, D. Dietzel, A. Schirmeisen, and E. Gnecco, Spinning and translational motion of Sb nanoislands manipulated on MoS\textsubscript{2}, Nanotechnology 24 (2013) 325302

**SESSION S.NM06.02: Excitonic and Optical Properties in 2D Materials**

On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

5:00 AM **S.NM06.02.01

\textbf{Spatial and Temporal Imaging of Exciton Transport in Two-Dimensional Heterostructures} Libai Huang; Purdue University, United States

Charge-transfer (CT) excitons at hetero-interfaces play a critical role in light to electricity conversion using nanostructured materials. However, how CT excitons migrate at these interfaces is poorly understood. Atomically thin and two-dimensional
(2D) nanostructures provide a new platform to create architectures with sharp interfaces for directing interfacial charge transport. Here we investigate the formation and transport of interlayer CT excitons in van der Waals (vdW) heterostructures based on semiconducting transition metal dichalcogenides (TMDCs) employing transient absorption microscopy (TAM) with a temporal resolution of 200 fs and spatial precision of 50 nm.

We have recently imaged the transport of interlayer CT excitons in 2D organic-inorganic vdW heterostructures constructed from WS₂ layers and tetracene thin films. To investigate driving force for exciton dissociation, we perform measurements on heterostructures constructed with different WS₂ thickness ranging from 1 layer to 7 layers. Photoluminescence (PL) measurements confirm the formation of interlayer excitons with a binding energy of ~ 0.3 eV. Electron and hole transfer processes at the interface between monolayer WS₂ and tetracene thin film are very rapid, with time constant of ~ 2 ps and ~ 3 ps, respectively. TAM measurements of exciton transport at these 2D interfaces reveal coexistence of delocalized and localized CT excitons, with diffusion constant of ~ 1 cm²s⁻¹ and ~ 0.04 cm²s⁻¹, respectively. The high mobility of the delocalized CT excitons could be the key factor to overcome large CT exciton binding energy in achieving efficient charge separation.

We have also investigated interlayer exciton dynamics and transport modulated by the moiré potentials in WS₂-WSe₂ heterobilayers in time, space, and momentum domains using transient absorption microscopy combined with first-principles calculations. Experimental results verified the theoretical prediction of energetically favorable K-Q interlayer excitons and unraveled exciton-population dynamics that was controlled by the twist-angle-dependent energy difference between the K-Q and K-K excitons. Spatially- and temporally-resolved exciton-population imaging directly visualizes exciton localization by twist-angle-dependent moiré potentials of ~ 100 meV. Exciton transport deviates significantly from normal diffusion due to the interplay between the moiré potentials and strong many-body interactions, leading to exciton-density- and twist-angle-dependent diffusion length. These results have important implications for designing vdW heterostructures for exciton and spin transport as well as for quantum communication applications.

5:15 AM S.NM06.02.04
Stable Long-Range Diffusion of Photocarriers in 2D MoS₂ Injected by 0D Charge Sources Ilka Krieger1,2, Michele Ghini1, Nicholas Borys3,4, Kehao Zhang5,6, Adam W. Jansons6, Brandon M. Crockett6, Kristopher W. Koskela6, Edward S. Barnard2, Erika Penzo2, James E. Hutchison6, Joshua A. Robinson5,6, Librato Manna1 and P James Schuck3; 1Italian Institute of Technology, Italy; 2Lawrence Berkeley National Laboratory, United States; 3Columbia University, United States; 4Montana State University, United States; 5The Pennsylvania State University, United States; 6University of Oregon, United States

We present stable long-range diffusion of photocarriers in an innovative 0D-2D heterostructure through contactless all solid state photodoping. We implement 0D indium tin oxide nanocrystals (ITO NCs) as light-driven charge injection sources for localized contactless injection of carriers into the underlying monolayer of molybdenum disulfide (2D MoS₂). This technique gives us the opportunity to follow carrier diffusion in the 2D transition metal dichalcogenide without the need of invasive and broad physical contacts. With light beyond the bandgap we locally excite the nanocrystals within a diffraction limited excitation spot, promoting electrons from the valence band to the conduction band of ITO. The photogenerated holes spontaneously transfer to the underlying 2D material with charge injection densities comparable to p-type doping in electronically gated MoS₂ (in the range of 6x10¹²cm⁻²). We collect hyperspectral maps of the 0D-2D hybrid, before and after light-driven charge injection to spatially resolve variations in the emission of the monolayer MoS₂. We observe a blue-shift of more than 35 meV of the photoluminescence peak energy and a significant variation in the relative contribution of excitons and trions to the emission, as a consequence of the annihilation of negatively charged excitons. Remarkably, the injected carriers diffuse tens of microns through the monolayer, covering long distances away from the local micron sized excitation spot. The excited holes accumulate preferably in regions that are initially higher in n-doping and preferentially along edges and grain boundaries, following the initial local electronic landscape of the two-dimensional layer. The comparison between hyperspectral maps collected immediately after the photodoping and after months shows no significant variation in the photoluminescence, indicating that the photodoping process is irreversible and stable up to, at least, 73 days. These works demonstrate a new possibility to remotely and locally dope two-dimensional transition metal dichalcogenides in a contact-less way. The accumulation of carriers in specific regions of the monolayer, as observed by us, might play an important role in unveiling the contributions of structural defects, vacancies and strain to the optical properties of 2D materials and in the same time open novel design principles for future applications in the field of energy storage and contactless light-driven nanoelectronics.

5:25 AM S.NM06.02.06
Correlative Mapping of Photonic Properties in 2D Semiconductor-Based Optoelectronics Timothy Ismael1, Kazi Islam1, Nathan Grinolds1 and Matthew Escarra1; 1Tulane University, United States; 2High Point University, United States

2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
A variety of techniques have proven to be important in characterizing the optical and electronic properties of atomically thin transition metal dichalcogenides (TMDCs). Among these two-dimensional (2D) materials, molybdenum disulfide (MoS2) is considered a good candidate for applications in optoelectronics and photovoltaics. However, predicted device performance is significantly affected by localized defects such as grain boundaries and non-uniformity in large-area films, including regions with varying number of atomic layers. Improvement of techniques for spatially localized investigation of these materials will help accelerate device development from these materials.

In this work, we demonstrate an optical microscope setup capable of transmittance, photoluminescence (PL), and photocurrent spectroscopy with ~1 μm spatial resolution. This spatial-spectral mapping of 2D materials is shown for the visible and near-infrared part of the spectrum. By correlating each of these measurements over the same material and device region, we can draw connections between material properties and device performance. We do this by studying optoelectronic and photovoltaic (PV) devices fabricated on chemical vapor-deposition (CVD) grown MoS2 samples. We concurrently measure the fundamental properties of various excitons, e.g. transmission at the A, B and C peaks, and identify spatial regions of peak photoresponsivity leading to efficient photocurrent generation in MoS2 photodetectors.

Our light source is a supercontinuum laser (Fianium/NKT Photonics) with laser line tunable filter, facilitating wavelength dependent excitation and optical studies of our MoS2. PL mapping of MoS2 flakes and films within the device active area is carried out by exciting single and few-layer thick MoS2 samples with a monochromatic 532 nm excitation; emitted PL is measured using an Ocean Optics QePro spectrometer. Transmittance measurements are carried out with Thorlabs FDS1010-CAL calibrated photodiode mounted 1mm beneath the sample on a transparent stage. Device photocurrent is measured using a Keithley 2450 sourcemeter.

While each technique individually yields insightful information on the uniformity and properties of the 2D material, the integrated setup enables spatial correlation of properties as they relate to the performance of 2D PV, photodetectors, and other optoelectronics. From correlated PL and transmission measurements we extract absorption and photogeneration information that enables mapping localized external radiative efficiency. Transmittance measurements probe wavelength dependent absorption and reflectance and their dependence on local defects, while correlated spatial mapping of absorption and photocurrent vs. wavelength reveals the effects on carrier collection and device performance resulting from material uniformity, contact choice, grain boundaries, surface treatments, and defects. Localized layering of materials is visualized through mapping PL intensity and percentage transmittance. We are using this correlative mapping of photonic properties to better understand, design, model, and prototype advanced optoelectronics from 2D materials.

5:35 AM S.NM06.02.08
Quasiparticle Electronic Structure, Exciton and Optical Absorption of Atomically Thin Blue Phosphorus Ji Zhou, Tian-Yi Cai and Sheng Ju; Soochow University, China

Two-dimensional (2D) van der Waals layered materials have attracted wide interest in condensed matter physics, materials, chemistry and engineering. For allotropes of phosphorus, besides black phosphorus with narrow band gap, a single layered phosphorus with bulked honeycomb structure and wide band gap was studied recently and was called blue phosphorus. Here, by considering many-body effects arising from strong electron-electron and electron-hole interactions in low-dimensional systems, we have studied the electronic and optical properties of 2D blue phosphorus. The intrinsic indirect quasiparticle band gap is 3.76 eV, with a sharp bright and strongly bound exciton located at 2.85 eV, with a binding energy of 0.9 eV. By applying the isotropic strain within 6%, the 1s exciton could be tuned effectively from 2.4 eV to 3.2 eV. In addition, the band topology and winding numbers have been illustrated, explaining the existence of p-like excitons with relatively high oscillator strength. Given recent advances in the successful production of two-dimensional blue phosphorus crystals, we expect them to be profoundly applied in sensor, solar, and lighting technologies.

SESSION S.NM06.03: Chemical and Physical Properties and Applications
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM06

5:00 AM S.NM06.03.02
Electron Transmission Along Circular Arcs in Semiconducting Graphene Nanoribbons Jie Zhang and Eric P. Fahrenthold; University of Texas, United States

The electrical properties of deformed graphene nanoribbons (GNR) are of central interest in the development of high mass
specific conductivity wiring [1], chemiresitive sensors [2], nanoscale strain gauges, and nanoelectromechanical systems. Despite considerable experimental and computational research, understanding of electromechanical coupling effects in GNR is limited. Recent computational research [3] has developed a general description of electron transmission along circular arcs in semiconducting (3M-1) aGNRs. The computational results suggest that: (1) length and total rotation (along a circular arc) are orthogonal generalized coordinates which determine the resistance of a semiconducting nanowire, (2) the ratio of the curved GNR conductance to that of a corresponding flat nanowire is a linear function of the total rotation over a wide operating range, and (3) at low rotations, the current in a curved GNR can exceed that of a corresponding flat nanowire, due to bandgap effects. The computational results have been shown to be consistent with published data obtained from lifting experiments on 5-aGNRs. An analytical conductance model developed from the computational results generalizes the well known exponential decay law for semiconducting nanowires, and may be applied in the design of experiments and new nanoscale devices.


This work was supported by the Office of Naval Research (Grant N00014-16-2357). Computer time support was provided by the Department of Defense High Performance Computing Modernization Program (Project ONRDC40983493) and the Texas Advanced Computing Center (Project G-815029) at the University of Texas at Austin.

5:10 AM S.NM06.03.03
Phase and Quantum Confinement Dependent Structural, Electronic and Magnetic Properties of Layered CrTe2
Yuhang Liu1, Hang Chi2,3, Yunbo Ou2, Mahesh R. Neupane3,4, George D. Coster3, Charles Rong3, Patrick Folkes3 and Jagadeesh Moodera2,2; 1University of California, Riverside, United States; 2Massachusetts Institute of Technology, United States; 3CCDC US Army Research Laboratory, United States

CrTe2 is a novel magnetic layered transition metal dichalcogenide that has been recently synthesized in a metastable 1T bulk form [1]. While promising strain-tunable magnetic ordering has been proposed in 1T monolayers [2], detailed theoretical insights into the phase and layer thickness dependent electronic and magnetic properties are imperative [3]. In this work, we have investigated the effect of phase type and quantum confinement on the structural, electronic, and magnetic properties of CrTe2-based systems using first-principle simulations. In the 1T phase, although the inclusion of spin-orbit coupling (SOC) opens up a gap at the K-point in the Brillouin zone, the relaxed structures appear to be insensitive to quantum confinement and maintain metallic from the bulk towards the monolayer limit. This weak metallic behavior is generally consistent with thickness dependent resistivity measurements in the few-monolayer regime on e.g., exfoliated 1T-CrTe2 flakes as recently reported in the literature [4], as well as on our in-house prepared CrTe2-based thin films. The 1H and 2H phases, on the other hand, typically have finite and thickness-tunable energy gaps. Surprisingly, the 1H-CrTe2 is nonmagnetic with a finite gap of 0.3-0.4 eV with thickness ranging from 1 to 5 layers, which becomes ferromagnetic and metallic at and above six layers. These tunable, anomalous electronic and magnetic properties controlled by the layer thickness and phase make the extended family of chromium tellurides a particularly rich and intriguing platform for further exploration of spintronic and topologically enabled devices.

Building an understanding of the mechanics of the van der Waals interface is critical to these next generation devices. In this heterostructures and leads to membranes which are orders of magnitude more deformable than conventional 3D materials. Taken together, these experiments show that interfacial slip strongly impacts the mechanics of 2D materials and electronics made from crumpled 2D heterostructure devices.

Structural damping in superlubric twisted bilayer graphene resonators have damping coefficients more than twice than that of the commensurate counterparts. The extra dissipation in the twisted interface is well described by a structural damping model.
common in macroscale vibrating components arising from small slips at mechanical joints [5,6]. In the twisted bilayer graphene, the damping arises from inelastic sliding between layers during vibration. From this structural damping model, we extract an upper limit for the interlayer friction stress to be 0.86 mN/m, in good agreement with the reported value obtained in static measurements of interlayer sliding [2]. Additionally, by measuring the mechanical quality factor versus temperature, we observe that friction decreases with decreasing temperature, down to a value < 0.1 mN/m, in agreement with theoretical predictions of a phonon limiting mechanism for superlubric friction. These results unveil the important role of the superlubric interface in mechanical dissipation and provides a principle for designing nanoelectromechanical systems with 2D heterostructures.


5:25 AM S.NM06.04.04
Mechanical Behavior of Strain Engineered Transition Metal Dichalcogenides for Phase Change Transistors Shoieb Ahmed Chowdhury, Ahmad Azizimanesh, Stephen Wu and Hesam Askari; University of Rochester, United States

Switching mechanism in transistors based on transformation of transition metal dichalcogenides (TMD) between semiconducting and semi-metallic phases may offer superior performance by eliminating static and dynamic power consumption problems associated with scaling of conventional field effect transistors. It has been shown recently that the transformation between semi-metallic TMD 1T’-MoTe2 and semiconducting MoTe2 using nanoscale strain engineering results in such switching behavior at device scale. Since strain is the key factor in controlling such electrical properties in these multilayer materials, we use a combination of modelling and experimental approaches to examine and quantify the efficiency of strain transfer in multilayer TMDs and how strain is tied to electrical properties. In this study, molecular dynamics (MD) models are used to predict properties of both monolayer and multilayer structured TMDs under different mechanical loading such as uniaxial, biaxial strain, and nanoindentation. Using the reactive empirical bond order (REBO) potential available in literature along with local structural identification methods such as polyhedral template matching, phase transformation behavior is studied under mechanical loading. Additionally, nanoindentation is used for experimental measurement of properties of different structure types of TMDs (2H and 1T’) for verifying, as well as developing, interlayer van der Waals interaction parameters for atomistic models. Results from the atomistic model coupled with experimental observations using optical microscopy and Raman spectroscopy reveals the mechanism of strain transfer at device scale and its efficiency in various setups.

5:35 AM S.NM06.04.06
Lattice Green’s Function for Atomistic Scale Modeling of Strain Field Due to a Vacancy in a 2D Material Vinod K. Tewary and Edward J. Garboczi; National Institute of Standards and Technology, United States

Modern 2D (two-dimensional) materials such as graphene and beyond are nanoscale materials of strong topical interest. They are recognized as materials with strong potential for diverse industrial applications ranging from quantum to structural material systems. In order to exploit their full potential, it is necessary to develop efficient techniques for their characterization and for atomic-scale understanding of lattice defects in these materials. One lattice defect of primary importance in 2D materials is a monovacancy. It can be treated as a building block of more complicated and extended defects in the materials.

Vacancies and their aggregates, such as antidots and Stonewall defects, play a pivotal role in determining mechanical, thermal, as well as electronic characteristics of 2D materials. One parameter that plays an important role in aggregation and coalescence of vacancies, is the strain field in the material due to the vacancy. Modeling of a monovacancy and its strain field is, therefore, of central interest for 2D materials. Over the last several years, we have developed powerful techniques at NIST for calculation of Green’s functions (GF) for multiscale modeling of different materials and their application to mechanical and thermal problems. A major advantage of a GF based technique is its computational efficiency. Using this technique, we can model large crystallites containing several
million atoms even on a desktop. Modeling large crystallites is especially important for 2D materials because these materials show a significant size effect. It arises because of the logarithmic nature of the response of these materials to a point stimulus. Lattice GF method makes it numerically convenient to account for the size effect. Further, since the GF gives the response of the whole solid at multiscales, it has been shown to seamlessly link the atomistic structure and bulk material performance.

In this talk, we will describe the lattice GF and its application to calculation of the lattice distortion and the strain field in 2D materials. We will present numerical results for silicone, phosphorene and, of course, graphene. Our model crystallite consists of about 2 million atoms. An important input to the GF calculation is the interatomic potential. We have used the functional form of the potentials as available in the literature.

One especially interesting feature of the GF is the possibility of its direct measurement. It has been proposed that the GF is not just a mathematical artefact but a physical entity that can be measured for 2D materials [Tewary et. al., “Green's function modeling of response of two-dimensional materials to point probes for scanning probe microscopy”; Physics Letters A380 (2016) 1750]. If this can be verified, the GF will become a very practical tool for characterization and atomistic scale modeling of 2D materials. This work is another step in that direction.

5:45 AM S.NM06.04.07
Improving the Electrical Performance of MoS2 Transistors Using Tensile Strain
Isha Datye1, Alwin Daus1, Kevin Brenner1,2, Ryan W. Grady1 and Eric Pop1; 1Stanford University, United States; 2Southern Methodist University, United States

Transition metal dichalcogenides (TMDs) such as molybdenum disulfide (MoS2) have gained much interest for scaled nanoelectronics, but their mobilities and drive currents must be improved in order to compete with existing technologies. Theoretical studies predict that tensile strain can increase the mobility of TMDs due to changes in band structure, leading to reduced intervalley scattering [1]. However, such mobility improvement has not yet been experimentally demonstrated. In this work, we utilize uniaxial tensile strain to improve the electrical performance of monolayer (1L) MoS2 transistors on flexible substrates. Using a two-point bending apparatus, we apply multiple strain levels between 0% and ~0.7%, which we estimate from the curvature radius of the bent substrates. We confirm these strain levels by Raman spectroscopy, using the known red-shift of the MoS2 in-plane E’ Raman peak of ~2 cm⁻¹ per percent of tensile strain [2].

We fabricate our devices on polyethylene naphthalate (PEN) flexible substrates. First, the gate metal is lithographically patterned, and then we form the gate dielectric with ~20 nm of Al2O3 by atomic layer deposition (ALD). Monolayer MoS2, grown by chemical vapor deposition (CVD) on separate SiO2/Si substrates [3] is then transferred to the flexible substrates using a polymer scaffold [4]. Finally, we pattern source and drain contacts onto the MoS2 films, followed by an O2 plasma etch to define the channels.

We characterize the effects of tensile strain on MoS2 transistors with channel lengths from 1 to 15 μm, by extracting the field-effect mobility. Relatively long channels are used to limit extrinsic contributions of contact resistance. We obtain a continuous mobility improvement up to ~85% with increasing tensile strain up to ~0.7%, leading to a drain current I_D increase of ~2x at the same carrier density. Furthermore, we find that the effects are fully reversible as the device characteristics return to their initial state after strain release. The mobility increase with tensile strain also indicates that these devices could be used as strain sensors. An I_D change of ~2x at 0.7% strain corresponds to a gauge factor of nearly ~150, which is the highest value reported so far for piezoresistive 1L CVD MoS2 strain sensors [5-6].

These results demonstrate the largest mobility and on-state current improvements to MoS2 transistors using strain to date, revealing that strain engineering is a promising way to tune the electrical performance of TMD-based devices. Furthermore, using MoS2 transistors as strain sensors can facilitate the realization of flexible and transparent sensor systems for strain mapping.

Keynote: Interfacial Engineering of Chemically Reactive Two-Dimensional Materials  
Mark C. Hersam; Northwestern University, United States

Following the success of ambient-stable two-dimensional (2D) materials such as graphene, hexagonal boron nitride, and transition metal dichalcogenides, new classes of chemically reactive layered solids are being explored since their unique properties hold promise for improved device performance [1] and quantum phenomena [2]. For example, chemically reactive 2D semiconductors (e.g., black phosphorus (BP) and indium selenide (InSe)) have shown enhanced field-effect mobilities and optoelectronic properties under controlled conditions that minimize ambient degradation [3,4]. In addition, 2D boron (i.e., borophene) is an anisotropic metal with a diverse range of theoretically predicted phenomena including confined plasmons, charge density waves, and superconductivity [5], although its high chemical reactivity has limited experimental studies to inert ultrahigh vacuum conditions [6-9]. Therefore, to fully study and exploit the vast majority of 2D materials, methods for mitigating or exploiting their relatively high chemical reactivity are required [10]. In particular, covalent organic functionalization of BP minimizes ambient degradation, provides charge transfer doping, and enhances field-effect mobility [11], while noncovalent organic functionalization of borophene leads to the spontaneous formation of electronically abrupt lateral borophene-organic heterostructures [12]. On the other hand, sequential deposition of atomic carbon and boron on silver substrates results in rotationally commensurate vertical borophene-graphene heterostructures where the graphene adlayer provides robust encapsulation for the underlying borophene [13]. By combining organic and inorganic encapsulation strategies, even highly chemically reactive 2D materials (e.g., InSe and CrI3) can be studied and utilized in ambient conditions [14].

potential energy surfaces spanned by the imaginary mode eigenvectors to estimate the barrier associated with the transition and to track the route to the CDW phase. By treating these structures all at the same high level of theory, we can try to explain why specific phases undergo CDW transition and what the driving force is.

Our results successfully show that though TiTe$_2$ bulk has no lattice instability, its monolayer has an instability similar to but much weaker than that present in TiSe$_2$, highlighting the origin of a very weak coupling CDW. The semimetallic overlap in the electronic band structure of TiTe$_2$ monolayer is only 0.2 eV smaller than that in the bulk supporting the idea that narrow band overlaps thermodynamically drive the CDW distortion. This is the first attempt to perform a complete study of ab-initio electronic and lattice dynamics calculations of the two compounds within the same level of theory. The presence of phonon instability only in the structures that undergo CDW transition shows that the CDW distortion in these compounds is brought about by a lattice instability, and the semimetallic overlap is the key factor that determines how favoured the transition is. These results could have impact in prediction and understanding of CDW instabilities in other systems, particularly the methodology of following imaginary modes to track the transitions between phases.

4P. Chen et al., Nat. Commun., 2015, 6, 8943.

5:10 AM S.NM06.06.05
Lattice Dynamics of Moire Pattern Graphene Ben Xu$^1$, Nan Feng$^1$, Ce-Wen Nan$^1$, Dong Zhang$^2$ and Kai Chang$^2$; $^1$Tsinghua University, China; $^2$Institute for Semiconductors, Chinese Academy of Science, China

Recent experiments found signatures of superconductivity in 'magic angle' twisted bilayer graphene and ABC-trilayer graphene/ hexagonal boron nitride moiré superlattice. Several theoretical works point that the electron-phonon coupling is strong enough to introduce this superconducting phenomenon. In our presentation, phonon spectrum and corresponding phonon modes will be demonstrated by molecular dynamics simulation. These illustrations will help the understanding the interaction between electron and phonon in these multi-layered materials.

5:00 AM S.NM06.07.02
Accurate Molecular Models for MoS$_2$ and Battery Oxides (NMC) to Predict Interfacial Properties up to the Large Nanometer Scale Juan Liu and Hendrik Heinz; University of Colorado Boulder, United States

We introduce reliable force fields and applications to electrolyte and organic interfaces for molybdenum sulfide and battery oxides, including lithium cobalt oxide as well as nickel and manganese substituted lithium cobalt oxides. Such models, except for MoS$_2$, have not been available and are necessary to understand the dynamics and charge transport properties up to the large nanometer scale. Specifically, the parameters for MoS$_2$ reliably account for structural, interfacial, and mechanical properties and are compatible with many force fields for molecular simulations (Interface force field, CVFF, PCFF, CHARMM, AMBER, OPLS-AA, TEAM). We reproduce chemical bonding, X-ray structure, cleavage energy, infrared spectrum, bulk modulus, Young’s modulus, and interfacial properties with polar and nonpolar solvents within 0.1% to 5% deviation from measurements. Compared to prior models, structural and mechanical instabilities of the nanoscale layers were eliminated, and large deviations in computed interfacial properties (>50%) were reduced to quantitative agreement with experiment (<5%). Computed contact angles of water and diiodomethane agree within ±2° with experimental measurements on freshly cleaved MoS$_2$ surfaces. Similarly, new force field parameters for lithium cobalt oxide as well as Co-Ni-Mn mixed oxide phases are shared that reproduce lattice constants, surface energies, contact angles, and mechanical properties in excellent agreement with experiment. The models can be used as part of multiple force fields (IFF, CHARMM, AMBER, OPLS-AA, PCFF, TEAM) for accurate predictions of fully dynamic, large scale interfacial properties and local analysis by quantum mechanics.
The parameters rely on quantitative representation of chemical bonding using atomic charges, using methods that reach much higher accuracy than DFT calculations, bonded parameters from experimental data, and a consistent interpretation of Lennard-Jones parameters that lead to wide compatibility for multiphase materials. All parameters are supported by a physical chemical interpretation. As an example, we discuss the binding mechanism and adsorption energies of peptides on the MoS₂ basal plane using strongly binding and weakly binding sequences derived from phage display. Adsorption is driven by direct surface contact and replacement of surface-bound water molecules, with very widely tunable adsorption energies between -86 and -6 kcal/mol. Weak electrostatic interactions of backbone and side chains with the surface, hydrogen bonds between electrolyte-facing side groups and water, and contributions by hydrophobic groups play a key role to tune the interaction strength.

The models can be applied to any biomaterials and nanomaterials including these 2D compounds, including embedding in electrolytes, polymer matrices, understanding of charge transport, local defects and changes in stoichiometry. The accuracy is comparable to DFT methods at millionfold larger time and length scales, and extensions are feasible for reactive simulations (IFF-R). The models for battery oxides can help overcome problems in designing materials with a higher storage capacity.

5:10 AM *S.NM06.07.03
Molecule Functionalization and Intercalation in 2D Materials Judy Cha; Yale University, United States

Owing to the large surface area and layered nature, the electrical and catalytic properties of 2D materials can be tuned greatly by surface functionalization with tailored molecules with specific redox potentials and intercalation of various intercalants. The utility of surface functionalization and intercalation has been amply demonstrated in 2D transition metal dichalcogenides (TMDCs), including the modulation of carrier densities in monolayer MoS₂ field-effect transistors (FETs) and the enhancement of catalytic activities of hydrogen evolution reaction in Li⁺-intercalated WS₂. However, fundamental mechanistic understandings that govern molecule-TMDC interactions or intercalation-induced structural and electrical phase transformations remain basic.

In this talk, I will present our approach to elucidate the underlying mechanisms that govern surface functionalization and intercalation in 2D TMDCs, using MoS₂ as a material choice. For surface functionalization, we compare doping powers of a family of organic electron donors (OEDs) on MoS₂ to understand the OED-MoS₂ interactions. This requires accurate knowledge of surface coverage of OEDs, change in the carrier density after functionalization, and the nature of the OED bonding to MoS₂. For intercalation, we electrochemically intercalate Li⁺ ions into individual monolayer or heterostructure FETs and follow the change in crystal structure and electrical properties of the host 2D systems as a function of intercalation.

We uncover a host of interesting phenomena, such as the role of a hBN/MoS₂ interface on intercalation kinetics and physics, phase transformation in WSe₂ by intercalation, and competition between intercalation kinetics and thermodynamics in MoS₂/graphene heterostructures. A central theme of our approach to understanding surface functionalization and intercalation is the integration of device physics with electrochemistry.

5:25 AM S.NM06.07.04
Effect of Structural Disorder and Nitrogen Doping on the Li Storage Capacity of Graphene Nanomaterials—A First-Principles Study Yu-Jen Tsai and Chin-Lung Kuo; National Taiwan University, Taiwan

We employed first-principles calculations based on density functional theory to investigate the effect of structural disorder and nitrogen doping on the Li storage capacity of graphene nanomaterials as the anodes of Li-ion batteries. Our calculated results first revealed that the Li storage capacity of monolayer graphene does not necessarily increase with the number of carbon vacancy created but highly depends on the local geometry of the defect sites. The achievable Li capacity limit per vacancy contributed was found to decrease from four to one as the monovacancy grows into a hexavacancy complex, which implies that the coalescence of vacancy defects may tend to lower down the Li storage capacity of monolayer graphene. Our electronic structure analysis further revealed that the enhanced Li storage capacity by the carbon vacancy is mainly attributed to the increased amount of density of states lying just above the Fermi level, which can be much more increased by the local structural disorder around the vacancy sites. Moreover, our calculations also showed that the Li storage capacity of monolayer graphene can be effectively enhanced by the local ring disorder such as the Stone-Wales defect without the
presence of any carbon vacancy, which appeared to increase proportionally to the number of the Stone-Wales defect on the basal plane. Our calculations further demonstrated that the amorphous graphene structure can possess a relatively high Li storage capacity primarily owing to the presence of many non-hexagonal ring defects therein. These topological disorders were found to create many electron-deficient regions on the basal plane, which can effectively induce p-type doping on graphene to accommodate more electrons from Li, thereby greatly enhancing the Li storage capacity of the graphene-based nanomaterials. On the other hand, our calculated results also indicate that nitrogen-doping can effectively reduce the vacancy formation energy in graphene, thereby increasing the amount of carbon vacancy to enhance the Li storage capacity. Moreover, the migration energy barriers of vacancy defects were found to increase by nitrogen-doping, which can thus suppress the Li capacity loss induced by the coalescence of vacancy defects in graphene. Nevertheless, our calculations also indicated that it is energetically favorable for nitrogen dopants to aggregate on the vacancy sites, which can thus result in significant irreversible capacity loss of Li because of its extremely high adsorption energy on the vacancy site. Our theoretical findings suggest that the concentration of nitrogen-doping should be carefully controlled in order to obtain optimal Li storage capacity of graphene-based materials.

5:35 AM S.NM06.07.05
Dimensionality-Dependent Electrochemical Kinetics at the Single-Layer Graphene–Electrolyte Interface Prab Bandaru1, Hidenori Yamada1 and Rajaram Narayanan1,2; 1University of California, San Diego, United States; 2Applied Materials, Inc., United States

The theories to describe the rate at which electrochemical reactions proceed, to date, do not consider explicitly the dimensionality or the discreteness and occupancy of the energy levels of the electrodes. We show experimentally that such quantum mechanical aspects are important for dimensionally confined nanostructured materials and yield unusual variation of the kinetic rate constants with applied voltage in single-layer graphene. The observed divergence from conventional electrokinetics was ascribed to the linear energy dispersion as well as a nonzero density of states at the Dirac point in the graphene. The obtained results justify the use of density of states-based rate constants and considerably add to Marcus–Hush–Chidsey kinetics. The talk includes theoretical, computational, and experimental results.

5:45 AM *S.NM06.07.06
Influence of Atomic Vacancies on Catalytic and Transport Properties of 2D Transition Metal Dichalcogenides Manish Chhowalla; University of Cambridge, United Kingdom

Single atom chalcogen vacancies are common in chemical vapor deposited monolayer transition metal dichalcogenides (TMDs). In some ways, the properties of two dimensional TMDs appear to be not influenced by the presence of up to 1-3% vacancies in the monolayers. That is, it is possible to achieve gate modulation and mobilities of tens of cm²-V⁻¹-s⁻¹ at room temperature in field effect transistors (FETs) with single layer TMD channels. Here, we describe the evolution of photoluminescence and FET characteristics as a function of single atom vacancy defects concentration. We find that the monolayer TMDs are defect tolerant – capable of preserving their properties up to defect concentration of ~ 10¹⁴ cm⁻². We also measure the catalytic properties of monolayer TMDs and find that the overall activity increases with number of atomic vacancies – with the best performance (lowest overpotential and highest turnover frequency for the reaction) occurring at a concentration where semiconductor to metal transition occurs. I will describe how our results provide new insights into the defect tolerance of 2D TMDs and how atomic structure engineering can be used to tune their properties.

6:00 AM S.NM06.07.09
Ambient Stable Phosphorenes and Covalently Linked Phosphorene-MoX2 (X = S or Se) Nanocomposites with Enhanced H₂ Evolution Activity Pratap Vishnoi1,2 and C. N. R. Rao1; 1Jawaharlal Nehru Centre for Advanced Scientific Research, India; 2University of California Santa Barbara, United States

The phosphorene is a 2D puckered sheet composed of sp³ phosphorus with each P atom is covalently bonded to three P atoms in the plane. The phosphorus atoms contain lone-pair electrons. It exhibits high charge carrier mobility as well as a thickness tuneable band-gap in the 0.3-2.0 eV range.[1] The conduction band minimum of phosphorene is appropriately positioned to effectively catalyze the H₂ evolution reaction by water splitting. Besides, phosphorus is an earth-abundant and environmentally benign non-metal element. Therefore, it is of great interest to exploit the potential of phosphorene as a metal-free photocatalyst for H₂ evolution. However, pristine phosphorene is ambient instable and it produces trace amounts of H₂ by water splitting.[2,3]

The advantage of the lone-pair electrons is that they can be utilized for chemical functionalization of phosphorene without
significantly affecting its intrinsic properties. In this work, we present synthesis of ambient stable η–ν adducts of phosphorene, covalently cross-linked phosphorene-MoX$_2$ (X = S or Se) nanocomposites, and their HER activity. The phosphorenes functionalized with InCl$_3$ and B(C$_6$F$_5$)$_3$ as well as ylide with a benzyl group are ambient stable and disperse well in aqueous medium.[3] Their photocatalytic HER activity is enhanced significantly exhibiting H$_2$ yields of 6.6 mmol h$^{-1}$g$^{-1}$ in the case of phosphorene-B(C$_6$F$_5$)$_3$ (hydrogen yields for pristine phosphorene is 0.6 mmol h$^{-1}$g$^{-1}$). Phosphorene-MoX$_2$ nanocomposites are synthesized by forming amide as the cross-linkages.[4] Due to improved charge-transfer and suppressed charge recombination rate, phosphorene-MoS$_2$ exhibits excellent photochemical HER activity with H$_2$ yields of 26.8 mmol h$^{-1}$g$^{-1}$, while only a negligible amount is produced by their physical mixture. The phosphorene-MoS$_2$ composite shows high electrochemical HER activity with an onset overpotential of 110 mV, closer to that of Pt/C catalyst. The onset overpotential of a 1:1 physical mixture of phosphorene and MoS$_2$ is 450 mV. The enhanced HER activity of phosphorene-MoS$_2$ nanocomposite can be attributed to the ordered cross-linking of the 2D sheets, leading to increased interfacial area as well as the charge-transfer interaction between phosphorene and MoS$_2$ layers.


SESSION S.NM06.08: Design and Synthesis of Functional 2D Materials

On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

S-NM06

5:00 AM *S.NM06.08.01
Revealing the Full Spectrum Layered Materials with Super-Human Predictive Abilities Gowoon Cheon and Evan J. Reed; Stanford University, United States

We have utilized data mining approaches to elucidate over 1000 2D materials and several hundred 3D materials consisting of van der Waals bonded 1D subcomponents, or molecular wires. We find that hundreds of these 2D materials have the potential to exhibit observable piezoelectric effects, representing a new class of piezoelectrics. A further class of layered materials consists of naturally occurring vertical hetero structures, i.e. bulk crystals that consist of stacks of chemically dissimilar van der Waals bonded layers like a 2-D super lattice. We further combine this data set with physics-based machine learning to discover the chemical composition of an additional 1000 materials that are likely to exhibit layered and two-dimensional phases but have yet to be synthesized. This includes two materials our calculations indicate can exist in distinct structures with different band gaps, expanding the short list of two-dimensional phase change materials. We find our model performs five times better than practitioners in the field at identifying layered materials and is comparable or better than professional solid-state chemists. Finally, we find that semi-supervised learning can offer benefits for materials design where labels for some of the materials are unknown.

5:15 AM *S.NM06.08.03
Water-Based and Biocompatible 2D Inks for Printed Electronics Cinzia Casiraghi; University of Manchester, United Kingdom

Solution processing of graphene [1] allows simple and low-cost techniques such as inkjet printing [2, 3] to be used for fabrication of heterostructures of arbitrary complexity. However, the success of this technology is determined by the nature and quality of the inks used.

In this work we show a general formulation engineering approach to achieve highly concentrated, and inkjet printable water-based 2D crystal formulations, which also provide optimal film formation for heterostructure fabrication [4]. Examples of all-inkjet printed devices, such as large area arrays of photosensors on plastic [4], programmable logic memory devices [4], strain sensors on paper [5], capacitors [6] and transistors [7] will be discussed. In addition, our approach allows easy production of defects-free and biocompatible graphene flakes with positive or negative charge [4,8-10], which can find use in biomedical applications.
Low Temperature NbS2/NbS3 Heterostructure Fabrication by Atomic Layer Deposition

Saravana Balaji Basuvalingam,
Yue Zhang, Matthew Bloodgood, Jan P. Hofmann, Marcel Verheijen, Erwin Kessels and Ageeth A. Bol; Eindhoven University of Technology, Netherlands

Two-dimensional transition metal dichalcogenides (TMDCs) such as MoS2 and WS2, among others, have gained a lot of attention due to their phase and thickness dependent electrical and optical properties. There is also another class of two-dimensional materials involving similar elements as in TMDCs, which are known as transition metal trichalcogenides (TMTCs). Contrary to TMDCs, TMTCs are quasi-1D materials, which gives added benefits for applications as they have strong anisotropy in both electrical and optical properties. Among the various transition metal chalcogenides systems, some TMDCs exhibits metallic properties, while their TMTCs counterparts exhibits semiconducting properties (or vice versa). An example are Nb based sulfides: NbS2 is metallic, whereas NbS3 is semiconducting.

Lately, the prospects of combining metal-semiconductor transition metal chalcogenides to form heterostructures have gained momentum for future applications in opto-electronics. However, there are many challenges associated with the current heterostructure synthesis processes, such as process scalability, control over the thickness of the individual layers and high processing temperatures. Atomic layer deposition (ALD) can address most of the aforementioned challenges as it offers uniformity over large area substrates, precise thickness control, and low-temperature processing.

In this work, we focus on fabricating metallic NbS2, semiconducting NbS3 heterostructures by ALD. NbS2 and NbS3 thin films were synthesized with control over the phase by plasma-enhanced atomic layer deposition (PE-ALD) using a metalorganic precursor and H2S (+H2) plasma at low temperatures (200 – 450 °C). The phase-control between NbS2 and NbS3 was achieved by two methods, first by varying the temperature (which we have also shown for TiS2/TiS3). Second, by careful optimization of H2S:H2 gas mixture ratio in the plasma co-reactant while maintaining a constant deposition temperature. For demonstrating this, the deposition temperature was maintained at 300 °C. The H2S:H2 ratio was varied from 1:0 to 0:1 while maintaining a constant total flow. A high H2S gas fraction led to the synthesis of NbS3, otherwise, NbS2 was deposited. It was observed with optical emission spectroscopy that the increased H species in the plasma mixture could act as an S reducing agent and cause NbS2 growth at low temperatures. We used this phase-controlled growth of NbS2 on NbS3 (or vice versa) by modulating the H2S:H2 ratio as a function of ALD cycles to form NbS2/NbS3 heterostructures. The formation of heterostructures was confirmed by high-resolution transmission electron microscopy (TEM) along with electron diffraction. Our experiments demonstrate that ALD enables the controlled synthesis of both TMDCs and TMTCs, while also enabling metal-semiconductor heterostructure formation at low temperatures over large scale substrates. This opens up new avenues to include both TMDCs and TMTCs in nano- or optoelectronic applications.

Transition from 3D to 2D and Fractal to Compact Domains of CVD Grown MoSe2

Sayema Chowdhury, Anupam Roy and Sanjay K. Banerjee; University of Texas at Austin, United States

Atomically thin two-dimensional transition metal dichalcogenides (TMDs) have been extensively researched in recent years...
due to their unique thickness dependent optical and electronic properties, showing remarkable applications in FETs, digital logic circuits, memory devices, photovoltaics, sensors, flexible devices etc. The selenides are garnering a greater interest particularly for the applications in optoelectronics owing to a narrower bandgap and higher optical absorbance compared to sulfides [1]. Although mechanically exfoliated monolayer TMDs are widely used for different proof-of-concept experiments, scaling up the production of large area uniform TMDs to an industrial level still requires an optimized growth method. Several bottom up synthesis processes such as molecular beam epitaxy (MBE) [2] and chemical vapor deposition (CVD) [3] have already been reported in literature, but while the low grain sizes in MBE grown TMDs limits device performances [4], CVD comes with its own challenges e.g., poor control over thickness, low repeatability of growth results etc. In order to achieve large area repeatable growth of TMDs with precise thickness control, a detailed understanding of the role of different parameters influencing the growth dynamics is of utmost importance.

In this work we demonstrate atmospheric pressure CVD (APCVD) growth of MoSe2 on Si/SiO2 substrates, and investigate the effect of growth temperature and metal/chalcogen flux. We observe that the growth temperature strongly influences the morphology of the domains and the compact triangular or hexagonal domains ramify into fractals as the growth temperature is decreased. We also observe that higher substrate temperature helps reduce the formation of grain boundaries, which hinder carrier mobilities and introduce defects in the crystal domains by suppressing the nucleation density. The effect of chalcogen environment is studied where growth in a Se-rich environment helps restrict Mo-rich nuclei formation promoting lateral growth. Raman and Photoluminescence (PL) spectroscopy confirms the formation of crystalline monolayer MoSe2. For the growth in Se-deficient environment, several multilayer islands are seen to form on the domains, showing vertical growth of multilayer MoSe2 which can be attributed to insufficient Se-passivation. Atomic force microscopy (AFM) study confirms the lateral (monolayer) versus vertical growth under Se-rich and Se-deficient conditions, respectively. XPS analysis show a near perfect stoichiometry (Mo:Se=1:1.97) of MoSe2 under Se-rich growth environment, whereas in the Se-deficient condition a ratio of Mo:Se=1:1.77 is observed indicating a deviation from the stoichiometric MoSe2. This also supports our claim of forming metal rich nuclei (Mo1+xSe2-x) under Se-deficient condition leading to 3D island formation. This work offers a deeper understanding of the effects of several important growth parameters and proposes an optimized growth window for synthesizing large area 2D TMD compounds.

This work was supported in part by the Army Research Office (ARO) Grant # W911NF-17-1-0312 (MURI) and NSF NNCI (done at the Texas Nanofabrication Facility at the University of Texas at Austin supported by NSF grant NNCI-1542159).


5:50 AM *S.NM06.08.06
Engineering Atomic Structures of MoS2 for Neuromorphic Applications Zhi Gen Yu1, Shuai Chen1, Hangbo Zhou1, Lin Wang2, Xuewei Feng2, Yongqing Cai1, Xiangjun Liu4, Gang Zhang1, Kah Wee Ang2,2 and Yong-Wei Zhang1,1 Institute of High Performance Computing, Singapore; 2National University of Singapore, Singapore; 3University of Macau, China; 4Donghua University, China

Two-dimensional (2D) semiconducting materials, such as MoS2, WS2, phosphorene, etc., hold great potential for many important applications, such as in nanoelectronics, molecular and bio-sensors, thermoelectric conversion and solar energy harvesting. It is well recognized that structures and defects of these 2D materials play an important role in dictating the electronic, optical, magnetic and thermal properties. To fully explore the functionalities and potentials of 2D materials, their structure and defect engineering is often required, which can greatly widen their applications.

Neuromorphic computing, which mimics the biological neural architectures, is promising to address some of the challenges facing von Neumann computing system, such as energy efficiency, computational power, and robust learning. 2D materials are promising materials for use in such new computational paradigm.

In this talk, we report our work on the development of multi-terminal MoS2-based memtransistor for neuromorphic computing. By combining first-principles calculations and theoretical modelling, we investigate the structures and energetics of intrinsic point defects in MoS2, their evolution and reaction under thermal and electric fields, and their effects on the changes in electrical properties, such as electrical conductivity and Schottky barrier. We further examine the origin of synaptic behavior in the MoS2-based multi-terminal memtransistor and the performance of such memtransistors, such as, long-term potentiation, long-term depreciation, etc. We also report our realization of an aerosol jet printed Ag/MoS2/Ag
memristor capable of storing and processing data on flexible substrates. This memresistor is realized in a cross bar structure by developing a scalable and low-temperature printing technique utilizing a functional MoS2 ink platform. Interestingly, the MoS2 memresistor exhibits both volatile and nonvolatile resistive switching behavior. By using first-principles calculations and kinetic Monte Carlo simulations, we further examine the role of defects and structures in the functionalities and performance of the memresistor.

Our studies here show that these nanodevices are capable of efficiently mimicking many interesting behaviors of biological synapses, demonstrating their potential to enable energy efficient artificial neuromorphic computing.

6:05 AM S.NM06.08.08
Exploring Strain-Stabilization of the Conducting 1T Phase in Pulsed Laser Deposited MoS2 Thin Film on Different Single Crystal Substrates Swati Parmar1,2, Suresh Gosavi1 and Satishchandra Ogale; 1Savitribai Phule Pune University, India; 2Indian Institute of Science Education and Research, India

The metallic 1T phase of MoS2 has excellent electrical conductivity but it is thermodynamically unstable. Hence there is great interest in realization and stabilization of this phase in different forms such as nanomaterials and thin films for various device applications. The thin film platform affords the element of substrate-induced strain as a tunable parameter that can control the phase equilibria. In the work reported here, we therefore examine the possibility of stabilizing the desirable 1T phase of MoS2 in the case of thin films grown by pulsed laser deposition (PLD) on different crystalline substrates, namely c-Al2O3 (0001), LaAlO3 (001), SrLaAlO4 (001), SrTiO3 (001) and MgO (001). The percent (%) lattice parameter mismatch between the most favorable growth planes of MoS2 and these different substrates varies from 5% to 16%. c-Al2O3, LaAlO3, SrLaAlO4 are noted to induce tensile strain whereas SrTiO3 and MgO cause compressive strain in MoS2 thin film. Interestingly, Raman and X-ray Photoelectron spectroscopy reveal much enhanced and stable 1T phase contribution in MoS2 thin films grown on SrTiO3 and SrLaAlO4 substrates. The X-ray diffraction, X-ray reflectivity, and atomic force microscopy data reveal high crystalline quality of MoS2 thin films. The most enhanced 1T phase film of MoS2 is noted in the case of the film grown on SrLaAlO4, which also shows a reduction in room temperature resistivity and semi-metal behavior. The valence band spectroscopy (VBS) data for this case are also consistent with the expected metal-like nature of the 1T phase MoS2 thin film. Furthermore, while increasing the thickness, structural transition from mixed 1T/2H phase to pure 2H hexagonal phase is observed; a consequence of strain relaxation, which clearly establishes the role of substrate-induced strain in 1T phase stabilization via octahedral rotation. This study will pave the way for making the vast family of transition-metal chalcogenides tetragonal phase thin films and brings out the potential of 1T phase thin film for unfolding phenomenon and technological applications.

References:

6:15 AM S.NM06.08.09
Pulsed Laser Deposition of Two-Dimensional Materials Denys Miakota1, Huu Phuoc Le1, Yu-Chuan Lin2, Raymond R. Unocic2, Fabian Bertoldo1, Kristian Thygesen1, Alexander Puretzky2, Ilia N Ivanov2, Jorgen Schou1, David B. Geohegan2 and Stela Canulescu1; 1Technical University of Denmark, Denmark; 2Oak Ridge National Laboratory, United States

Two-dimensional of transition metal dichalcogenides (2D-TMDCs) stand out from the class of 2D materials due to their appealing properties, including atomic-scale thickness, direct band gap and strong spin-orbit coupling. The precise control of the atomic layer structure can pave new avenues for the integration of TMDCs in future optoelectronic devices, such as light-emitting diodes and van der Waals photovoltaics. In this paper, we present our recent progress on the growth of 2D-TMDCs including MoS2, WS2, MoSe2 and their alloys, by a bottom-up approach, namely Pulsed Laser Deposition (PLD). PLD is a well-established technique for the growth of functional oxide structures1 and superlattices2. It relies on vapor-phase transfer of a material from a target to substrate3. Furthermore, this catalyst-free approach has recently been used for the growth of layered TMDCs4. Nevertheless, the optoelectronic properties of 2D-TMDCs, particularly photoluminescence (PL) emission, are often poor. A good control of the chalcogenide vacancies at the monolayer limit is important to realize the full potential of 2D materials and their heterostructures in devices. In this paper we will discuss the PLD-synthesis of large area, crystalline 2D-TMDCs on sapphire and SiO2/Si. PLD synthesis
at high temperature (~600°C and above) using this one-step approach results in the formation of continuous monolayers with
grain boundaries, as compared to the triangular-shaped structures, specific to the chemical vapor deposition process. We
profile the vacancy concentration in MoS$_2$ monolayer on an atomic scale using annular-dark-field electron microscopy, with
an absolute detection sensitivity of one to two sulfur vacancies. A rich variety of defects, including single and double sulfur
vacancies, anti-site defects, as well as grain boundaries with periodic rings 8-4-4- rings defects are revealed. Room
temperature PL spectra of MoS$_2$ monolayer exhibit two-distinct exciton peaks that can be used to qualitatively assess the as-
grown monolayers. Finally, we will discuss the PLD growth of 2D materials using chalcogen-enriched targets as a path
towards defect engineering of 2D materials.


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**SESSION S.NM06.09: Emerging 2D Materials and Devices**

**On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020**

*S-NM06*

**5:00 AM S.NM06.09.02**

**Encapsulation and Transfer Schemes for Epitaxial Xenes** [Deepyanti Taneja]¹, Gabriele Farone², Md. Hasibul Alam¹, Christian Martella², Carlo Grazianetti², Emiliano Bonera¹, Alessandro Molle² and Deji Akinwande¹; ¹The University of Texas at Austin, United States; ²CNR IMM, Unit of Agrate Brianza, Italy; ³Università degli Studi di Milano-Bicocca, Italy

Epitaxial Xenes are an emerging class of two-dimensional crystals made of elements spanning group III to group VI of the periodic table (e.g. borophene, silicene, phosphorene, antimomene, tellurene etc) [1]. These materials are synthesized by epitaxy on various substrates and are subject to degradation in environmental conditions. Our work is centered around Xenes grown on noble metal surfaces that are supported by mica, as they can readily undergo delamination and transfer on other substrates for device related studies. In particular, we focus on silicene-on-silver [2] and epitaxial phosphorene [3] as representative cases to establish a stabilization and transfer scheme. Encapsulation of the unstable Xenes is a critical step for achieving transfer of the Xene layer from its pristine growth substrate to a device or functional substrate. We propose the use of an Al$_2$O$_3$encapsulation as a stabilization strategy that can be universally applied to the whole class of Xenes. The integrity of the Xene layer after encapsulation is validated by means of Raman spectroscopy and X-ray photoelectron spectroscopy. We then propose a few different transfer schemes and present experimental results of film transfer. A technical step in the delamination and transfer process is the time-controlled etching of the metal substrate. We achieve this using an optimized KI/I$_2$silver etchant with a controllable etch rate. Finally, we demonstrate the stability of air-exposed multilayer silicene, prepared using our developed methods, via Raman spectroscopy, validating our successive delamination and transfer protocol.

References:

**5:10 AM S.NM06.09.03**

**Optical Properties of Group-14 Xenes on Al$_2$O$_3$(0001)** [Carlo Grazianetti]¹, Christian Martella¹, Stefano Lupi² and Alessandro Molle¹; ¹CNR-IMM, Italy; ²CNR-IOM, Italy

The class of two-dimensional (2D) graphene-like lattices made of atoms out of carbon, collectively known as Xenes, today
Two-dimensional layered materials have received much interest in recent years due to their ease of miniaturization by mechanical exfoliation along with strong light-matter interactions and tunable electronic properties. Quasi-one-dimensional...
Materials hint towards gas-sensing and energy storage applications. The dependent properties of this nature show promise as filters and polarizers, while high surface areas associated with 2D crystallographic directions using a tip of an atomic force microscopy (AFM) probe. In the AFM experiments, it was possible to slide the 2D TiS₃ layers relative to each other as well as to remove selected 1D chains from the layers. Further, their characterization by Raman spectroscopy shows a reliable, internally standardized shift of a few cm⁻¹ from monolayer to bulk demonstrating tunability typical of conventional layered materials. Devices made from this material show promising electronic properties with predicted mobilities in excess of 10,000 cm²V⁻¹s⁻¹ with low edge-scattering, as well as in optoelectronics with strong light-matter interactions, particularly along the crystallographic b-axis (anisotropic). Orientation-dependent properties of this nature show promise as filters and polarizers, while high surface areas associated with 2D materials hint towards gas-sensing and energy storage applications.

5:45 AM *S.NM06.09.08
Manipulation of Molecules with Tuned-Oscillator Atomic Force Microscopy—A New Pathway to Catalysis Research
Omur E. Dagdeviren¹,²; ¹Yale University, United States; ²McGill University, Canada

Since the first demonstration of atomic resolution in ultrahigh vacuum conditions more than twenty years ago, frequency modulation-based noncontact atomic force microscopy (FM-NC-AFM) has significantly matured and is now routinely applied to study problems that benefit from high-resolution surface imaging. In FM-NC-AFM, control of the tip’s vertical position is accomplished by detecting a shift in the cantilever’s resonance frequency upon approach to the sample. Consistently ensuring reliable distance control during extended data acquisition periods has nevertheless remained challenging, as most FM-mode-based control schemes employ three feedback loops that may interfere. As a consequence, sample throughput in FM-NC-AFM is often low compared to ambient condition AFM, where the easy-to-implement amplitude-modulation (AM) control scheme is predominantly used. Transfer of the AM methodology to high-resolution measurements in vacuum is, however, difficult as with AM-AFM, instabilities during approach are common; in addition, the lack of viscous air damping and the related significant increase of the cantilever’s quality factor generates prolonged settling times that cause the system’s bandwidth to become impractical for many applications. Here we introduce a greatly simplified approach to NC-AFM imaging and quantitative tip-sample interaction force measurement that prevents instabilities while simultaneously enabling data acquisition with customary scan speeds by externally tuning the oscillator’s response characteristics [1]. After discussing the background and basic measurement principles, examples for its application to controlled manipulation of molecules are provided. We will show that the manipulation path can be chosen at will and energy barriers between potential minima on that pathway can be quantified, as can the energy landscape around the molecule before and after manipulation. To explore the practicality of this novel pathway to catalysis research, we selected benzene molecules on a Cu (100) surface as a model system. We first choose a specific manipulation path and then move the tip at constant but continuously reduced heights z-along this path (y-coordinate) while recording the oscillation amplitude and phase as a function of the tip-sample interaction potential [2-5]. Analyzing the full (x, z, A, phi) data array then allows recovery of the potential energy U(x,z) acting between the tip and the sample, the force on the tip normal to the surface vertical tip-sample force F_n(x, z), and the force F_l(x, z) that acts on the tip along the manipulation path (i.e., lateral) with meV, pN, and pm resolution [4,5]. In 54 distinct manipulation events, the molecules were either pushed, pulled, jumped to the tip, or did not move depending on the chemical surrounding of the molecule and the chemical identity of the tip. For further insight, we compared the experimentally measured energy landscapes and manipulation outcomes with computational results, which highlights the decrease of the energy barrier with the variation of the chemical environment of the molecule.

References:

6:00 AM S.NM06.09.09
Energy Dissipation on Suspended Graphene Quantum Dots
Marcin Kisiel, Alexina Ollier, Urs Gysin and Ernst Meyer;
Understanding nanoscale energy dissipation is nowadays among few priorities particularly in solid state systems. Breakdown of topological protection, loss of quantum information and disorder-assisted hot electrons scattering in graphene are just few examples of systems, where the presence of energy dissipation has a great impact on the studied object [1]. It is therefore critical to know, how and where energy leaks. Pendulum geometry Atomic Force Microscope (pAFM), oscillating like a pendulum over the surface, is perfectly suited to measure such tiny amount of dissipation [2,3], since a minimum detectable power loss is of the order of aW.

Here we report on a low temperature (T=5K) measurement of striking singlets or multiplets of dissipation peaks above graphene nanodrums surface. The stress present in the structure leads to formation of few nanometer sized graphene quantum dots (GDS) and the observed dissipation peaks are attributed to tip-induced charge state transitions in quantum-dot-like entities. The dissipation peaks strongly depend on the external magnetic field (B=0T-2T), the behavior we attributed to crossover from quantum dot carrier confinement to the confinement by magnetic field.


SESSION S.NM06.10: Poster Session: Theory and Characterization of 2D Materials—Bridging Atomic Structure and Device Performance
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
5:00 AM - 8:00 AM
S-NM06

S.NM06.10.01 Structural Characterization of 2D Layered Complex Hetero-Ion Systems
Ryan Mbagna Nanko¹, Matthew Cheng² and Vinayak Dravid²; ¹University of Maryland, Baltimore County, United States; ²Northwestern University, United States

The motivation behind this project is to study the structure of complex hetero ion based lamellar materials and their physical properties, including ferroelectricity and ferromagnetism, at the 2D limit. By mechanically exfoliating bulk single crystals of CuInP₂S₆, CuCrP₂S₆, and CuCrP₂S₆, a top down approach is used to obtain flakes that are as thin as possible. By isolating a monolayer of these materials, future studies will be conducted to probe for the existence of subnanometer ferroelectric, ferromagnetic, or magnetoelastic multiferroic responses from each respective material systems. Furthermore, studies on heterostructures formed from stacking different monolayers of material in order to study the coupling between different layers are also considered. In hope of its success, we can formulate a device that can take advantage of its magnetoelastic coupling in applications of spintronics and capacitors for more advanced computing.

Using Atomic Force Microscope (AFM) and Raman Spectroscopy, I developed a system to measure the thickness of flakes and to correlate them to Raman spectra and optical images. Despite its challenges, I have successfully measured a range of flake thickness that correlates to a trend in the intensity of the Raman spectra. This allows us a way to identify thin flakes of materials to pursue future studies on the multiferroic character of these materials systems at the 2D limit.

S.NM06.10.03 Simulation of Chalcogen Ion Laser Plasma Plumes—Fine-Tuning Plasma Conditions for Modification and Heterostructure Formation in Transition Metal Dichalcogenides
Joseph A. Edoki¹, Jacob H. Paiste², Sumner B. Harris², Robert R. Arslanbekov³ and Renato P. Camata²; ¹Alabama A&M University, United States; ²The University of Alabama in Huntsville, United States; ³CFD Research Corporation, United States
Among the many chemical and physical processes capable of modifying 2D materials, laser plasma processing provides an attractive suite of unique experimental parameters. Using appropriate laser irradiation conditions of a solid target, the ionization fraction, density, temperature, and kinetic energy of a laser-generated plasma can all be adjusted. These plasmas can be used to modify atomically-thin materials. This approach has been employed in the use of a laser-generated sulfur plume for alloying and creation of lateral heterostructures in transition metal dichalcogenides (TMDs) [1]. Further development in this area may be possible with a quantitative understanding of the formation/expansion process of laser-produced chalcogen plumes. In this work, we report on full-scale fluid dynamic simulations of laser-generated chalcogen ion plasmas from initial light-matter interactions to long-range expansion away from a solid target. Contrary to previous studies, our simulation is carried out to centimeter distances, which is the length scale relevant for materials modification. The simulation makes use of implicit partial differential equation solvers and is implemented in a state-of-the-art, multidimensional adaptive Cartesian mesh (ACM) framework. The ACM approach is essential since the spatial resolution required in the early stage of laser-matter interaction is a fraction of a micron while the entire computational domain is several centimeters. As the plasma begins to expand, the fine resolution at the target surface is no longer required, allowing the grid to be coarsened. A dense mesh is still required at the moving plasma front throughout the entire domain and so the ACM follows the front, and allows a coarse mesh elsewhere. The ACM technique makes the computation fast and enables large scale, multidimensional simulations. We simulate the plasma produced during pulsed nanosecond ablation (e.g., KrF excimer) of elemental tellurium and selenium and calculate the kinetic energy distribution of neutral and ionic species, analyzing in detail the evolution of their spatial dynamics. Compared to other metals like copper, bulk tellurium and selenium have drastically lower melting and boiling points as well as mass density. The result of these physical properties is that plasma absorption of the laser pulse begins earlier in the ablation process, and is sustained for longer times, leading to greater vapor densities and temperatures. For instance, at the surface of a copper target, vapor densities are in the $10^{23}$ m$^{-3}$ range while a selenium or tellurium target irradiated with the same laser power exhibits vapor densities that are an order of magnitude higher, with a greater number of highly ionized species. Both 1D and 2D-axisymmetric simulations show that singly and doubly ionized species expand outwards with high kinetic energy ahead of the high-density neutral vapor. At high vacuum conditions, reducing the laser irradiance below the plasma absorption threshold minimizes the number of energetic species and the thermal component of the plume is dominant. Simulations such as these provide quantitative understanding of the physical properties of chalcogen ion plasmas and can guide experiments in laser plasma modification of TMDs.


S.NM06.10.07

Influence of Strain on Mesoscopic 2D Film Growth from Phase Field Methods Tara M. Boland, Gabriel Munro-Ludders and Arunima Singh; Arizona State University, United States

The emergence of two dimensional (2D) materials opened up many potential avenues for novel device applications such as nanoelectronics, topological insulators, field effect transistors, microwave and terahertz photonics and many more. To date there are over 1,000 theoretically predicted 2D materials. Of those theoretical materials, only 55 have been experimentally synthesized. The incorporation of this technology into device applications has been hindered due to the difficulty synthesizing and stabilizing the 2D materials. Traditional methods such as chemical vapor deposition result in films with defects and grain boundaries. Controlling the growth of these films requires a systematic understanding of the crucial factors of the film-substrate adhesion strength and mismatch strain. In this work, we present a multi-scale computational approach to model the mesoscopic growth mechanisms of 2D materials on various substrates using density functional theory calculations with van der Waals corrections and phase field methods capturing both atomistic and mesoscopic materials properties.

Various 2D materials are placed epitaxially on substrate surfaces which possess hexagonal symmetry. The 2D materials are pre-screened to ensure that each 2D material will not possess a strain that is more than 10%. For all substrate-2D systems the binding and formation energy is computed using a high-throughput approach to density functional theory performed within the atomate framework. These parameters, coupled with the elastic constants for the 2D material are used to fit phase field models to predict the mesoscopic growth of various 2D materials.

1. We gratefully acknowledge ASU’s HPC staff for support and assistance with computing resources along with the Extreme Science and Engineering Discovery Environment (XSEDE), for support by National Science Foundation grant number ACI-1548562, through award number TG-DMR-150006.

S.NM06.10.08
From last decade, the interest of graphene is rising spanning almost all research areas due to its outstanding electrical, optical, mechanical, etc. properties inherited by its 2D structure [1]. Due to this remarkable discovery, the material graphene oxide (GO) became famous as a precursor for graphene synthesis, even though it was discovered about 150 years ago [2]. The GO is oxygenated form of graphene with many oxygen-containing groups (O-groups) and lattice defects. Hence, to fabricate graphene from GO, removal of these O-groups and repairing of the lattice defects is vital. This process is known as reduction [3]. However, to obtain pristine graphene from GO is the most challenging task due to the difficulty in complete removal of O-groups and repairing of lattice defects by conventional reduction method. It has been reported that, reduction of GO by high temperature annealing (>1500 °C) is an effective reduction method, particularly in producing conducting RGO films [4]. However, high temperature annealing transforms into high-energy consumption. Further, high temperatures cannot be used on all types of substrates in making graphene films. Therefore, the road to make pristine graphene like material by reducing GO still poses obstacles. As an alternative strategy, thermal annealing of GO in the presence of a carbon source (C-source) such as, ethanol, methane, ethylene, and acetylene via chemical vapour deposition (CVD) has been reported (<1000 °C) [5,6]. In our previously published work, fabrication of conducting RGO films by the restoration of graphitic structure via ethanol-CVD was reported [7]. As a continuation of this work, here we report, with the objective to understand the restoration behaviour of lattice defects, thermal annealing of GO in the presence of various organic solvents such as ethanol, methanol, isopropanol, tert-butanol, ethylene glycol, and toluene. To mention the methodology in brief, first a dispersion of GO was spin-coated on SiO2/Si substrates and thermal annealing was done in the presence of the above solvents using a CVD device. Characterization of the synthesized samples was done by Raman spectroscopy, atomic force microscopy (AFM) along with Kelvin probe force microscopy (KPFM), and X-ray photoelectron spectroscopy (XPS). Preliminary results showed that there is a significant effect on restoration of lattice defects depending on the organic solvent used. Particularly, the Raman spectroscopic results show the evolution of the G’-peak, which is an indication of restoration of lattice defects, and depending on the C-source the spectral properties change (intensity of G’-peak increases with more carbon atoms). The AFM results showed that the thickness of a single GO sheet has reduced from 1 nm to 0.4 nm due to removal of O-groups upon thermal treatment. Further, conductivity measurements of the synthesized RGO films will be carried out to clarify the solvent dependence on the restoration of lattice defects.

References
[2] Brodie, B.C., Phil. Trans. R. Soc. Lond., 1859, 149, 249-259

S.NM06.10.09
Symmetry Dependent Kinetics of 2D Materials’ Growth and Etching Jichen Dong1 and Feng Ding1,2; 1Center for Multidimensional Carbon Materials, Institute for Basic Science, Korea (the Republic of); 2Ulsan National Institute of Science and Technology, Korea (the Republic of)

The unique structures of 2D materials make them to show many excellent electronic, chemical and thermal properties that are absent from their 3D counterparts. To date, tremendous efforts have been devoted to the synthesis of large-area high-quality 2D materials. Moreover, studies have shown that etching, which has been one of the key techniques in the semiconductor society, can be used to create various structures in 2D materials, which can not be obtained by direct growth (PNAS 110 20386 (2013)). Therefore, A deep understanding on the growth and etching behaviors of 2D materials is crucial for their controllable fabrication. Here, we propose a general model for the growth and etching of two dimensional (2-D) crystals. In this model, low index edges are treated as the basis, while high index ones are described to be composed of terraces along the basis directions and kinks that connect the terraces. Considering the high formation energy penalty of forming a 1D nucleus on a terrace and the easy addition or removal of atoms to or from the kink sites, symmetry dependent edge growth and etching rate profiles of 2D crystals are constructed. By applying the kinetic Wulff construction (KWC) for growth and our modified KWC for etching, we simulated the shape evolutions of 2-, 3-, 4- and 6-fold symmetric 2D crystals during their growth and etching processes, which are well consistent with many experimental observations. This proposed model is expected to be a standard model for the growth and etching of 2D crystals.
Robustness of Atomic Scale Phosphorous Delta Layers—Toward Room Temperature Operation

David A. Scrymgeour, Connor Halsey, Daniel Ward, DeAnna Campbell, Evan Anderson, Scott W. Schmucker, Jeffrey A. Ivie, Ezra Bussmann, Suzey Gao, Tzu-Ming Lu and Shashank Misra; Sandia National Labs, United States

Atomic precision phosphorus doping of silicon by scanning tunneling microscope (STM) based hydrogen resist lithography is a promising fabrication platform for creating advanced silicon based electrical and quantum structures. In this process, termed atomic precision advanced manufacturing (APAM), the doping is accomplished by selective depassivation of bound hydrogen with the STM tip, incorporation of phosphine molecules, and capping with epitaxial silicon. APAM devices could provide a platform to learn about the device physics relevant to future transistor technologies. Moreover, these structures can carry a surprising 2 mA/μm of current, potentially enough to integrate APAM structures and devices with modern CMOS transistors. However, these devices have limited applicability because they only operate at cryogenic temperatures, and their ability to withstand the operational environments of CMOS is an open question. In this work, we report on our attempts to demonstrate room temperature devices realized in silicon-on-insulator devices and delta layer analogs, and the discuss the robustness and failure mechanisms at elevated temperature and current densities. These results show utility and challenges of this material platform for future discovery platforms.

This work was supported by the Laboratory Directed Research and Development Program at Sandia National Laboratories and was performed, in part, at the Center for Integrated Nanotechnologies, a U.S. DOE, Office of Basic Energy Sciences user facility. Sandia National Labs is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government.

Fabrication and Characterization of DNA Origami-Based Metal-Semiconductor Junctions

Basu R. Aryal, Dulashani R. Ranasinghe, Tyler R. Westover, Robert C. Davis, John N. Harb and Adam T. Woolley; Brigham Young University, United States

DNA-assisted bottom-up nanofabrication has demonstrated promise in creating both metal and non-metal nanostructures with diverse applications. To date, different-shaped and electrically connected metal nanostructures have been created and electrically characterized. However, the self-assembly and electrical measurement of semiconducting materials on DNA at the nanoscale have not been demonstrated. We have examined the fabrication yield and electrical properties of various Au nanowire structures created on DNA origami tiles by site-specific attachment of Au nanorods to molecularly programmed sites. We are now working with metals and semiconductors on these DNA nanostructures. We have attached Au and Te nanorods to designated locations on individual DNA origami templates and connected the nanorods via electroless Au deposition technique to create metal-semiconductor junctions. In addition, two-point probe electrical measurements were performed to verify the electrical continuity of the junctions, and non-linear current vs voltage curves were obtained. This work is a step toward self-assembling metals and semiconductors at the nanoscale using DNA origami structures, with potential future nanoelectronics applications.

Reference

Tailoring the Electronic Transport Properties of MoS2 Thin Film by Oxygen Plasma Treatment

Bhim Chamlagain and Saiful I. Khondaker; University of Central Florida, United States

Controlled and meticulous tunability of electronic properties of layered two-dimensional (2D) transition metal dichalcogenides (TMDs) is essential challenge to fabricate TMDs functional devices for the specific applications. Structural defects, crystallinity of the film and dopants used in two-dimensional (2D) transition metal dichalcogenides (TMDs) can significantly modify the material properties. Significant effort has been done to tune the optical and electrical properties of MoS2 with plasma exposure by manipulating the defects, doping and band structure. However, the observation of structural defects repair and phase change of MoS2 by plasma exposure has been still debatable. In this study, we will present the tunability of the electrical properties MoS2 thin film prepared by low pressure chemical vapor deposition (LPCVD) method with low power oxygen plasma treatment. Our electrical transport measurements elucidate the effect of the mild oxygen to
the MoS\textsubscript{2} film and able to tune the transport properties of the MoS\textsubscript{2}.

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**S.NM06.10.25**

**Non-Destructive Thickness Mapping of Insulating 2D Materials Down to a Monolayer** Andrea Crovetto\textsuperscript{1}, Patrick Whelan\textsuperscript{1}, Ruizhi Wang\textsuperscript{2}, Miriam Galbiati\textsuperscript{1}, Stephan Hofmann\textsuperscript{2} and Luca Camilli\textsuperscript{1}; \textsuperscript{1}Technical University of Denmark, Denmark; \textsuperscript{2}Cambridge University, United Kingdom

Characterization of the thickness and continuity of wide band gap 2D materials with monolayer sensitivity over large areas has proven to be very challenging. A prime example is 2D hexagonal boron nitride (hBN). Optical contrast methods suffer from the lack of visible absorption in the material; Raman spectral signatures are weak and often not conclusive; and electrical measurements are not possible due to a high electrical resistivity. In this contribution, we will demonstrate an experimental method based on the ellipsometry technique, which makes it possible to map the thickness and continuity of large-area hBN monolayers and bilayers transferred to Si/SiO\textsubscript{2} substrates. The method has sub-monolayer thickness sensitivity, is relatively fast, non-destructive, and can be easily automated. Importantly, artifacts in the measured thickness due to polymer residuals from the transfer process can be deconvolved under most conditions. With some assumptions on the optical functions of hBN, the thickness of an as-transferred hBN monolayer on SiO\textsubscript{2} is measured as 4.1 Å ± 0.1 Å, whereas the thickness of an air-annealed hBN monolayer on SiO\textsubscript{2} is measured as 2.5 Å ± 0.1 Å. The most likely cause of this discrepancy is the presence of a water layer trapped between the SiO\textsubscript{2} surface and the hBN layer in the latter case. The number of hBN layers measured in this study has been confirmed by Raman spectroscopy, x-ray photoemission spectroscopy, and by a series of ellipsometry control experiments. We will present a workflow of our experimental procedure, so that other researchers can extend this characterization method to other 2D materials and hopefully accelerate their development.

**S.NM06.10.27**

**Molecular Modeling of Biomaterial Degradation in Two Dimensions** Falk Hoffmann, Rainhard Machatschek, Stefanie Barbirz and Andreas Lendlein; Helmholtz-Zentrum Geesthacht, Germany

Modern medical applications require the design of multifunctional polymers. These substances shall fulfill several roles while implanted in the human body, for example as mechanically supporting devices that can release a drug, followed by a full, non-toxic degradation. A concept for implanting multiple functions is molecular integration through well-defined polymer architectures. Here, structure parameters, which can be varied include composition and ratio of different molecular building blocks as well as the branching type. Moreover, the aqueous biological environment can influence polymer behavior, like hydrogel swelling in water that may trigger both drug release and subsequent degradation.

Material design therefore implies knowledge on structure-function relationships that enable rapid prediction of material properties under specific conditions and external stimuli over sufficiently long time scales. Especially, polymer degradation has major impact on material physicochemical properties and requires thorough understanding of the molecular processes [1]. Importantly, degradation at the polymer surface links to medical applications. For example, medical drugs are delivered in the human body without functional loss if they are encapsulated in a polymer matrix which degrades at the surface without effecting its bulk composition. Recent experimental studies have shown that defined two-dimensional thin film polymer layers are highly suitable to quantitatively study degradation kinetics with Langmuir techniques [2]. In this work we now apply computational simulations to provide an all-atomic description of the polymer degradation process at the two dimensional interface. A molecular modeling approach is used to show how a molecular monolayer polymer surface film at the water interface behaves at different stages of the degradation process. The models are validated by exploring chemically established commercially available implant materials such as PLGAs (poly(lactide-co-glycolide)s and PCL (poly(\(\varepsilon\)-caprolactone)). The validation takes random chains as well as end-chain cutting as degradation mechanisms into consideration.

Finally, the model will be used as a predictive tool for digitally assembled copolyesters comprising the same repeating units, but aligned in sequence structure, which in part are challenging to synthesize such as strictly alternating structures. The gained knowledge will form the basis for the design of the next generation of degradable implant materials.

**S.NM06.10.28**

**Exploring the Role of Dimensional Variation in Molybdenum Disulphide (MoS\textsubscript{2}) by Relating the Structural, Morphological and Optical Characteristics** Margi Jani, Dhyey Raval, Abhijit Ray and Indrajit Mukhopadhyay; Pandit
Deendayal Petroleum University, India

Molybdenum disulphide (MoS$_2$) as a transition metal dichalcogenides (TMDCs) sketching a wide research interests with unique optical and electronic properties then a bulk. Bandgap engineering technique is a potential way for tuning to its optimization. MoS$_2$ owing to band gap tailoring from 1.3 to 1.9 eV for bulk (indirect) and single-layered (direct) structures makes it a promising material in the field of energy applications. The present article deals with variation in the properties along with dimensional (1-3D) change in molybdenum disulphide nanostructure. Syntheses, structural, morphological, optical properties of bulk to few layers of nanostructures are investigated. The exfoliation of MoS$_2$ Flake like nanostructure has been studied for its unique properties. Uniform 3D flower like nanostructures has been prepared by one-pot hydrothermal method. Nanostructure flakes by a solution based exfoliation method are compared with a bulk MoS$_2$. Structural, morphological and optical properties were investigated by XRD, FESEM, EDAX, UV–Visible for the bulk and nanostructures properties.

**SYMPOSIUM S.NM07**

Two-Dimensional Quantum Materials Out of Equilibrium  
November 21 - December 1, 2020

Symposium Organizers  
Ariando Ariando, National University of Singapore  
Christianne Beekman, Florida State University  
Jaime Gomez-Rivas, Technische Universiteit Eindhoven  
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Symposium Support  
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* Invited Paper

SESSION Tutorial S.NM07: Electronic, Optical and Magnetic Properties of Quantum Materials  
Session Chairs: Liqin Ke, Philip Kim and Jigang Wang  
Saturday Afternoon, November 28, 2020  
S.NM07

2:45 PM *  
Topological Quantum Materials for Quantum Electronic Devices Philip Kim; Harvard University, United States

Modern electronics has been heavily relied on the technology to confine electrons in the interface layers of materials. The unique properties of these low dimensional systems are generally understood by considering enhanced quantum effects and increased correlations due to the reduction of available phase space. Quantum effect in low dimensional materials also provides topological states of matter where entangled quantum states that can be transformed smoothly with protected symmetries, resulting in robust invariants. In this presentation, we will discuss some of the key physical phenomena such as the Berry phase, quantum Hall, and the quantum spin Hall effect. Topology and collective phenomena give quantum materials emergent functions that provide a platform for developing next-generation quantum devices with novel functionality, such as electronics without power dissipation and fault-tolerant quantum computing. We will discuss the prospect of quantum technology based on topological quantum materials.

3:45 PM BREAK
4:00 PM *
Terahertz Light Control and Nano-Imaging of Quantum Materials Jigang Wang; Iowa State University, United States

The recent development of ultrafast THz spectroscopy and nano-imaging tools facilitates discovering and understanding collective excitations and emergent phenomena in quantum materials. In this tutorial, I will discuss strategic advantages, with recent examples, of applying single- and few-cycle THz pulses to probe and control several systems of current focus, including unconventional superconductors, topological matter and perovskite photovoltaic semiconductors. Particularly, THz light-driven coherence and dynamic symmetry breaking allows the observation of quantum beats forbidden by equilibrium symmetry and quantum phases hidden by conventional tuning methods. Finally I will discuss far-reaching consequence of THz spectroscopy tools at the space-time limit on quantum matter discovery and dynamic control.

5:00 PM BREAK

5:15 PM *
Magnetism in Quantum Materials—Computation Approach Liqin Ke; Ames Laboratory, United States

The magnetic 2D van der Waals materials have received great attention due to their potential applications in spintronics. In this tutorial, I will give an introduction to computational magnetism. In particular, I will focus on the ab initio methods that used to compute and resolve intrinsic magnetic properties, such as exchange coupling, magnetocrystalline anisotropy, and magnetic susceptibility. We will discuss the underlining magnetic mechanisms that may guide the bandstructure engineering to improve the magnetic properties in these systems.

12:30 PM *S.NM07.01.02
Uniaxial Stress Effect on a Transition Metal Dichalcogenide, WTe2 Na Hyun Jo, Lin-lin Wang, Peter P. Orth, Sergey L. Bud'ko, Adam Kaminski and Paul C. Canfield; Ames Laboratory/Iowa State University, United States

Strain describes the deformation of a material as a result of applied stress. It has been widely employed to probe transport properties of materials, ranging from semiconductors to correlated materials. In order to understand, and eventually control, transport behavior under strain, it is important to quantify the effects of strain on the electronic band structure, carrier density and mobility. Here, we demonstrate that much information can be obtained by exploring a novel experimental observable: magneto-elastoresistance (MER), which refers to magnetic field-driven changes of the elastoresistance. We use this powerful approach to study the combined effect of strain and magnetic fields on the semi-metallic transition metal dichalcogenide WTe2. We discover that WTe2 shows a large and temperature non-monotonic elastoresistance, driven by uniaxial stress, that can be tuned by magnetic field. Using first-principle and analytical low-energy model calculations, we provide a semi-quantitative understanding of our experimental observations. We show that in WTe2 the strain induced change of the carrier density dominates the observed elastoresistance. In addition, the change of the mobilities can be directly accessed using MER. Our analysis also reveals the importance of a heavy hole band near the Fermi level on the elastoresistance at intermediate temperatures.

12:42 PM *S.NM07.03.12
Ultrafast Manipulation of Surface Transport in Topological Insulators by Mid-Infrared and Terahertz Pulses Jigang Wang; Iowa State Univ and Ames Lab, United States

The demand for disorder-tolerant quantum logic and spin electronics can be met by generating and controlling dissipativeless spin currents protected by topology. Dirac fermions with helical spin-locking surface transport offer a way of achieving such goal. Yet a challenge remains on how to selectively control surface helical spin transport and surface-bulk coupling. Here we use the mid-infrared and terahertz (THz) photoexcitation of intraband transitions and/or coherence optical phonons to enable ultrafast manipulation of surface THz conductivity in a topological insulator. We will also discuss how to extend the ultra-broadband, wavelength-selective pumping to emerging topological semimetals. Imposing electronic and vibrational
coherence into topological matter may become a universal light control principle for reinforcing the protected quantum transport.

12:54 PM *S.NM07.09.03
Manipulating Valley-Selective Photon Dressed States in Monolayer Semiconductors Nathaniel P. Stern; Northwestern University, United States

Control over the interactions between light and matter underlies many classical and quantum applications. In recent years, 2D layered semiconductors have gained prominence for optoelectronics because of their strong excitonic features and capacity for van der Waals assembly in layered heterostructures. Through integration with various photonics devices, the interactions between these materials and light can be tailored and new physical regimes can be achieved, highlighting the importance of understanding photonic dressed states of 2D materials. One of the unique features of monolayer materials such as transition metal dichalcogenides is the valley pseudospin addressable by circularly-polarized light. Understanding how this valley polarization can be manipulated is an exciting goal with implications for devices and quantum information science. Here, I discuss hybrid light-matter dressed states, or exciton-polaritons, in transition metal dichalcogenides embedded in dielectric microcavities. These strongly-coupled polaritons preserve the valley pseudospin known from bare monolayers [1]. Distinct behavior of valley-polarized exciton-polaritons can be accessed with microcavity engineering by tuning system parameters such as cavity decay rate and exciton-photon coupling strength. In the opposite dressed state regime of weak light-matter coupling, intense off-resonant light can be used to shift energy levels though the Stark effect [2]. Applied to valley-sensitive states, this shift can be used for coherent manipulation of valley pseudospin. I will show how this approach can be translated to valley-selective exciton-polaritons. Cavity reflectance spectra exhibit a simultaneous shift of both polariton branches when ultrafast coincident pump and probe pulses are co-circularly-polarized, and no appreciable shift when they are cross-polarized. This valley-selective polariton Stark shift combines both dressed state regimes of strong, near resonant interactions with weak, off-resonant optical interactions, providing a new tool for state control in coherent valleytronics. Exploiting photonic dressed states can be viewed as another approach in the toolbox for manipulating the optoelectronic properties of 2D materials and their heterostructures.

This work was supported by DOE (DE-SC0012130) and ONR (N00014-16-1-3055).


1:06 PM *S.NM07.08.04
Local Site Magnetic Susceptibility on Quantum Materials by Polarized Neutron Diffraction Huibo Cao; Oak Ridge National Laboratory, United States

Understanding the interactions leading to magnetic quantum phenomena in a wide range of quantum materials is extremely important for development of new quantum materials and future technologies. Although neutron scattering is a powerful tool for this purpose, it also faces a range of challenges, such as the lack of sizable high-quality crystals, limited high pressure capabilities, and the difficulty in disentangling the intrinsic quantum phenomena versus effects from defects and site-disorder. Recently we have introduced the local magnetic susceptibility methods for studying quantum materials, which can be used for small crystals and powder samples. A single crystal neutron diffractometer DEMAND at the High Flux Isotope Reactor at the Oak Ridge National Laboratory has been upgraded for studying magnetic materials under various extreme sample environment conditions. In this talk, I will introduce the local site magnetic susceptibility methods, the current capabilities at the DEMAND, and our recent studies on two-dimensional quantum materials.

1:18 PM *S.NM07.09.05
Quantum Oscillations in Resistivity and Magnetization in Kondo Insulators Lu Li; University of Michigan, United States

In metals, orbital motions of conduction electrons on the Fermi surface are quantized in magnetic fields, which is manifested by quantum oscillations in electrical resistivity. This Landau quantization is generally absent in insulators. Here we report a notable exception in an insulator — ytterbium dodecaboride (YbB₁₂). The resistivity of YbB₁₂ exhibits distinct quantum oscillations despite having a much larger magnitude than in metals. This unconventional oscillation is shown to arise from the insulating bulk, even though the temperature dependence of the oscillation amplitude follows the conventional Fermi liquid theory of metals. The large effective masses indicate the presence of a Fermi surface consisting of strongly correlated...
electrons. Quantum oscillations are also observed in the magnetization of YbB12. Our result reveals a mysterious dual nature of the ground state in YbB12: it is both a charge insulator and a strongly correlated metal.

1:30 PM *S.NM07.09.01
Spin Excitations in Magnetic 2D van der Waals Materials—Nonlocal Electron Correlation Effects Liqin Ke; Ames Laboratory, United States

The recent experimental realization of magnetic two-dimensional van der Waals (m2DvdW) materials has generated significant interest in exploiting such systems for novel 2D magnetism and for developing applications such as energy-efficient ultra-compact spin-based electronics. A better understanding of the magnetic interactions in these systems may help to accelerate the discovery of materials with higher magnetic ordering temperatures, moving these novel systems closer to practical applications. Using linear-response ab initio methods, we investigate the magnetic interactions and spin excitations in various m2DvdW systems, such as CrI3, CrGeTe3, V13, and Fe3GeTe2. Dynamical transverse spin susceptibility is calculated to directly compare with available Inelastic Neutron Scattering (INS) measurements. Accurate descriptions of electronic structure can provide reliable predictions of electronic and magnetic properties. Due to confinement, electrons in these 2D systems are likely to be strongly correlated, and electron screening anisotropic, so that their description may require advanced ab initio methods beyond density functional theory (DFT). Therefore, we also use the quasiparticle self-consistent GW (QSGW) method, a self-consistent many-body perturbation method, to describe the electronic structure and calculate magnetic properties. In contrast to DFT, the electron-electron interaction is evaluated explicitly by calculating the dynamically-screened Coulomb interaction W. We found that the nonlocal electron correlations, which are not included in methods such as DFT+U, have profound effects on the electronic and magnetic properties in these m2dvdW materials. A more elaborate description of electron interactions helps better describe the magnetic interactions in these 2D quantum systems. By comparing the electronic structures obtained in QSGW and DFT, we discuss the applicability and limitations of the widely-used DFT+U methods for these systems. We will also discuss the effects of spin-orbit coupling, the Dzyaloshinskii-Moriya interaction, impurities, pressure, and electric fields on the magnetic interactions and excitations in relevant systems.

1:42 PM *S.NM07.01.01
High Pressure Driven Structural and Electronic Phase Transitions in 2D Materials and Structures Junqiao Wu, Yang Gao and Penghong Ci; University of California, Berkeley, United States

High pressure is a powerful, reversible and “clean” way to drive materials away from equilibrium, exposing new phases, new states, new effects and new physics that would not exist in ambient condition. For layered materials where neighboring layers are held together by weak van der Waals forces, high pressure are particularly effective in creating these new effects. In this talk, we will discuss some of our findings in using high hydrostatic pressure to modulate the structure and electronic/optical properties of a variety of 2D materials, ranging from single or few layers of transition metal dichalcogenides, and their heterostructures, to new 2D materials created by intercalating non-2D materials.

1:54 PM *S.NM07.05.02
Fluctuations in Quantum Materials—From Skyrmions to Superconductivity Joshua J. Turner1,2; 1Stanford University, United States; 2SLAC National Accelerator Laboratory, United States

Quantum materials offer not only a vast array of potential for technological advancement, but also provide a testbed for the laws of nature in condensed matter. One area to advance the frontier in this area is through the measurement of fast, spontaneous fluctuations of quantum order. This is at the heart of the essential physics in these types of solids, but has remained largely unexplored. The key component we use is the application of a newly developed coherent scattering method which can access these fluctuations on the relevant energy scales. This new tool has been demonstrated on a topological magnetic material, and early results point to the tremendous potential for this approach to provide important new insight into fundamental open questions in condensed matter. It allows for the direct, element-specific and momentum-resolved measurement of the fluctuations of a complex material and to connect them to the requisite response functions calculated from first principles. By analyzing subtle X-ray variations known as "speckle", statistics is used to extract the stochastic fluctuation information of the system. This offers the ability to address a range of important current problems in materials. In this talk, we will first discuss the newly developed tools which are used to measure the material properties, based on short pulses from an x-ray free electron laser. We will then present how this has been applied to skyrmions and the measurement of nanosecond fluctuations. This will be followed by an examination of new results on skyrmion physics near the critical point of the skyrmion ordered lattice phase. We will end with an outlook of how this progress can help to tackle the question of fluctuations in unconventional superconductors.
This work at SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, through the Materials Sciences and Engineering Division, contract DEAC02-76SF00515. J. J. Turner acknowledges support from the U.S. Department of Energy, Office of Science, Basic Energy Sciences through the Early Career Research Program.

2:06 PM *S.NM07.03.05
Investigation of Coherent Magnons in Antiferromagnetic Iridate Sr$_2$IrO$_4$ Richard D. Averitt; University of California, San Diego, United States

The spin-orbit coupled Mott insulator Sr$_2$IrO$_4$ has attracted considerable interest because of its exotic $J_{\text{eff}} = 1/2$ Mott state arising from the interplay of on-site Coulomb repulsion and strong spin-orbit coupling. We have investigated magnetization dynamics of this enigmatic compound. Specifically, we measured coherent magnons of the $J_{\text{eff}} = 1/2$ Mott state using Kerr rotation following excitation with either mid-infrared 9 μm (below the charge gap), or near-infrared 1.3 μm (above the charge gap) circularly polarized pulses. For both pump wavelengths, the 2D in-plane $B_{2g}$ coherent magnon oscillation of frequency ~0.5 THz is observed. In this talk, we show that the excitation pathways are different for these two excitation wavelengths. In particular, coherent magnon excitation with 9 μm pulses arises from the inverse Faraday effect that, microscopically, is related to two-magnon processes. Notably, coherent magnon generation with 9 μm pulses is nearly an order of magnitude more efficient in comparison to 1.3 μm pulses, without excitation of carriers across the Mott gap.

Acknowledgement: This research is supported by the Army Research Office MURI grant ARO W911NF-16-1-0361, “Floquet engineering and metastable states.”

2:18 PM *S.NM07.08.01
Non-Equilibrium Effects in Quantum Magnets Kate Ross and Steffen Saeubert; Colorado State University, United States

The study of non-equilibrium properties of quantum phases of matter is important in the context of future quantum technologies, since all devices operate in the non-equilibrium limit. Theoretically, the transverse field Ising model (TFIM) and its disordered variants provide a tractable platform to study effects of quantum quenches (a rapid variation of a non-thermal parameter, leading to interesting transient effects), or quantum annealing (a slow variation of a non-thermal parameter, leading to efficient optimization). While there is enormous theoretical interest in these ideas, they have not yet been thoroughly tested on real Ising magnetic systems. There are well-known magnetic material realizations of the TFIM, CoNb2O6 and LiHoYF4, which display quantum critical points in accessible transverse magnetic field ranges. We have studied these materials following various protocols of time variation of the magnetic field, using ac susceptibility and neutron scattering as probes. I will discuss the non-equilibrium effects we have observed in these TFIM materials.

SESSION S.NM07.12: Live Keynote II: Two-Dimensional Quantum Materials Out of Equilibrium
Session Chairs: Christianne Beekman and Srinivasa Rao Singamaneni
Monday Morning, November 30, 2020
S.NM07

8:00 AM *S.NM07.04.02
Magnetic Field Induced Berezinskii-Kosterlitz-Thouless Correlations in Three-Dimensional Manganites Subray Bhat$^1$, Bhagyashree KS$^1$ and Arjun Ashoka$^2$; $^1$Indian Institute of Science, India; $^2$University of Cambridge, United Kingdom

Ideal two-dimensional (2D) Heisenberg magnets lack long range order [1]. However, the XY model with spins confined to a plane shows a topological phase transition at a finite temperature corresponding to binding and unbinding of vortices [2,3]. Experimental evidence for such Berezinskii-Kosterlitz-Thouless (BKT) transitions has been difficult to obtain in condensed matter systems, where, even a weak interlayer coupling that is invariably present leads to long-range order, pre-empting the BKT transition. The BKT signatures are still discernible above the long-range ordering temperature, however, in the characteristic exponential temperature dependence of the coherence length of the fluctuations. In this work we report that an applied magnetic field can induce such BKT correlations not only in quasi 2-dimensional systems but also in nominally 3-dimensional manganites undergoing antiferromagnetic transitions. We arrive at this unexpected conclusion based on our
studies of temperature dependence of electron spin resonance (ESR) linewidth $\Delta H(T)$ of $\text{Cr}^{3+}$ doped bismuth strontium manganite $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x=0.04, 0.1$) (BSMCO).

BSMCO [4] belongs to the family of mixed valent manganites of the type $\text{ReAMnO}_3$ where $\text{Re}$ is a trivalent rare earth ion or $\text{Bi}^{3+}$ and $\text{A}$ is a divalent alkaline earth ion, which are intensely studied in the last few years [5]. $\Delta H(T)$ provides the most important probe to study the spin interactions in these strongly correlated spin systems. We find that $\Delta H(T)$ observed in BSMCO (current work), as well as in $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ and $\text{CaMnO}_3$ [6] is better (than the usually adopted critical state model) described by the BKT scenario which predicts [7]

$$\Delta H_{\text{BKT}}(T) = \Delta H_0 \exp \left[ \frac{3b}{T/T_{\text{BKT}} - 1} \right] + mT + \Delta H_{\text{ind}}, \quad T > T_{\text{BKT}}$$

where $T_{\text{BKT}}$ is the BKT transition temperature and $b = \pi/2$ for a square lattice and the last two terms are included to account for the high temperature and temperature independent behaviour. This is unexpected as these manganites have a 3D structure and the BKT model addresses systems with spin and spatial dimensions of two. We understand this result in terms of an effective symmetry reduction induced by i) the magnetic field applied in the ESR experiment and ii) the intrinsic anisotropy arising from microscopic details such as doping and phase separation - contributing to an effectively 2-dimensional XY easy plane anisotropy. Nanometric scale spin clusters similar to the ones observed in La doped $\text{CaMnO}_3$ [8] could conceivably play the role of vortices in these 3D materials. The sensitivity of the BKT behaviour to applied field is also supported by a re-analysis of the field dependence of the $\Delta H(T)$ in the quasi-2D antiferromagnetic compound $\text{BaNi}_2\text{V}_2\text{O}_8$ reported by Heinrich et al., [9]. For undoped manganites we find $T_{\text{BKT}}$ is of the order of the magnetic interaction energy, suggesting that the applied field could be the sole origin of the BKT behaviour [10]. We shall also address the interesting observation that in BSMCO ($x=0.04, 0.1$), $T_{\text{BKT}}$ is composition-independent while the magnetic properties are quite sensitive to composition.

SVB and AA thank the Indian National Science Academy, the National Academy of Sciences, India and the Indian Academy of Sciences for support.

References:

8:12 AM *SNM07.08.08
Ultrafast Energy- and Momentum-Resolved Dynamics of Magnetic Correlations in the Photo-Doped Iridates Mark P. Dean; Brookhaven National Laboratory, United States

Measuring how the magnetic correlations evolve in doped Mott insulators has greatly improved our understanding of the pseudogap, non-Fermi liquids and high-temperature superconductivity. Recently, photo-excitation has been used to induce similarly exotic states transiently. However, the lack of available probes of magnetic correlations in the time domain hinders our understanding of these photo-induced states and how they could be controlled. This talk will describe our implementation of magnetic resonant inelastic X-ray scattering at free-electron lasers to directly determine the magnetic dynamics after photo-doping the Mott insulators Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$ [1-3]. We find that the non-equilibrium states host strong 2D magnetic correlations even in cases where 3D long-range magnetic order is completely suppressed [1]. The marked difference in these 2D and 3D timescales implies that the dimensionality of magnetic correlations is vital for our understanding of ultrafast magnetic dynamics. We also uncover distinct differences in the magnetic dynamics between insulators Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$, which we attribute to a "spin-bottle-neck" effect [3].

8:24 AM *SNM07.03.01
Ultrafast Optical Studies of Two-Dimensional Quantum Materials Rohit Prasankumar; Los Alamos National Laboratory, United States

Ultrafast optical spectroscopy has attained prominence due to its ability to resolve dynamics in conventional metals and semiconductors at the fundamental time scales of electron and lattice motion. In recent years, ultrafast optical techniques have become more sophisticated, making it possible to directly access fundamental material parameters in a non-contact
manner. In this talk, I will discuss the use of ultrafast optical spectroscopy to track and potentially control carrier dynamics through both space and time in two-dimensional (2D) quantum materials. This will include unraveling charge transfer and diffusion across the interface between lateral transition metal dichalcogenide (TMD) monolayers as well as driving structural dynamics in a topological insulator with intense terahertz (THz) pulses, along with other studies of these fascinating nanosystems.

8:36 AM *S.NM07.05.01
Keynote: Topological Defects in Twisted van der Waals Interfaces Philip Kim; Harvard University, United States

Controlling the interlayer twist angle in artificial two-dimensional (2D) van der Waals (vdW) heterostructures offers an experimental route to create moire superlattice. One can create exotic electronic states by minimizing electronic band width with tunable moire length scale. However, in the small twist angle regime, vdW interlayer interaction can cause significant structural reconfiguration at the interface, creating the arrays of domain structures. In this presentation, we will discuss the atomic reconstruction at twisted vdW interfaces and its effect on electronic structure and electrical transport behavior. Furthermore, we note that multiple domain boundaries at the reconstructed interface join together to create energetically unfavorable nodes forming vortex-like structures. We will discuss our recent efforts to understand the topological nature of those defects.

8:48 AM *S.NM07.03.04
Tracking Non-Equilibrium Magnetism in Quantum Materials John Freeland; Argonne National Laboratory, United States

Non-equilibrium phases have developed as an important topic in the realm of layered materials, especially in the two-dimensional limit. Of particular interest is the case of magnetism in the single layer limit[1]. Using external inputs ranging from static to dynamic, the states in these systems can be strongly manipulated to drive transitions between different spin configurations[2]. However, the challenge is to follow the emergent or collapses of specific phases in systems that are at the two-dimensional limit. Here I will focus on using X-rays to explore the magnetic order parameter directly for the cases involving antiferromagnetic and ferromagnetic states. The use of polarized X-rays in either scattering or absorption experiments, has a long history of probing magnetic states. With synchrotron and free-electron laser sources, we can extend this to the ultrafast domain to follow the dynamic response of the magnetic configuration. Here I will present examples involving dynamic collapse of antiferromagnetic order in nickelates to the optical conversion of antiferromagnetic to ferromagnetic order in manganites[3]. I will use these ultrathin oxide films as examples of exploration of magnetism in the two-dimensional limit using X-rays.

The work at Argonne is supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357. The development of the materials and ultrafast experiments is supported by the U.S. Department of Energy, Office of Basic Energy Sciences under Award Number DE-SC-0012375.

References:

9:00 AM *S.NM07.02.01
New Adventures in a Small World—Metals at the Atomic Limit Joshua A. Robinson; The Pennsylvania State University, United States

The last decade has seen an exponential growth in the science and technology of two-dimensional materials. Beyond graphene, there is a huge variety of layered materials that range in properties from insulating to superconducting that can be grown over large scales for a variety of electronic devices and quantum technologies, such as topological quantum computing, quantum sensing, and neuromorphic computing. In this talk, I will discuss the synthesis of a range of 2D layers over large areas for sensing and electronic devices, as well as recent breakthroughs in novel 2D heterostructures and realization of unique 2D allotropes of 3D materials. I will introduce a novel synthesis method, dubbed confinement heteroepitaxy (Chet), that enables the creation of atomically thin metals, enabling a new platform for creating artificial quantum lattices (AQLs) with atomically sharp interfaces and designed properties.
9:12 AM OPEN DISCUSSION

9:24 AM *S.NM07.07.01
Keynote: Light-Matter Interaction in Two-Dimensional Semiconductors Vinod Menon; City College and Graduate Center of CUNY, United States

Owing to their large oscillator strength and strong exciton binding energy, two-dimensional (2D) transition metal dichalcogenides (TMDs) have emerged as an attractive material platform for studying strong light-matter coupling and associated phenomena. Following up on our previous work on strong light-matter coupling in 2D TMDs [1, 2], here we will present results on enhancing the nonlinear interaction between the quasiparticles (exciton-polaritons). This is achieved using excited states of excitons (Rydberg states) which have larger Bohr radii. We will also present our recent results on controlling the valley pseudospin via the pseudomagnetic fields in optical cavities and our work on realizing an electrically pumped polariton LED [3]. Finally, we will first present our work on realizing single photon emitters (SPEs) in hexagonal boron nitride (hBN), a van der Waals material, via strain engineering [4] and coupling of these SPEs to high Q silicon nitride microresonators [5].


SESSION S.NM07: Pressure/Strain Dependent Properties
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM07

5:00 AM *S.NM07.01.01
High Pressure Driven Structural and Electronic Phase Transitions in 2D Materials and Structures Junqiao Wu, Yang Gao and Penghong Ci; University of California, Berkeley, United States

High pressure is a powerful, reversible and “clean” way to drive materials away from equilibrium, exposing new phases, new states, new effects and new physics that would not exist in ambient condition. For layered materials where neighboring layers are held together by weak van der Waals forces, high pressure are particularly effective in creating these new effects. In this talk, we will discuss some of our findings in using high hydrostatic pressure to modulate the structure and electronic/optical properties of a variety of 2D materials, ranging from single or few layers of transition metal dichalcogenides, and their heterostructures, to new 2D materials created by intercalating non-2D materials.

5:15 AM *S.NM07.01.02
Uniaxial Stress Effect on a Transition Metal Dichalcogenide, WTe2 Na Hyun Jo, Lin-lin Wang, Peter P. Orth, Sergey L. Bud'ko, Adam Kaminski and Paul C. Canfield; Ames Laboratory/Iowa State University, United States

Strain describes the deformation of a material as a result of applied stress. It has been widely employed to probe transport properties of materials, ranging from semiconductors to correlated materials. In order to understand, and eventually control, transport behavior under strain, it is important to quantify the effects of strain on the electronic band structure, carrier density and mobility. Here, we demonstrate that much information can be obtained by exploring a novel experimental observable: magneto-elastoresistance (MER), which refers to magnetic field-driven changes of the elastoresistance. We use this powerful approach to study the combined effect of strain and magnetic fields on the semi-metallic transition metal dichalcogenide WTe2. We discover that WTe2 shows a large and temperature non-monotonic elastoresistance, driven by uniaxial stress, that can be tuned by magnetic field. Using first-principle and analytical low-energy model calculations, we provide a semi-quantitative understanding of our experimental observations. We show that in WTe2 the strain induced change of the carrier density dominates the observed elastoresistance. In addition, the change of the mobilities can be directly accessed using MER. Our analysis also reveals the importance of a heavy hole band near the Fermi level on the elastoresistance at intermediate temperatures.
Microscale Synthesis of Photoluminescent Silicated Quantum Dots for Particulate-Flow Tracking
Clara Reed, Lance Hubbard, Nic Uhnak, Trevor Cell, Ryan Sumner, Martin Liezers, Nathaniel Smith, Michael Foxe, April Carman and Caleb Allen; Pacific Northwest National Laboratory, United States

Particulate flow measurements require environmentally inert and size-selected particles, with unique identifiers. Agglomerated microscale silica covered quantum dots (QDs) were synthesized and used for explosive mass-deposition measurements within fabricated enclosures. Experimental determination of luminescent intensity, as well as chemical-environmental tolerance, were conducted to ensure the inert nature and unique identifier for each size-selected band. Reagent concentration control was used to produce silicated/QD luminescent particles with bands centered from 100 nm to 4 microns. The ability to uniformly size particles and link the size to an easily identifiable characteristic, such as luminescence, allows for the creation of flow-based particle distribution description. This is a valuable tool for the analysis of turbulent flow in highly variable cavities. Future modeling with these particles can be used to predict the deposition and settling location of particulates and the environmental flow of debris in turbulent fluid environments.

New Adventures in a Small World—Metals at the Atomic Limit
Joshua A. Robinson; The Pennsylvania State University, United States

The last decade has seen an exponential growth in the science and technology of two-dimensional materials. Beyond graphene, there is a huge variety of layered materials that range in properties from insulating to superconducting that can be grown over large scales for a variety of electronic devices and quantum technologies, such as topological quantum computing, quantum sensing, and neuromorphic computing. In this talk, I will discuss the synthesis of a range of 2D layers over large areas for sensing and electronic devices, as well as recent breakthroughs in novel 2D heterostructures and realization of unique 2D allotropes of 3D materials. I will introduce a novel synthesis method, dubbed confinement heteroepitaxy (CHet), that enables the creation of atomically thin metals, enabling a new platform for creating artificial quantum lattices (AQLs) with atomically sharp interfaces and designed properties.

Ultrafast Optical Studies of Two-Dimensional Quantum Materials
Rohit Prasankumar; Los Alamos National Laboratory, United States

Ultrafast optical spectroscopy has attained prominence due to its ability to resolve dynamics in conventional metals and semiconductors at the fundamental time scales of electron and lattice motion. In recent years, ultrafast optical techniques have become more sophisticated, making it possible to directly access fundamental material parameters in a non-contact manner. In this talk, I will discuss the use of ultrafast optical spectroscopy to track and potentially control carrier dynamics through both space and time in two-dimensional (2D) quantum materials. This will include unraveling charge transfer and diffusion across the interface between lateral transition metal dichalcogenide (TMD) monolayers as well as driving structural dynamics in a topological insulator with intense terahertz (THz) pulses, along with other studies of these fascinating nanosystems.
5:15 AM *S.NM07.03.02
Ultrafast Dynamical Processes in Antiferromagnets
Manfred Fiebig; ETH Zurich, Switzerland

At the time of its discovery, antiferromagnetic (AFM) order was considered as an interesting but essentially useless phenomenon in terms of application. Now, however, the AFM state is being regarded as highly promising for spintronic applications. The fully compensated magnetic order makes it robust against external magnetic fields and at the same time leads to vanishing magnetic stray fields, thus reducing crosstalk between neighbouring AFM domains. Furthermore, the AFM order permits spin dynamics in the THz-regime with AFM switching processes on the picosecond timescale. Because of the absence of a macroscopic magnetization, ultrafast detection of the AFM state is challenging, however. In my talk, I present various laser-optical approaches to overcome this. On the one hand, linear and nonlinear laser-optical processes allow us to track the ultrafast three-dimensional motion of the AFM order parameter through space. By doing that, we show that, in stark contrast to ferromagnets, damping effects play an important role during the optical excitation of the AFM state and offer an efficient handle for all-optical AFM order-parameter switching ("writing an AFM bit") [1]. Furthermore, THz time-domain spectroscopy offers a novel approach for studying the competition of AFM order and a magnetically screened spin-liquid state with the formation of heavy fermions and their disintegration near the quantum-critical points in materials like CeCu$_6$$_x$Au$_{1-x}$ and YbRh$_2$Si$_2$ [2, 3].


5:30 AM *S.NM07.03.04
Tracking Non-Equilibrium Magnetism in Quantum Materials
John Freeland; Argonne National Laboratory, United States

Non-equilibrium phases have developed as an important topic in the realm of layered materials, especially in the two-dimensional limit. Of particular interest is the case of magnetism in the single layer limit[1]. Using external inputs ranging from static to dynamic, the states in these systems can be strongly manipulated to drive transitions between different spin configurations[2]. However, the challenge is to follow the emergent or collapses of specific phases in systems that are at the two-dimensional limit. Here I will focus on using X-rays to explore the magnetic order parameter directly for the cases involving antiferromagnetic and ferromagnetic states. The use of polarized X-rays in either scattering or absorption experiments, has a long history of probing magnetic states. With synchrotron and free-electron laser sources, we can extend this to the ultrafast domain to follow the dynamic response of the magnetic configuration. Here I will present examples involving dynamic collapse of antiferromagnetic order in nickelates to the optical conversion of antiferromagnetic to ferromagnetic order in manganites[3]. I will use these ultrathin oxide films as examples of exploration of magnetism in the two-dimensional limit using X-rays.

The work at Argonne is supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357. The development of the materials and ultrafast experiments is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC-0012375.

References:

5:45 AM *S.NM07.03.05
Investigation of Coherent Magnons in Antiferromagnetic Iridate Sr$_2$IrO$_4$
Richard D. Averitt; University of California, San Diego, United States

The spin-orbit coupled Mott insulator Sr$_2$IrO$_4$ has attracted considerable interest because of its exotic $J_{eff}$ = 1/2 Mott state arising from the interplay of on-site Coulomb repulsion and strong spin-orbit coupling. We have investigated magnetization dynamics of this enigmatic compound. Specifically, we measured coherent magnons of the $J_{eff}$ = 1/2 Mott state using Kerr rotation following excitation with either mid-infrared 9 μm (below the charge gap), or near-infrared 1.3 μm (above the charge gap) circularly polarized pulses. For both pump wavelengths, the 2D in-plane $B_2g$ coherent magnon oscillation of frequency...
~0.5 THz is observed. In this talk, we show that the excitation pathways are different for these two excitation wavelengths. In particular, coherent magnon excitation with 9 μm pulses arises from the inverse Faraday effect that, microscopically, is related to two-magnon processes. Notably, coherent magnon generation with 9 μm pulses is nearly an order of magnitude more efficient in comparison to 1.3 μm pulses, without excitation of carriers across the Mott gap.

Acknowledgement: This research is supported by the Army Research Office MURI grant ARO W911NF-16-1-0361, “Floquet engineering and metastable states.”

6:00 AM S.NM07.03.06
Ultra-Thin van der Waals Crystals as Semiconductor Quantum Wells Samuel Magorrian, Johanna Zultak, Vladimir Falko and Roman Gorbachev; National Graphene Institute, University of Manchester, United Kingdom

The confinement of electrons in semiconductor quantum wells, and the resulting quantization of motion and energy, allows the engineering of electronic band structure and resulting device properties. However, this possibility has remained largely unexplored for the case of ultra-thin two-dimensional (2D) van der Waals crystals. Here, we apply the quantum well concept to 2D materials, using the thickness of exfoliated 2D crystals to control the quantum well dimensions in few-layer indium selenide. This approach allows high-precision control of the subband energies, with their uniformity giving high quality electronic transport properties to the system.

Here, for the first time, we present a comprehensive study of the full subband structure of atomically thin 2D semiconductors, applied to InSe[1]. The subbands of the conduction band are fully mapped using resonance tunneling spectroscopy, in agreement with theoretical density of states calculations. On the valence band side, we map the subbands using photoluminescence excitation (PLE), interpreting the results using theoretical calculations of the optical absorption and comparing them with ARPES data. Further evidence of quantum confinement is explored, including quantum-confined Stark shifts of the subbands on application of a bias across the crystal, and an increase in the binding energy of the excitonic resonance in absorption in the thinnest films is seen.

The analogy between ultra-thin van der Waals crystals and conventional semiconductor quantum wells can be clearly traced, with this work paving the way to the application of 2D materials in infrared and terahertz light sources employing intersubband optical transitions.


6:10 AM S.NM07.03.07
Exciton Polarons in Two-Dimensional Hybrid Metal-Halide Perovskites Ajay Srimath Kandada1,2, Felix Thouin3 and Carlos Silva2; 1Wake Forest University, United States; 2Istituto Italiano di Tecnologia, Italy; 3Georgia Institute of Technology, United States

Owing to strong electronic and dielectric confinement effects, strongly bound two-dimensional excitons are observed in layered hybrid organic-inorganic perovskites[1,2]. Given the relevance of polaronic effects in their 3D counterparts, here we ask if such effects are consequential for excitons in 2D HOIPs. We argue that the peculiar lattice interactions are manifested intrinsically in the exciton spectral structure, which is comprised of multiple non-degenerate resonances with distinct photophysical characteristics[2]. We highlight their population[3] and dephasing dynamics[4] that point to the apparently deterministic role of polaronic effects. We contend that an interplay of long-range and short-range exciton-lattice couplings give rise to exciton polarons, which fundamentally establishes their effective mass and radius, and consequently, their quantum dynamics[2]. Finally, we highlight opportunities for developing rigorous description of exciton polarons in 2D-HOIPs to advance their fundamental understanding as model systems for materials with strong lattice-mediated correlations.

Two dimensional electron gases (2DEG) in graphene\(^1\) and black Phosphorus (bP)\(^2\) have been explored in quantum transport measurements, yet unlike graphene, the optical properties 2DEGs in bP are relatively unknown. The crystal structure of bP is anisotropic\(^3\), so it is a candidate material to exhibit naturally-occurring tunable hyperbolic dispersion. According to calculations\(^4\), plasmons (low energy collective mode excitations) in bP exist in the mid to far-infrared regime and exhibit hyperbolic dispersion and anisotropy in different frequency windows.

In order to probe plasmonic resonances we have performed far-field infrared spectroscopy measurements (with both thermal source and synchrotron beam at ALS, Berkeley) to observe gate-tunable polarized absorption in patterned bP nano-resonators encapsulated with hBN (to prevent oxidation). Ribbons of bP 100-150nm wide were fabricated via electron beam lithography and reactive ion etching, aligned to its two principal crystal axes identified with polarized Raman spectroscopy and characterized with SEM. A vertical Fabry-Perot resonator was also used to enhance the weak plasmonic absorption. Polarized infrared extinction shows clear anisotropy in the 35-50\(\mu\)m regime, along with characteristic Fabry-Perot (F-P) peaks. Finite difference time domain (FDTD) simulations show good agreement with experimental results. However, these measurements are limited by two factors – patterning bP induces scattering centers leading to higher damping; dry etching of bP limits the accessible wave vectors, leading to resonances in the far IR with poor signal to noise ratio. To circumvent these limitations we designed a structure comprised of unpatterned bP (giving much higher quality 2DEGs) placed close to metallic resonators, which can be made at the 30-50nm scale, cladded by hBN spacer layers, enabling excitation of acoustic plasmons. FDTD simulations predict gate-tunable anisotropic/hyperbolic plasmonic resonances in 10-20\(\mu\)m range. Higher order optical modes from the metallic resonators and bP plasmon-hBN phonon coupling are observed. Fabrication techniques for such devices will be discussed, along with characterization techniques like polarized Raman spectroscopy, SEM and two-terminal field effect transport measurements. Also, polarized infrared extinction and its dependence on charge density, duty cycle and hBN spacer thickness will be shown if time permits. Taken together, these optical studies offer a thorough understanding of low energy excitations in bP and suggest the potential for infrared fingerprinting in the THz range.

We report a novel 0D-2D hybrid heterostructure displaying light-driven capacitive charging dynamics through solid state photodoping. We exploit the coupling between indium tin oxide (ITO) nanocrystals and two-dimensional molybdenum disulfide (MoS2) to absorb and directly store the energy of the incoming light as extra charges within the ultra-thin heterostructure. By illuminating this hybrid system with light beyond the bandgap of ITO photo-electrons and holes are generated inside the nanocrystal and rapidly separated from each other. Photo-generated holes are quenched at the surface of the semiconductor and injected into the MoS2 monolayer, which acts as a hole collector. The photo-excited electrons accumulate in the ITO nanocrystal leading to the photodoping of the hybrid nanostructure. Multiple electrons can be excited and permanently stored displaying the behavior of a light-driven miniaturized capacitor. During the photodoping process we detect variations in the relative contributions of excitons and trions to the emission of 2D-MoS2: while the overall photoluminescence peak shifts over time to higher energies the exciton population is enhanced and the trion population suppressed. We extract the temporal evolution of the free carriers in the MoS2, which mimics the charging kinetics of a capacitive system. Further studies unveiled that the solid state photodoping process occurs over two main timescales, with most of the variations happening in the first 30 seconds and remaining established after the photoexcitation is switched off. Moreover, by probing the system with light at different wavelengths we identify two distinct processes competing with each other: one reversible due to the interaction between the MoS2 and air molecules and one irreversible due to the injection of extra holes transferred from the ITO nanocapacitors. Quantitative analysis suggests that each nanocrystal can store, in average, 40 optically generated electrons and that the p-type photodoping of 2D MoS2 reaches values compatible with electrostatic gating. These studies present an innovative step towards a light-driven hybrid 0D-2D nanocapacitor, opening prospects for the development of new solutions to directly store the solar energy.

6:50 AM #S.NM07.03.12
Ultrafast Manipulation of Surface Transport in Topological Insulators by Mid-Infrared and Terahertz Pulses Jigang Wang; Iowa State Univ and Ames Lab, United States

The demand for disorder-tolerant quantum logic and spin electronics can be met by generating and controlling dissipativeless spin currents protected by topology. Dirac fermions with helical spin-locking surface transport offer a way of achieving such goal. Yet a challenge remains on how to selectively control surface helical spin transport and surface-bulk coupling. Here we use the mid-infrared and terahertz (THz) photoexcitation of intraband transitions and/or coherence optical phonons to enable ultrafast manipulation of surface THz conductivity in a topological insulator. We will also discuss how to extend the ultra-broadband, wavelength-selective pumping to emerging topological semimetals. Imposing electronic and vibrational coherence into topological matter may become a universal light control principle for reinforcing the protected quantum transport.

7:05 AM #S.NM07.03.13
Many-Body Contributions to the Valley-Selective Optical Stark Effect in Monolayer WS2 Paul D. Cunningham1, Aubrey Hanbicki1,2, Thomas L. Reinecke1, Kathleen M. McCrery1 and Berend T. Jonker1; 1U.S. Naval Research Laboratory, United States; 2University of Maryland, United States

Valley pseudo-spin and broken inversion symmetry leads to valley-specific optical and transport properties in monolayer transition metal dichalcogenides (TMDC). Selective population of the degenerate K and K’ valleys via right- and left-hand circularly polarized light has fueled interest in the potential of TMDCs for Valleytronic applications, where the momentum state is manipulated to perform logical operations.

Intense circularly polarized light fields can break the valley degeneracy, allowing the energy levels of each valley to be independently tuned via a valley-selective form of the optical Stark effect.1,2 These strong light-matter interactions have historically been described by a two-level dressed-atom picture, which works well for semiconductors far from resonance where the Rabi frequency is larger than the exciton formation rate. Recently, the need to extend this model to include the additional energy levels associated with intervalley biexcitons has been demonstrated,3 however the basic assumption of non-interacting particles remained. Here, we report that this assumption is not applicable for excitation near resonance in monolayer WS2,4 where an excitonic model5 of the optical Stark effect that includes many body effects is required.

We use ultrafast transient absorption spectroscopy to show that the valley-selective optical Stark effect produces a blue shift for both below- and above-resonant excitation.4 This coherent light-matter interaction is inconsistent with the two-level dressed-atom picture, which predicts a change in the direction of the optical Stark shift when tuning through resonance.
Instead, our observations are well described by an excitonic model of the optical Stark effect that includes exciton-exciton interactions in addition to the exciton photon interaction. Here, we confirm the prediction from this theory that repulsion between virtual excitons will be the dominant contribution to the optical Stark effect when the excitation wavelength is detuned from resonance by less than the exciton binding energy. This observation demonstrates the need to include many-body Coulomb effects when describing the optical Stark effect in low-dimensional semiconductors that support bound excitons.

References

7:15 AM *S.NM07.03.15
Optical Control of Interlayer Exchange Interaction and Tunneling through Floquet States Wang-Kong Tse; University of Alabama, United States

Floquet states are photon-dressed electronic states that emerge when driven by a time-periodic optical excitation. The presence of these states changes the equilibrium picture of electronic transitions into one where transitions between Floquet states are allowed. We have recently studied the indirect exchange (RKKY) interaction between ferromagnetic chains mediated by itinerant electrons that are driven strongly out of equilibrium by circularly polarized light. Emergence of non-equilibrium Floquet states leads to new and qualitatively different regimes of RKKY coupling, in which the sign (ferromagnetic or antiferromagnetic) and the period of the RKKY oscillation become tunable through the frequency and amplitude of the laser. Another phenomenon where Floquet driving plays a distinctive role is the tunneling dynamics in a tunneling junction. We have investigated the tunneling current between graphene layers under strong polarized radiation, predicting periodic suppression of the photon-assisted tunneling current when the bias voltage is equal to integer multiples of the photon frequency. Our findings on these Floquet systems demonstrate the feasibility of optically controlling the indirect exchange interaction and tunneling in van der Waals materials with coherent laser fields.

7:30 AM S.NM07.03.16
Tuning the Kinetic Energy of Pulsed Laser Deposition Plasmas to Selectively Convert Atomically Thin Transition Metal Dichalcogenides and Form Janus Monolayers Yu-Chuan Lin1, Yiling Yu1, Chenze Liu1,2, Eva Zarkadoula1, Mina Yoon1, Alexander Puretzky1, Iliia N Ivanov1, Christopher Rouleau1, Harry Meyer1, Matthew Chisholm1, Gerd Duscher1,2, Kai Xiao1 and David B. Geohegan1; 1Oak Ridge National Laboratory, United States; 2The University of Tennessee, Knoxville, United States

Janus two-dimensional (2D) materials present a new form of quantum materials predicted to exhibit topological phases and the Rashba-type spin-orbit-coupling. Despite the fact that Janus monolayers have now been experimentally realized, the reliable synthesis of these metastable materials requires precise synthetic control. Pulsed laser deposition (PLD) plasma plumes offer hyperthermal kinetic energies that have been used for decades to synthesize thin films of many materials and are currently being explored for the growth of 2D transition metal dichalcogenides (TMDC) in metastable phases, alloys, and heterostructures. Here, we demonstrate PLD for the selective replacement of sulfur by selenium in monolayer (ML) WS2 crystals at low (250-600 °C) temperatures to form 2D Janus TMDCs. Using in situ plasma diagnostics, the kinetic energy of Se species generated by pulsed laser ablation of Se targets was moderated in the < 20 eV/atom range by collisions with inert Ar atoms in order to determine the thresholds for top- and bottom-layer selenization of monolayer WS2 crystals on both TEM grids and SiO2/Si substrates. Subsequent analysis by Z-contrast STEM images, XPS, PL, and Raman spectroscopy were used to measure the degree of alloying and confirm the Janus monolayer formation as a function of kinetic energy, revealing discrete kinetic energy thresholds: (1) for irreparable damage to the monolayers, (2) for replacement of S atoms on both the top and bottom of the monolayer to enable full or partial conversion into WSe2; and (3) for the selective replacement of only the top S atoms (facing the Se beam), enabling the formation of high-quality Janus WSeS and MoSeS monolayers. The experimental thresholds are consistent with both density functional theory calculations of energy barriers for Se migration through WS2, and with molecular dynamic simulations the selenization process. The generalization of this synthetic approach to many other Janus monolayer systems will be described. Synthesis science was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division. Characterization science at CNMS was supported by the Scientific User Facilities Division, BES.
Disorder-induced magnetoresistance (MR) effect is quadratic at low perpendicular magnetic fields and linear at high fields. This effect is technologically appealing, especially in the two-dimensional (2D) materials such as graphene, since it offers potential applications in magnetic sensors with nanoscale spatial resolution. However, it is a great challenge to realize a graphene magnetic sensor based on this effect because of the difficulty in controlling the spatial distribution of disorder and enhancing the MR sensitivity in the single-layer regime. Here, we report a room-temperature colossal MR of up to 5,000% at 9 T in terraced single-layer graphene. By laminating single-layer graphene on a terraced substrate, such as TiO₂ terminated SrTiO₃, we demonstrate a universal one order of magnitude enhancement in the MR compared to conventional single-layer graphene devices. Strikingly, a colossal MR of >1,000% was also achieved in the terraced graphene even at a high carrier density of ~10¹² cm⁻². Systematic studies of the MR of single-layer graphene on various oxide- and non-oxide-based terraced surfaces demonstrate that the terraced structure is the dominant factor driving the MR enhancement. Our results open a new route for tailoring the physical property of 2D materials by engineering the strain through a terraced substrate.

5:00 AM S.NM07.04.01
Characteristics of Interlayer Charge-Transfer in Correlated Oxide Heterostructures Ganesh Ji Omar and Ariando Ariando; National University of Singapore, Singapore

Electronic devices in the form of high mobility conducting channel with charge carriers can be regulated through the internal charge transfer or chemical doping. Using interlayer interaction through the internal charge transfer to control functional heterostructures with atomic-scale design has become one of the most effective interface-engineering strategies nowadays. Here, we demonstrate the effect of a crystalline LaFeO₃ buffer layer on amorphous and crystalline LaAlO₃/SrTiO₃ heterostructures with different characteristic length of interlayer charge transfer. The LaFeO₃ buffer layer acts as an energetically favored electron acceptor in both LaAlO₃/SrTiO₃ systems, resulting in modulation of interfacial carrier density and hence metal-to-insulator transition. For the amorphous and crystalline LaAlO₃/SrTiO₃ heterostructures, the corresponding metal-to-insulator transition is found when the LaFeO₃ buffer layer thickness crosses 3 and 6 unit cells, respectively. Such different critical LaFeO₃ thicknesses are explained in terms of distinct characteristic lengths of the redox-reaction-mediated and polar-catastrophe-dominated charge transfer, controlled by the interfacial atomic contact and Thomas-Fermi screening effect, respectively. Our results not only shed light on the complex interlayer charge transfer across oxide heterostructures, but also establish a new route to precisely tailor the charge-transfer process at a functional interface by atomically engineered buffer layers.

5:10 AM S.NM07.04.02
Magnetic Field Induced Berezinskii-Kosterlitz-Thouless Correlations in Three-Dimensional Manganites Subray Bhat¹, Bhagyashree KS¹ and Arjun Ashoka²; ¹Indian Institute of Science, India; ²University of Cambridge, United Kingdom

Ideal two-dimensional (2D) Heisenberg magnets lack long range order [1]. However, the XY model with spins confined to a plane shows a topological phase transition at a finite temperature corresponding to binding and unbinding of vortices [2,3]. Experimental evidence for such Berezinskii-Kosterlitz-Thouless (BKT) transitions has been difficult to obtain in condensed matter systems, where, even a weak interlayer coupling that is invariably present leads to long-range order, pre-empting the BKT transition. The BKT signatures are still discernible above the long-range ordering temperature, however, in the characteristic exponential temperature dependence of the coherence length of the fluctuations. In this work we report that an applied magnetic field can induce such BKT correlations not only in quasi 2-dimensional systems but also in nominally 3-dimensional manganites undergoing antiferromagnetic transitions. We arrive at this unexpected conclusion based on our studies of temperature dependence of electron spin resonance (ESR) linewidth ΔH(T) of Cr⁺⁺ doped bismuth strontium manganese Bi₁₀₋₅Sr₅₋₂Mn₁₋ₓCrₓO₃ (x = 0.04, 0.1) (BSMCO).
BSMCO [4] belongs to the family of mixed valent manganites of the type ReAMnO$_3$ where Re is a trivalent rare earth ion or Bi$^{3+}$ and A is a divalent alkaline earth ion, which are intensely studied in the last few years [5]. $\Delta H(T)$ provides the most important probe to study the spin interactions in these strongly correlated spin systems. We find that $\Delta H(T)$ observed in BSMCO (current work), as well as in La$_{0.5}$Ca$_{0.5}$MnO$_3$ and CaMnO$_3$ [6] is better (than the usually adopted critical state model) described by the BKT scenario which predicts [7]

$$\Delta H_{\text{BKT}}(T) = \Delta H_\infty \exp \left[ 3b/(T/T_{\text{BKT}} - 1)^{0.5} \right] + mT + \Delta H_{\text{int}}, \ T > T_{\text{BKT}}$$

where $T_{\text{BKT}}$ is the BKT transition temperature and $b = \pi/2$ for a square lattice and the last two terms are included to account for the high temperature and temperature independent behaviour. This is unexpected as these manganites have a 3D structure and the BKT model addresses systems with spin and spatial dimensions of two. We understand this result in terms of an effective symmetry reduction induced by i) the magnetic field applied in the ESR experiment and ii) the intrinsic anisotropy arising from microscopic details such as doping and phase separation - contributing to an effectively 2-dimensional XY easy plane anisotropy. Nanometric scale spin clusters similar to the ones observed in La doped CaMnO$_3$ [8] could conceivably play the role of vortices in these 3D materials. The sensitivity of the BKT behaviour to applied field is also supported by a re-analysis of the field dependence of the $\Delta H(T)$ in the quasi-2D antiferromagnetic compound BaNi$_2$V$_2$O$_8$ reported by Heinrich at al., [9]. For undoped manganites we find $T_{\text{BKT}}$ is of the order of the magnetic interaction energy, suggesting that the applied field could be the sole origin of the BKT behaviour [10]. We shall also address the interesting observation that in BSMCO (x=0.04, 0.1), $T_{\text{BKT}}$ is composition-independent while the magnetic properties are quite sensitive to composition.

SVB and AA thank the Indian National Science Academy, the National Academy of Sciences, India and the Indian Academy of Sciences for support.

References:

5:25 AM S.NM07.04.03

Magnetic Properties of Proton Irradiated van der Waals Mn$_3$Si$_2$Te$_6$ Luis M. Martinez$^1$, Rubyann Olmos$^1$, Hector Iturriaga$^1$, Lin Shao$^2$, Yu Liu$^3$, Cedomir Petrovic$^3$ and Srinivasa Rao Singamaneni$^1$; $^1$The University of Texas at El Paso, United States; $^2$Texas A&M University, United States; $^3$Brookhaven National Laboratory, United States

Van der Waals (vdW) magnetism is the topic of intense research interest in the community of 2D magnetic materials. Proton irradiation is an effective tool in controlling the magnetic properties of vdW magnets by modifying the spin-lattice coupling. In the present work, the magnetic properties of vdW magnet, such as Mn$_3$Si$_2$Te$_6$ (MST) have been studied at varying proton irradiation fluences of 1x10$^{15}$, 5x10$^{15}$, 1x10$^{16}$, and 1x10$^{18}$ H+/cm$^2$. The magnetization changes more prominently in the ferrimagnetic region (temperature < 74 K, where the saturation magnetization ($M_S$) reaches a maximum value of 25.1 emu/g (53% increase) at the fluence of 5x10$^{15}$ H+/cm$^2$ and decreases with further increase in the fluence. Electron Paramagnetic Resonance (EPR) spectroscopy was used to probe whether proton irradiation caused defects that may alter the magnetic properties of MST. From the EPR measurements taken at 80 K and 50 K, no signals corresponding to defects arose from the pristine and all the fluence rate spectra except for two intrinsic Mn signals. Raman spectroscopy suggests a change in the in-plane Tellurium vibrational modes, as reflected from a similar trend between the $M_S$ and the Raman $E_g$ peak. Additionally, XPS spectroscopy shows a decrease in the Te 3d5 peaks' intensity as the fluence changes. The changes observed in the $M_S$ are suggested to come from the modified Mn-Te interactions through spin-lattice coupling.

5:35 AM S.NM07.04.04

Multi-Frequency Electron Spin Resonance Studies of van der Waals Layered CrX$_3$ (X = Cl, Br, I) Christian Saiz$^1$, Sohan Hennadige$^1$, Michael A. McGuire$^2$, Fazel Fallah Tafti$^3$, Johan van Tol$^4$ and Srinivasa Rao Singamaneni$^1$; $^1$The University of Texas at El Paso, United States; $^2$Oak Ridge National Laboratory, United States; $^3$Boston College, United States; $^4$Florida State University, United States
van der Waals layered magnets such as CrX₃ (X = Cl, Br, I) have received a great deal of research excitement in the recent past due to their exfoliable nature and layer dependent magnetic properties, as well as their potential applications in future data storage devices. Interestingly, these compounds reveal strong halogen size dependent magnetic properties due to the introduction of strong spin-orbit coupling as one moves from Cl to I. This variation can be perfectly captured by employing electron spin resonance (ESR) spectroscopy, which is highly sensitive to underlying magnetic interactions. In this work, we report the ESR properties of these compounds such as g-value, line broadening, and signal intensity as a function of microwave frequency (9-240 GHz), temperature (4-500 K), and angle of rotation (0-360°). We compare and contrast the ESR properties of these three compounds and discuss their two-dimensional correlations across the magnetic ordering temperature, magnetic exchange interactions, and spin dynamics. The experimental findings collected from this work will have greater implications in understanding the few-layer magnetism in these materials, which is being intensely researched in the 2D magnetism community.

SESSION S.NM07.05: Charge Density Waves and Superconductivity
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM07

5:00 AM *S.NM07.05.01
Controlling Charge Density-Wave States in Single-Layer Transition-Metal Dichalcogenides Phil King; University of St Andrews, United Kingdom

Control over materials thickness down to the single-atom scale has emerged as a powerful tuning parameter for manipulating not only the single-particle band structures of solids, but increasingly also their interacting electronic states and phases. A particularly attractive materials system in which to explore this is the transition-metal dichalcogenides, both because of their naturally-layered van der Waals structures as well as the wide variety of materials properties which they are known to host. Yet, how their interacting electronic states and phases evolve when thinned to the single-layer limit remains a key open question in many such systems. Here, we use angle-resolved photoemission to investigate the electronic structure and charge density wave (CDW) phases of monolayer TiSe₂, TiTe₂, and VSe₂ epitaxial thin films grown by molecular-beam epitaxy.¹ Three-dimensionality is a core feature of the electronic structure of all of these parent compounds, but we show how their CDW phases not only persist, but are strengthened, in the monolayer limit. In TiSe₂, we observe a strong-coupling and orbital-selective CDW, necessarily without a kₓ-selectivity in band hybridisation that is of key importance for the bulk instability.² TiTe₂ is driven into a charge-ordered phase in the monolayer which is not stable in the bulk at all, but our measurements indicate that it is a much weaker-coupling instability than for the Se-based sister compound. In VSe₂, we show how the monolayer hosts a much stronger-coupling CDW instability than for the bulk compound, which in turn drives a metal-insulator transition, removing a competing instability to ferromagnetism.³ We show how ferromagnetism can, however, be re-established via proximity coupling.⁴ Together, these studies point to the delicate balance that can be realized between competing interacting states and phases in monolayer transition-metal dichalcogenides, and suggest new strategies for controlling these.

This work was performed in close collaboration with M.D. Watson, A. Rajan, K. Underwood, J. Feng, D. Biswas, W. Rahim, D.O. Scanlon, G. Vinai, G. Panaccione and colleagues from the Universities of St Andrews, Oxford, Keil, UCL, Diamond, Elettra, and SOLEIL.

¹ Rajan et al., arXiv:1910.03307
³ Feng et al., Nano Lett. 18 (2018) 4493

5:15 AM *S.NM07.05.02
Fluctuations in Quantum Materials—From Skyrmions to Superconductivity Joshua J. Turner¹,²; ¹Stanford University, United States; ²SLAC National Accelerator Laboratory, United States

Quantum materials offer not only a vast array of potential for technological advancement, but also provide a testbed for the laws of nature in condensed matter. One area to advance the frontier in this area is through the measurement of fast,
spontaneous fluctuations of quantum order. This is at the heart of the essential physics in these types of solids, but has remained largely unexplored. The key component we use is the application of a newly developed coherent scattering method which can access these fluctuations on the relevant energy scales. This new tool has been demonstrated on a topological magnetic material, and early results point to the tremendous potential for this approach to provide important new insight into fundamental open questions in condensed matter. It allows for the direct, element-specific and momentum-resolved measurement of the fluctuations of a complex material and to connect them to the requisite response functions calculated from first principles. By analyzing subtle X-ray variations known as "speckle", statistics is used to extract the stochastic fluctuation information of the system. This offers the ability to address a range of important current problems in materials. In this talk, we will first discuss the newly developed tools which are used to measure the material properties, based on short pulses from an x-ray free electron laser. We will then present how this has been applied to skyrmions and the measurement of nanosecond fluctuations. This will be followed by an examination of new results on skyrmion physics near the critical point of the skyrmion ordered lattice phase. We will end with an outlook of how this progress can help to tackle the question of fluctuations in unconventional superconductors.

This work at SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, through the Materials Sciences and Engineering Division, contract DEAC02-76SF00515. J. J. Turner acknowledges support from the U.S. Department of Energy, Office of Science, Basic Energy Sciences through the Early Career Research Program.

SESSION S.NM07.06/S.NM09.05: Keynote Session: Strong Correlation in Low-Dimensional Materials of TMPS3

5:00 AM *S.NM07.06/S.NM09.05.01
Strong Correlation in Low-Dimensional Materials of TMPS3 Je-Geun Park1,2; 1Institute for Basic Science (IBS), Korea (the Republic of); 2Seoul National University, Korea (the Republic of)

One of the most pressing questions in condensed matter physics is how electron correlations play out on two-dimension. For this question, the newly emerged magnetic van der Waals material can be helpful. In particular, TMPS3 with TM=transition metal elements have attracted significant attention as it exhibits all three fundamental magnetic models of magnetism; Ising (FePS3), XY (NiPS3) and Heisenberg (MnPS3) Hamiltonian. Using these materials, we have studied some of the fundamental theorems of modern magnetism: Onsager solution for the Ising model, The Berezinskii–Kosterlitz–Thouless transition for the XY model, and Mermin-Wagner theorem for the Heisenberg model. Besides, we have also investigated how correlation physics plays a role in optical spectroscopy data. In this talk, I will demonstrate how we can use this unique magnetic property of these materials to learn of the old physics.

5:15 AM *S.NM07.06/S.NM09.05.02
Keynote: Topological Defects in Twisted van der Waals Interfaces Philip Kim; Harvard University, United States

Controlling the interlayer twist angle in artificial two-dimensional (2D) van der Waals (vdW) heterostructures offers an experimental route to create moire superlattice. One can create exotic electronic states by minimizing electronic band width with tunable moire length scale. However, in the small twist angle regime, vdW interlayer interaction can cause significant structural reconfiguration at the interface, creating the arrays of domain structures. In this presentation, we will discuss the atomic reconstruction at twisted vdW interfaces and its effect on electronic structure and electrical transport behavior. Furthermore, we note that multiple domain boundaries at the reconstructed interface join together to create energetically unfavorable nodes forming vortex-like structures. We will discuss our recent efforts to understand the topological nature of those defects.
S.NM07.10.01
Pressure Induced Magnetic Properties of Crystal Cobalt-Ferrite  Dawn S. Blazer¹, Kinjal Gandha², Hector Iturriaga¹, Rubyann Olmos¹, Denis Prodius², Srinivasa Rao Singamaneni¹ and Cajetan Nlebedim²; ¹The University of Texas at El Paso, United States; ²Ames Laboratory, United States

Hydrostatic pressure is an effective way in tuning the physical properties of materials. This study examines the impact of hydrostatic pressure on the magnetic properties of 3-d transition metal oxide; CoFe₂O₄. The high cubic magnetocrystalline anisotropy, coercivity, moderate saturation magnetization, chemical stability, wear resistance, electrical insulation, and photo magnetic properties of CoFe₂O₄ have resulted in its study for engineering applications. The ease with which cobalt ferrite can be synthesized makes it suitable for scientific investigations and also increases its potential for cost-effective engineering applications. Our results show that the coercive field is decreased from 1600 Oe to 1000 Oe upon the application of 0.2 GPa, and the saturation magnetization is decreased from 91 emu/g to 88 emu/g, measured at cryogenic temperatures (4 K). The modification in the magnetic exchange interaction upon the application of pressure is believed to alter the magnetic properties. We will present our results based on magnetic experiments collected as a function of pressure (0-1 GPa), temperature (4-400 K), and magnetic field (3T).

S.NM07.10.02
Phase Transitions in Novel Li-Containing Honeycombs, Li₈Cr₂(Te/Sb)₂O₁₂  Hector C. Mandujano¹, Sandra L. Gonzalez¹, Narayan Poudel², Krzysztof Gofryk², Stuart A. Calder³ and Harikrishnan S. Nair¹; ¹The University of Texas at El Paso, United States; ²Idaho National Laboratory, United States; ³Oak Ridge National Laboratory, United States

Octahedral layers of metal atom separated and charge-compensated by alkali-metal ions have the ideal architecture to be used as electrodes for Li-ion batteries, ionic conductors, and visible light photocatalysts. Li₈M₂(Te/Sb)₂O₁₂ (M = transition metal) are relatively new members of this class. Forming honeycomb frameworks, they present interesting magnetic phenomena related to frustrated two-dimensional lattices of spins. In the present work, polycrystalline Li₈Cr₂Sb₂O₁₂ were synthesized by standard solid-state route. Powder X ray diffraction patterns were recorded to check the phase formation and purity. C₂/hm space group was confirmed using Rietveld analysis and lattice parameters are determined to be a = 5.141 Å, b = 8.884 Å, c = 5.143 Å, β = 109.5 Å for Li₈Cr₂Sb₂O₁₂, and a = 5.128 Å, b = 8.850 Å, c = 5.151 Å, β = 109.8 Å for Li₈Cr₂Te₂O₁₂, presenting diminished unit cell sizes compared to that of Li₈Co₂Te₂O₁₂ are a = 5.226 Å, b = 8.892 Å, c = 5.160 Å, β = 110.9 Å. In the case of Li₈Cr₂Sb₂O₁₂ a magnetic phase transition is present at 7.4 K as determined from the derivative, dC/dT. A similar transition is found in Li₈Co₂Te₂O₁₂ at 9.5 K. Neutron diffraction is underway for comprehending cationic ordering, crystal, and magnetic structure of Li₈Cr₂(Te/Sb)₂O₁₂ as well as its mixed occupancy of the 4g Wyckoff position in the C₂/hm space group. Our experimental results will highlight the magnetism of the honeycomb layers of Cr and the ionic diffusion of inter-layer Lithium and will be of interest to magnetism as well as battery research.

S.NM07.10.03
Fluence Dependent Magnetic Properties of Proton Irradiated CrSiTe₃  Hector Iturriaga¹, Rubyann Olmos¹, Dawn S. Blazer¹, Luis M. Martinez¹, Samir A. Muniz¹, Kinjal Gandhi², Cajetan Nlebedim², Yu Liu³, Cedimir Petrovic³, Lin Shao⁴, Qiang Wang⁵ and Srinivasa Rao Singamaneni¹; ¹The University of Texas at El Paso, United States; ²Ames Laboratory, United States; ³Brookhaven National Laboratory, United States; ⁴Texas A&M University, United States; ⁵West Virginia University, United States

Proton irradiation as a means of modifying the magnetic properties of layered van der Waals (vdW) materials has considerable, yet unexplored potential. Although vdW crystals display strong correlation and stability, their susceptibility to various kinds of stimuli promotes research into the flexible control of magnetism via proton irradiation for various applications. In this study, layered ferromagnetic vdW CrSiTe₃ (CST) crystals were subjected to proton irradiation at fluences ranging from 10¹⁶ to 10¹⁸ protons/cm². Low-temperature and isothermal magnetometry was conducted with a Quantum Design MPMS 3 on both pristine and irradiated samples. Direction dependent isothermal magnetization confirms the presence of magnetocrystalline anisotropy, with a stable easy axis along the in-plane direction. Furthermore, at the fluence of 5 x 10¹⁶ protons/cm², we have observed a 35% increase in saturation magnetization from 25 emu/g to 34 emu/g at T = 2 K. We will present and discuss our experimental findings on saturation magnetization, coercive field, magnetocrystalline anisotropy, and Curie temperature on proton irradiated CST.
S.NM07.10.04

Pressure Dependent Magnetic Properties of CrBr₃ Bulk Crystals
Rubyann Olmos¹, Hector Iturriaga¹, Kinjal Gandha², Cajetan Nlebedim², Fazel Fallah Tafti³ and Srinivasa Rao Singamaneni¹; ¹University of Texas at El Paso, United States; ²Ames Laboratory, United States; ³Boston College, United States

The van der Waals (vdWs) class of materials offer a new approach for two-dimensional magnetism allowing spin fluctuations to be tuned upon exfoliation of layers. The magnetic properties with pressure are investigated for the highly anisotropic MX₃ (M = Cr, V; X = Cl, Br, I) family. A clear understanding of the bulk magnetic structure and its tunability can be used as a means towards predicting material properties upon exfoliation. As research on pressure induced magnetic properties of exfoliated CrX₃ is at its nascent stage, hydrostatic pressure as a probe to induce a change in magnetic properties is employed in this study of bulk CrBr₃. Furthermore, pressure studies on CrI₃, VI₃, and Cr₂Ge₂Te₆ have appeared in literature reporting that pressure can modify the spin-lattice coupling and long-range magnetic order, however, the origin of magnetic behavior and whether pressure increases or decreases the long-range magnetic ordering is under debate. This study as a whole will take a deeper look into characterizing the magnetic properties of these crystals to understand the underlying magnetic behavior. Results for CrBr₃ upon the application of 0.4 and 0.8 GPa show a decrease in magnetization with no significant change in Curie temperature (T_C) with pressures of 0, 0.4, 0.8 GPa with T_C = 33, 32, 31 K, respectively. In the future, further insight will be collected by looking at the local electronic and magnetic structure of these materials by employing x-ray magnetic circular dichroism (XMCD) (Cr L₂,3 edge) measurements upon the application of pressure (0-10 GPa). In this work we will present all comprehensive experimental findings.

S.NM07.10.05

Magnetism in the Honeycomb Layers of Na₂Ni₂TeO₆ with Chiral Layers of Na
Nathan C. Episcopo¹, Kinley Wangmo¹, Narayan Poudel², Krzysztof Gofryk², Po-Hao Chang¹, Rajendra R. Zope¹, Ryan Klein³, Craig Brown⁴, Thomas W. Heitmann⁵ and Hari Nair¹; ¹The University of Texas at El Paso, United States; ²Idaho National Laboratory, United States; ³Ames Laboratory, United States; ⁴Boston College, United States; ⁵University of Missouri Research Reactor, United States

Low dimensional magnetic lattices offer the possibility of realizing flatbands in the magnon spectrum which can then lead to dissipation-less spin transport and associated magnon Hall effect. One could expect to find a magnon insulator, similar to a topological insulator. In the present work we present a rather less-studied honeycomb material Na₂Ni₂TeO₆ where our preliminary density functional theory calculations of magnetic structure shows departures from reported structures. Our samples of Na₂Ni₂TeO₆ confirmed hexagonal P6/mcm space group with refined lattice parameters, a=5.2023(1)Å and c=11.1552(8)Å. The bulk magnetism for the present sample is characterized using magnetic susceptability and specific heat, both of which confirm a phase transition at 28 K. Application of 8 T magnetic field only slightly polarizes the transition. We obtain a Curie-Weiss temperature of -9.7(2)K and effective paramagnetic moment of 2.24(4)mB/Ni. This matches well with the spin-only moment of Ni²⁺. Elastic and inelastic neutron scattering experiments are currently underway and reveal a rather flat spin wave excitation at 5 meV. Combining neutron diffraction with the DFT results, we would arrive at an accurate estimation of the exchange constants for Na₂Ni₂TeO₆.

S.NM07.10.06

Thermodynamically Driven Stacking of All-Inorganic Perovskite Nano-Sheets
Jacob Lee and Rajesh Sardar; Indiana University Purdue University Indianapolis, United States

The discovery of atomically thin carbon sheets known as graphene in 2004 has prompted intense scientific research on synthesizing and characterizing two-dimensional (2D) nanomaterials. It has been demonstrated both experimentally and theoretically that the 2D confinement of electrons offer distinct optoelectronic properties unlike their corresponding bulk materials including band-gap tunability and improved charge transport properties. Over the last 15 years several types of 2D nanomaterials such as metal oxides, transition metal dichalcogenides, layered metal hydroxides, and MXenes have been extensively studied. More recently organic-inorganic hybrid perovskite 2D sheets have been synthesized and characterized for their use in solution-processable photovoltaic devices. Perovskites possess defect tolerant electronic properties, wide band gap control, and large absorption coefficients necessary for many applications; however, lead free compositions along with combining 2D syntheses and assemblies need further research to reduce environmental toxicity. Cs₃Bi₂X₉ (X=Cl, Br, and I) is a perovskite family material with a hexagonal crystal structure. Herein, we report the synthesis of Cs₃Bi₂X₉ nanosheets with specific halide control by a low temperature colloidal synthetic method, for the first time. UV-visible absorption spectroscopy and powdered X-ray diffraction (XRD) characterizations, along with electron microscopy (EM) analyses, shows formation of atomically-thin perovskite nanosheets. EM analyses also observed formation of stacked nanosheets as superlattice structures. Furthermore, we conducted small angle X-ray scattering techniques to provide an in-depth study of the factors such as the
van der Waals forces induced from core stoichiometry, crystal structure, and ligand-ligand interactions between sheets impacting the self-assembly of 2D nanosheets into larger stacked superstructures. We hypothesize that these superstructures are self-assembled mainly through ligand-ligand interactions. The unique properties of the perovskite family, in combination with the well-studied benefits of 2D nanomaterials, suggest that our 2D Cs$_3$Bi$_2$X$_9$ will display well-controlled optoelectronic and charge transport properties leading to advanced solid-state device applications.

S.NM07.10.08
Particulate Mass Tracking with Ruggedized Nanoparticle Tracers for Explosive Events Lance Hubbard, Clara Reed, Nie Uhnak, Trevor Cell, Nathaniel Smith, Ryan Sumner, Martin Liezers, Michael Foxxe and April Carman; Pacific Northwest National Laboratory, United States

Tracing the flow of particulate matter through harsh conditions (such as a chemical explosions) requires a rugged tag that can be measured by a unique, identifiable signature. Small semiconductor core-shell particles of ZnS@CdSe provide a unique, tunable photoluminescent signature that can be adjusted by the material’s composition and core/shell thickness. The particles have been ruggedized by the growth of a silica layer around the quantum dots (QDs) that acts as a sacrificial layer during finite periods of elevated temperatures and pressures. Incorporating the QDs into a matrix allows for the identification of the debris by its unique photoluminescence. The silicated QD-bound powders were suspended in a hydrated silica gel pending incorporation into temperature-resistant paints and synthetic stone. Initial explosive testing of the tags embedded in enclosures and concrete showed the deposition and movement of particles based on size. The incorporation of temperature-resistant QD-bound powders has enabled unique identifiers, which allows for the tracking of mass through explosive events and other inaccessible environments.

SESSION S.NM07.07/S.EL06.06: Keynote Session: Light-Matter Interaction in Two-Dimensional Semiconductors
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM07

5:00 AM *S.NM07.07/EL06.06.01
Keynote: Light-Matter Interaction in Two-Dimensional Semiconductors Vinod Menon; City College and Graduate Center of CUNY, United States

Owing to their large oscillator strength and strong exciton binding energy, two-dimensional (2D) transition metal dichalcogenides (TMDs) have emerged as an attractive material platform for studying strong light-matter coupling and associated phenomena. Following up on our previous work on strong light-matter coupling in 2D TMDs [1, 2], here we will present results on enhancing the nonlinear interaction between the quasiparticles (exciton-polaritons). This is achieved using excited states of excitons (Rydberg states) which have larger Bohr radii. We will also present our recent results on controlling the valley pseudospin via the pseudomagnetic fields in optical cavities and our work on realizing an electrically pumped polariton LED [3]. Finally, we will first present our work on realizing single photon emitters (SPEs) in hexagonal boron nitride (hBN), a van der Waals material, via strain engineering [4] and coupling of these SPEs to high Q silicon nitride microresonators [5].


SESSION S.NM07.08: Neutron and X-Ray Scattering
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM07

2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
5:00 AM *S.NM07.08.01
Non-Equilibrium Effects in Quantum Magnets
Kate Ross and Steffen Saeubert; Colorado State University, United States

The study of non-equilibrium properties of quantum phases of matter is important in the context of future quantum technologies, since all devices operate in the non-equilibrium limit. Theoretically, the transverse field Ising model (TFIM) and its disordered variants provide a tractable platform to study effects of quantum quenches (a rapid variation of a non-thermal parameter, leading to interesting transient effects), or quantum annealing (a slow variation of a non-thermal parameter, leading to efficient optimization). While there is enormous theoretical interest in these ideas, they have not yet been thoroughly tested on real Ising magnetic systems. There are well-known magnetic material realizations of the TFIM, CoNb2O6 and LiHoYF4, which display quantum critical points in accessible transverse magnetic field ranges. We have studied these materials following various protocols of time variation of the magnetic field, using ac susceptibility and neutron scattering as probes. I will discuss the non-equilibrium effects we have observed in these TFIM materials.

5:15 AM S.NM07.08.03
Effect of Proton Irradiation on the Magnetocaloric Effect and Critical Phenomena of Transition Metal Trichalcogenides
Jose A. Delgado1, Rubyann Olmos1, Luis M. Martinez1, Christian Saiz1, Lin Shao2, Yu Liu3, Cedomir Petrovic3 and Srinivasa Rao Singamaneni1; 1University of Texas at El Paso, United States; 2Texas A&M University, United States; 3Brookhaven National Laboratory, United States

Proton irradiation as a form of defect engineering is used to inhibit the crystal structure of van der Waals crystals in order to provoke a change in the magnetic properties. In this study, the magnetocaloric effect, heat capacity, and critical behavior of transition metal trichalcogenides as a function of proton irradiation were analyzed for Mn3Si2Te6, Fe2.7GeTe3, and CrSiTe3. The crystals were irradiated at fluences of 1x1015, 5x1015, 1x1016 and 1x1018 H+/cm2 with a 2 MeV beam. Following proton irradiation, the Curie temperatures (TC) were obtained experimentally using heat capacity and magnetization as a function of temperature, and by critical exponent analysis. Critical exponents were calculated using the Kouvel-Fisher model and modified Arrott plot. In this work, the correlation between proton irradiation and the resulting critical behavior, magnetocaloric effect, and Curie temperatures will be discussed.

5:25 AM *S.NM07.08.04
Local Site Magnetic Susceptibility on Quantum Materials by Polarized Neutron Diffraction
Huibo Cao; Oak Ridge National Laboratory, United States

Understanding the interactions leading to magnetic quantum phenomena in a wide range of quantum materials is extremely important for development of new quantum materials and future technologies. Although neutron scattering is a powerful tool for this purpose, it also faces a range of challenges, such as the lack of sizable high-quality crystals, limited high pressure capabilities, and the difficulty in disentangling the intrinsic quantum phenomena versus effects from defects and site-disorder. Recently we have introduced the local magnetic susceptibility methods for studying quantum materials, which can be used for small crystals and powder samples. A single crystal neutron diffractometer DEMAND at the High Flux Isotope Reactor at the Oak Ridge National Laboratory has been upgraded for studying magnetic materials under various extreme sample environment conditions. In this talk, I will introduce the local site magnetic susceptibility methods, the current capabilities at the DEMAND, and our recent studies on two-dimensional quantum materials.

5:40 AM S.NM07.08.05
Nonequilibrium Synthesis of Mismatched 1T' Transition Metal Dichalcogenide Alloys for 2D Topological Insulators
Hui Cai, Yiling Yu, Raymond R. Unocic, Kunlun Hong, Alexander Puretzky, Wonhee Ko, Christopher Rouleau, David B. Geohegan and Kai Xiao; Oak Ridge National Laboratory, United States

Transition metal dichalcogenides (TMDC) are an emerging class of quantum materials because they are 2D topological insulators in the 1T' phase and Weyl semimetals in the Td phase. To optimize the properties of these materials, synthetic methods to tune their Fermi level and bulk gap opening are necessary. This can be realized by synthesizing alloys with a wide range of adjustable compositions. Mismatched alloys, such as MoS2-xTex, are alloys formed by elements far away from each other in the periodic table. Due to the large mismatch in atomic radius and electronegativity, a small addition of the alloying element can induce dramatic modifications in the electronic structure of the material. However, such immiscible alloys are hard to synthesize as bulk crystals by conventional crystal growth methods, especially in metastable phases such as the 1T'
Here, we report the bottom-up synthesis of 2D MoS$_2$-Te$_x$ mismatched alloys in the 1T' phase by chemical vapor deposition through non-equilibrium methods. We introduce K$^+$ during the synthesis to grow the 1T' phase, followed by fast cooling to stabilize this phase to room temperature. With this approach, MoS$_{2-x}$Te$_x$ alloys can be grown on various substrates including mica, sapphire and gold. The 1T' structure of the flakes are confirmed by Raman spectroscopy and scanning transmission electron microscopy. Our results open new opportunities in tailoring the structure and properties of quantum materials by alloying mismatched elements through non-equilibrium synthesis.

Research is sponsored by the U.S. Dept. of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Div. (synthesis science) and Scientific User Facilities Div. (characterization science).

5:50 AM *S.NM07.08.08

Ultrafast Energy- and Momentum-Resolved Dynamics of Magnetic Correlations in the Photo-Doped Iridates

Mark P. Dean; Brookhaven National Laboratory, United States

Measuring how the magnetic correlations evolve in doped Mott insulators has greatly improved our understanding of the pseudogap, non-Fermi liquids and high-temperature superconductivity. Recently, photo-excitation has been used to induce similarly exotic states transiently. However, the lack of available probes of magnetic correlations in the time domain hinders our understanding of these photo-induced states and how they could be controlled. This talk will describe our implementation of magnetic resonant inelastic X-ray scattering at free-electron lasers to directly determine the magnetic dynamics after photo-doping the Mott insulators Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$ [1-3]. We find that the non-equilibrium states host strong 2D magnetic correlations even in cases where 3D long-range magnetic order is completely suppressed [1]. The marked difference in these 2D and 3D timescales implies that the dimensionality of magnetic correlations is vital for our understanding of ultrafast magnetic dynamics. We also uncover distinct differences in the magnetic dynamics between insulators Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$, which we attribute to a “spin-bottle-neck” effect [3].

SESSION S.NM07.09: Theory, High Magnetic Fields and Optical Properties

On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

S-NM07

5:00 AM *S.NM07.09.01

Spin Excitations in Magnetic 2D van der Waals Materials—Nonlocal Electron Correlation Effects

Liqin Ke; Ames Laboratory, United States

The recent experimental realization of magnetic two-dimensional van der Waals (m2DvdW) materials has generated significant interest in exploiting such systems for novel 2D magnetism and for developing applications such as energy-efficient ultra-compact spin-based electronics. A better understanding of the magnetic interactions in these systems may help to accelerate the discovery of materials with higher magnetic ordering temperatures, moving these novel systems closer to practical applications. Using linear-response ab initio methods, we investigate the magnetic interactions and spin excitations in various m2DvdW systems, such as CrI$_3$, CrGeTe$_3$, VI$_3$, and Fe$_3$GeTe$_2$. Dynamical transverse spin susceptibility is calculated to directly compare with available Inelastic Neutron Scattering (INS) measurements. Accurate descriptions of electronic structure can provide reliable predictions of electronic and magnetic properties. Due to confinement, electrons in these 2D systems are likely to be strongly correlated, and electron screening anisotropic, so that their description may require advanced ab initio methods beyond density functional theory (DFT). Therefore, we also use the quasiparticle self-consistent GW (QSGW) method, a self-consistent many-body perturbation method, to describe the electronic structure and calculate magnetic properties. In contrast to DFT, the electron-electron interaction is evaluated explicitly by calculating the dynamically-screened Coulomb interaction W. We found that the nonlocal electron correlations, which are not included in methods such as DFT+U, have profound effects on the electronic and magnetic properties in these m2DvdW materials. A more elaborate description of electron interactions helps better describe the magnetic interactions in these 2D quantum systems. By comparing the electronic structures obtained in QSGW and DFT, we discuss the applicability and limitations of the widely-used DFT+U methods for these systems. We will also discuss the effects of spin-orbit coupling, the Dzyaloshinskii-Moriya interaction, impurities, pressure, and electric fields on the magnetic interactions and excitations in relevant systems.
Control over the interactions between light and matter underlies many classical and quantum applications. In recent years, 2D layered semiconductors have gained prominence for optoelectronics because of their strong excitonic features and capacity for van der Waals assembly in layered heterostructures. Through integration with various photonics devices, the interactions between these materials and light can be tailored and new physical regimes can be achieved, highlighting the importance of understanding photonic dressed states of 2D materials. One of the unique features of monolayer materials such as transition metal dichalcogenides is the valley pseudospin addressable by circularly-polarized light. Understanding how this valley polarization can be manipulated is an exciting goal with implications for devices and quantum information science. Here, I discuss hybrid light-matter dressed states, or exciton-polaritons, in transition metal dichalcogenides embedded in dielectric microcavities. These strongly-coupled polaritons preserve the valley pseudospin known from bare monolayers [1]. Distinct behavior of valley-polarized exciton-polaritons can be accessed with microcavity engineering by tuning system parameters such as cavity decay rate and exciton-photon coupling strength. In the opposite dressed state regime of weak light-matter coupling, intense off-resonant light can be used to shift energy levels though the Stark effect [2]. Applied to valley-sensitive states, this shift can be used for coherent manipulation of valley pseudospin. I will show how this approach can be translated to valley-selective exciton-polaritons. Cavity reflectance spectra exhibit a simultaneous shift of both polariton branches when ultrafast coincident pump and probe pulses are co-circularly-polarized, and no appreciable shift when they are cross-polarized. This valley-selective polariton Stark shift combines both dressed state regimes of strong, near resonant interactions with weak, off-resonant optical interactions, providing a new tool for state control in coherent valleytronics. Exploiting photonic dressed states can be viewed as another approach in the toolbox for manipulating the optoelectronic properties of 2D materials and their heterostructures.

This work was supported by DOE (DE-SC0012130) and ONR (N00014-16-1-3055).


Intrinsically two-dimensional materials have a variety of properties that make them attractive for potential topological devices, but the electronic and topological properties of this class of materials remains under-explored. Using density functional theory-based spin-orbit spillage, Wannier-interpolations, and related techniques, we identify topologically non-trivial intrinsic 2D materials in several classes, include magnetic and non-magnetic materials, as well as insulators and semimetals. Using JARVIS-DFT 2D material dataset we first identify materials with high spin-orbit spillage among 683 materials resulting in 108 materials with high-spillage values. Then we use Wannier-interpolation to carry-out Z2, Chern-number, anomalous hall conductivity, Curie temperature surface and edge state calculations to identify topological insulators and semimetals such as quantum spin-hall and anomalous-hall insulators (QSHI, QAHI), magnetic and non-magnetic semimetals. For a subset of predicted QAHI materials, we run GW+SOC and GGA+U calculations. We find that as we introduce many-body effects only few materials retain non-trivial band-topology suggesting the importance of high-level DFT methods in predicating 2D topological materials. However, as an initial step, the automated spillage screening and Wannier-approach provide useful predictions for finding new topological materials.

In metals, orbital motions of conduction electrons on the Fermi surface are quantized in magnetic fields, which is manifested by quantum oscillations in electrical resistivity. This Landau quantization is generally absent in insulators. Here we report a notable exception in an insulator — ytterbium dodecaboride (YbB12). The resistivity of YbB12 exhibits distinct quantum oscillations despite having a much larger magnitude than in metals. This unconventional oscillation is shown to arise from the insulating bulk, even though the temperature dependence of the oscillation amplitude follows the conventional Fermi liquid theory of metals. The large effective masses indicate the presence of a Fermi surface consisting of strongly correlated
electrons. Quantum oscillations are also observed in the magnetization of YbB$_{12}$. Our result reveals a mysterious dual nature of the ground state in YbB$_{12}$: it is both a charge insulator and a strongly correlated metal.

5:55 AM *S.NM07.09.07
Excitons in Nanophotonic Landscapes—Fluctuating, Diffusing, Annihilating Alberto G. Curto; TU/e – Eindhoven University of Technology, Netherlands

Excitons in two-dimensional semiconductors exhibit rich dynamics. Their fluorescence is sensitive to the nanoscopic environment. They are confined in the vertical direction while extending and diffusing along the atomically thin plane. Excitons can also interact with each other, notably to reduce light emission at high densities through exciton-exciton annihilation.

In this presentation, first, we will demonstrate that an atomically thin semiconductor can display substantial temporal fluctuations in fluorescence intensity influenced by its environment. We show blinking and flickering synchronized over monolayer domains tens of micrometers in size. We analyze the fluctuation statistics to draw analogies with blinking in conventional quantum dots.

Second, we will discuss strategies to increase the amount of photons emitted by a 2D semiconductor based on nanophotonic enhancement. We study how exciton diffusion impacts fluorescence enhancement using nanophotonic structures. As mobile excitons diffuse through optical hotspots, the careful balance of diffusion constants and nanophotonic geometry can lead to enhanced or suppressed fluorescence. Finally, we investigate the effect of nanophotonic enhancement on exciton-exciton annihilation.

Our results open new vistas for nanoscale photonics and optoelectronics with atomically thin semiconductors. Controlling exciton dynamics in the form of fluctuations, diffusion, or annihilation has direct implications for stable single-photon sources, molecular sensors based on excitonic fluorescence, or high-power light-emitting devices.

SESSION S.LP03.04: Live Poster Session: Nanoscale and Quantum Materials (S.NM07, S.NM09, S.NM10 and S.NM12)
Session Chairs: Christianne Beekman, Yuanyue Liu and Srinivasa Rao Singamaneni
Tuesday Afternoon, December 1, 2020
1:45 PM - 3:45 PM
S.NM07

S.NM07.10.01
Pressure Induced Magnetic Properties of Crystal Cobalt-Ferrite Dawn S. Blazer$^1$, Kinjal Gandha$^2$, Hector Iturriaga$^1$, Rubyann Olmos$^1$, Denis Prodous$^3$, Srinivasa Rao Singamaneni$^1$ and Cajetan Nlebedim$^2$; $^1$The University of Texas at El Paso, United States; $^2$Ames Laboratory, United States

Hydrostatic pressure is an effective way in tuning the physical properties of materials. This study examines the impact of hydrostatic pressure on the magnetic properties of 3-d transition metal oxide; CoFe$_2$O$_4$. The high cubic magnetocrystalline anisotropy, coercivity, moderate saturation magnetization, chemical stability, wear resistance, electrical insulation, and photo magnetic properties of CoFe$_2$O$_4$ have resulted in its study for engineering applications. The ease with which cobalt ferrite can be synthesized makes it suitable for scientific investigations and also increases its potential for cost-effective engineering applications. Our results show that the coercive field is decreased from 1600 Oe to 1000 Oe upon the application of 0.2 GPa, and the saturation magnetization is decreased from 91 emu/g to 88 emu/g, measured at cryogenic temperatures (4 K). The modification in the magnetic exchange interaction upon the application of pressure is believed to alter the magnetic properties. We will present our results based on magnetic experiments collected as a function of pressure (0-1 GPa), temperature (4-400 K), and magnetic field (3T).

S.NM07.10.02
Phase Transitions in Novel Li-Containing Honeycombs, Li$_8$Cr$_2$(Te/Sb)$_2$O$_{12}$ Hector C. Mandujano$^1$, Sandra L. Gonzalez$^1$, Narayan Poudel$^2$, Krzysztof Gofryk$^2$, Stuart A. Calder$^3$ and Harikrishnan S. Nair$^4$; $^1$The University of Texas at El Paso, United States; $^2$Idaho National Laboratory, United States; $^3$Oak Ridge National Laboratory, United States

Octahedral layers of metal atom separated and charge-compensated by alkali-metal ions have the ideal architecture to be used as electrodes for Li-ion batteries, ionic conductors, and visible light photocatalysts. Li$_8$M$_2$(Te/Sb)$_2$O$_{12}$ ($M =$ transition metal)
are relatively new members of this class. Forming honeycomb frameworks, they present interesting magnetic phenomena related to frustrated two-dimensional lattices of spins. In the present work, polycrystalline Li₈Cr₂(Te/Sb)₂O₁₂ were synthesized by standard solid-state route. Powder X-ray diffraction patterns were recorded to check the phase formation and purity. C₂m space group was confirmed using Rietveld analysis and lattice parameters are determined to be a = 5.141 Å, b = 8.884 Å, c = 5.143 Å, β = 109.5 Å for Li₈Cr₂Sb₂O₁₂, and a = 5.128 Å, b = 8.850 Å, c = 5.151 Å, β = 109.8 Å for Li₈Cr₂Te₂O₁₂, presenting diminished unit cell sizes compared to that of Li₈Co₂Te₂O₁₂ are a = 5.226 Å, b = 8.892 Å, c = 5.160 Å, β = 110.9 Å. In the case of Li₈Cr₂Sb₂O₁₂ a magnetic phase transition is present at 7.4 K as determined from the derivative, dCp/dT. A similar transition is found in Li₈Co₂Te₂O₁₂ at 9.5 K. Neutron diffraction is underway for comprehending cationic ordering, crystal, and magnetic structure of Li₈Cr₂(Te/Sb)₂O₁₂ as well as its mixed occupancy of the 4g Wyckoff position in the C₂m space group. Our experimental results will highlight the magnetism of the honeycomb layers of Cr and the ionic diffusion of inter-layer Lithium and will be of interest to magnetism as well as battery research.

S.NM07.10.03
Fluence Dependent Magnetic Properties of Proton Irradiated CrSiTe₃ Hector Iturriaga¹, Rubyann Olmos¹, Dawn S. Blazer¹, Luis M. Martinez¹, Samir A. Muniz¹, Kinjal Gandhi², Cajetan Nlebedim³, Yu Liu³, Cedomir Petrovic³, Lin Shao⁴, Qiang Wang⁵ and Srinivasa Rao Singamaneni¹; ¹The University of Texas at El Paso, United States; ²Idaho National Laboratory, United States; ³Brookhaven National Laboratory, United States; ⁴Texas A&M University, United States; ⁵West Virginia University, United States

Proton irradiation as a means of modifying the magnetic properties of layered van der Waals (vdW) materials has considerable, yet unexplored potential. Although vdW crystals display strong correlation and stability, their susceptibility to various kinds of stimuli promotes research into the flexible control of magnetism via proton irradiation for various applications. In this study, layered ferromagnetic vdW CrSiTe₃ (CST) crystals were subjected to proton irradiation at fluences ranging from 10¹⁶ to 10¹⁸ protons/cm². Low-temperature and isothermal magnetometry was conducted with a Quantum Design MPMS 3 on both pristine and irradiated samples. Direction dependent isothermal magnetization confirms the presence of magnetocrystalline anisotropy, with a stable easy axis along the in-plane direction. Furthermore, at the fluence of 5 x 10¹⁶ protons/cm², we have observed a 35% increase in saturation magnetization from 25 emu/g to 34 emu/g at T = 2 K. We will present and discuss our experimental findings on saturation magnetization, coercive field, magnetocrystalline anisotropy, and Curie temperature on proton irradiated CST.

S.NM07.10.04
Pressure Dependent Magnetic Properties of CrBr₃ Bulk Crystals Rubyann Olmos¹, Hector Iturriaga¹, Kinjal Gandhi², Cajetan Nlebedim², Fazel Fallah Tafti³ and Srinivasa Rao Singamaneni¹; ¹University of Texas at El Paso, United States; ²Ames Laboratory, United States; ³Boston College, United States

The van der Waals (vdWs) class of materials offer a new approach for two-dimensional magnetism allowing spin fluctuations to be tuned upon exfoliation of layers. The magnetic properties with pressure are investigated for the highly anisotropic MX₃ (M = Cr, V; X = Cl, Br, I) family. A clear understanding of the bulk magnetic structure and its tunability can be used as a means towards predicting material properties upon exfoliation. As research on pressure induced magnetic properties of exfoliated CrX₃ is at its nascent stage, hydrostatic pressure as a probe to induce a change in magnetic properties is employed in this study of bulk CrBr₃. Furthermore, pressure studies on CrI₃, V1₃, and Cr2Ge2Te6 have appeared in literature reporting that pressure can modify the spin-lattice coupling and long-range magnetic order, however, the origin of magnetic behavior and whether pressure increases or decreases the long-range magnetic ordering is under debate. This study as a whole will take a deeper look into characterizing the magnetic properties of these crystals to understand the underlying magnetic behavior. Results for CrBr₃ upon the application of 0.4 and 0.8 GPa show a decrease in magnetization with no significant change in Curie temperature (Tc) with pressures of 0, 0.4, 0.8 GPa with Tc = 33, 32, 31 K, respectively. In the future, further insight will be collected by looking at the local electronic and magnetic structure of these materials by employing x-ray magnetic circular dichroism (XMCD) (Cr L2,3 edge) measurements upon the application of pressure (0-10 GPa). In this work we will present all comprehensive experimental findings.

S.NM07.10.05
Magnetism in the Honeycomb Layers of Na₃Ni₃TeO₆ with Chiral Layers of Na Nathan C. Episcopo¹, Kinley Wangmo¹, Narayan Poudel¹, Krzysztof Gofryk², Po-Hao Chang¹, Rajendra R. Zope¹, Ryan Klein², Craig Brown², Thomas W. Heitmann³ and Hari Nair¹; ¹The University of Texas at El Paso, United States; ²Idaho National Laboratory, United States; ³National Renewable Energy Laboratory, United States; ⁴National Institute of Standards and Technology, United States; ⁵University of Missouri Research Reactor, United States
Low dimensional magnetic lattices offer the possibility of realizing flatbands in the magnon spectrum which can then lead to dissipation-less spin transport and associated magnon Hall effect. One could expect to find a magnon insulator, similar to a topological insulator. In the present work we present a rather less-studied honeycomb material Na$_2$Ni$_2$TeO$_6$ where our preliminary density functional theory calculations of magnetic structure shows departures from reported structures. Our samples of Na$_2$Ni$_2$TeO$_6$ confirmed hexagonal $P6_3/mcm$ space group with refined lattice parameters, $a=5.2023(1)\,\text{Å}$ and $c=11.1552(8)\,\text{Å}$. The bulk magnetism for the present sample is characterized using magnetic susceptibility and specific heat, both of which confirm a phase transition at 28 K. Application of 8 T magnetic field only slightly polarizes the transition. We obtain a Curie-Weiss temperature of $-9.7(2)\,\text{K}$ and effective paramagnetic moment of $2.24(4)\,\mu_\text{B}/\text{Ni}$. This matches well with the spin-only moment of Ni$^{2+}$. Elastic and inelastic neutron scattering experiments are currently underway and reveal a rather flat spin wave excitation at 5 meV. Combining neutron diffraction with the DFT results, we would arrive at an accurate estimation of the exchange constants for Na$_2$Ni$_2$TeO$_6$.

S.NM07.10.06
Thermodynamically Driven Stacking of All-Inorganic Perovskite Nano-Sheets Jacob Lee and Rajesh Sardar; Indiana University Purdue University Indianapolis, United States

The discovery of atomically thin carbon sheets known as graphene in 2004 has prompted intense scientific research on synthesizing and characterizing two-dimensional (2D) nanomaterials. It has been demonstrated both experimentally and theoretically that the 2D confinement of electrons offer distinct optoelectronic properties unlike their corresponding bulk materials including band-gap tunability and improved charge transport properties. Over the last 15 years several types of 2D nanomaterials such as metal oxides, transition metal dichalcogenides, layered metal hydroxides, and MXenes have been extensively studied. More recently organic-inorganic hybrid perovskite 2D sheets have been synthesized and characterized for their use in solution-processable photovoltaic devices. Perovskites possess defect tolerant electronic properties, wide band gap control, and large absorption coefficients necessary for many applications; however, lead free compositions along with combining 2D syntheses and assemblies need further research to reduce environmental toxicity. Cs$_3$Bi$_2$X$_9$ (X=Cl, Br, and I) is a perovskite family material with a hexagonal crystal structure. Herein, we report the synthesis of Cs$_3$Bi$_2$X$_9$ nanosheets with specific halide control by a low temperature colloidal synthetic method, for the first time. UV-visible absorption spectroscopy and powdered X-ray diffraction (XRD) characterizations, along with electron microscopy (EM) analyses, shows formation of atomically-thin perovskite nanosheets. EM analyses also observed formation of stacked nanosheets as superlattice structures. Furthermore, we conducted small angle X-ray scattering techniques to provide an in-depth study of the factors such as the van der Waals forces induced from core stoichiometry, crystal structure, and ligand-ligand interactions between sheets impacting the self-assembly of 2D nanosheets into larger stacked superstructures. We hypothesize that these superstructures are self-assembled mainly through ligand-ligand interactions. The unique properties of the perovskite family, in combination with the well-studied benefits of 2D nanomaterials, suggest that our 2D Cs$_3$Bi$_2$X$_9$ will display well-controlled optoelectronic and charge transport properties leading to advanced solid-state device applications.

S.NM07.10.08
Particulate Mass Tracking with Ruggedized Nanoparticle Tracers for Explosive Events Lance Hubbard, Clara Reed, Nic Uhnak, Trevor Cell, Nathaniel Smith, Ryan Sumner, Martin Liezers, Michael Foxe and April Carman; Pacific Northwest National Laboratory, United States

Tracing the flow of particulate matter through harsh conditions (such as a chemical explosions) requires a rugged tag that can be measured by a unique, identifiable signature. Small semiconductor core-shell particles of ZnS@CdSe provide a unique, tunable photoluminescent signature that can be adjusted by the material’s composition and core/shell thickness. The particles have been ruggedized by the growth of a silica layer around the quantum dots (QDs) that acts as a sacrificial layer during finite periods of elevated temperatures and pressures. Incorporating the QDs into a matrix allows for the identification of the debris by its unique photoluminescence. The silicated QD-bound powders were suspended in a hydrated silica gel pending incorporation into temperature-resistant paints and synthetic stone. Initial explosive testing of the tags embedded in enclosures and concrete showed the deposition and movement of particles based on size. The incorporation of temperature-resistant QD-bound powders has enabled unique identifiers, which allows for the tracking of mass through explosive events and other inaccessible environments.

S.NM10.05.02
High Temperature Synthesis of a Crystalline MXene with Ordered Surface Terminations Jacob Pawlik and Daniel Druffel; University of North Carolina, United States
In this work, a new MXene is experimentally described which exhibits uniform functionality on MX layers (-Cl), contrary to the mixed functionality (-F, -O, -OH) of traditional MXenes. Most MXenes contain random surface terminations, arising from the vigorous etching process of the MAX phase with acids such as HF. However, the present MXene Y2CCl2 is synthesized by a direct high temperature method followed by liquid exfoliation, which results in highly crystalline 2D flakes. This MXene has well-defined properties due to single moiety surface terminations, allowing for construction of simple computational models. Previous research in the field highlights the difficulty of predicting properties such as band gap and surface energy due to the unpredictable arrangement of surface terminations and complexity of computational models. A crystalline MXene with ordered terminations offers an easily synthesizeable target with properties that can be predictably tuned.

First, Y2CCl2 was directly synthesized by heating a pellet composed of Y, C, and YCl3 in a sealed tantalum tube at 950°C for 5 days according to literature procedures. Next, density functional theory (DFT) calculations were performed to predict the energy required to exfoliate Y2CCl2 into an MXene. The binding energy of Y2CCl2 (0.14 J/m²) is less than half the binding energy of graphite, indicating that Y2CCl2 should be easier to exfoliate than graphite. A common method for exfoliating graphite is sonication in a liquid with similar surface properties, so the material was sonicated in the polar aprotic solvent propylene carbonate. The mixture quickly forms a well-dispersed solution of 2D Y2CCl2 flakes. Transmission electron microscopy (TEM) shows flakes with lateral sizes of 2-5 µm, and electron diffraction confirms retention of the crystalline Y2CCl2 structure. The optical properties were evaluated by UV-Vis spectroscopy, which reveals an absorption peak at 1.64 eV that is close to the expected band gap of 1.56 eV, calculated using the HSE06 functional. Furthermore, X-ray photoelectron spectroscopy measurements reveal unusual oxidation states associated with yttrium (2+) and carbon (2-), suggesting interesting electrical properties.

This material has several attractive features that may be utilized. Y2CCl2 is easily exfoliated in mild conditions, avoiding the hazards of corrosive media such as HF and HCl. Also, the material absorbs light in the visible, making Y2CCl2 potentially useful for light harvesting and photocatalytic applications. More broadly, Y2CCl2 is part of a larger class of metal carbide halide materials with the stoichiometry M2CX2 (M = Y, Sc, Gd; X = F, Cl, Br, I) that share similar structure and properties. Through preliminary calculations, we predict that other metal carbide halides may be exfoliable and contain similar properties to Y2CCl2. Overall, Y2CCl2 and other similar metal carbide halides offer a new class of MXenes with ordered surface terminations.

S.NM10.05.04
Investigating Chemical Reactivity of MXenes Using Gas Chromatography Shuohan Huang, Gabriel Hulliung and Vadym Mochalin; Missouri University of Science and Technology, United States

MXenes are a new family of two-dimensional (2D) materials discovered in 2011. Because of their 2D structure and many outstanding properties [1], MXenes have raised significant interest for various applications, such as batteries, optoelectronic devices [2], supercapacitors, lasers [3,4], sensors [5], etc. It was found that titanium carbide MXene flakes in aqueous solutions spontaneously transform into TiO2 and recently, it has been demonstrated that water plays the main role in the reactions leading to this chemical transformation [6]. Thus, studying MXene reactivity is important for prolonged shelf life of MXene colloidal solutions, as well as for robust performance of MXene based devices. In this work, we demonstrate the use of gas chromatography technique to study reactivity of MXenes. Several hypotheses have been put forward to explain the degradation of MXenes in aqueous environments. However, no studies of the gaseous products of this reaction have been reported. The analysis of gases produced during MXene degradation, using gas chromatography, allows for a better understanding of the degradation process. The chemical reactivity of MXenes with different monolayer thickness was also investigated at different pH and temperatures. Our results have led to new, important conclusions about the chemical reactivity of MXenes in aqueous solutions. This knowledge will have significant impacts on the development of MXenes and other 2D materials for many applications.

References
S.NM10.05.10
Raman Spectroscopy Reveals the Effect of Synthesis Conditions on Ti3C2
Asia Sarycheva and Yury Gogotsi; Drexel University, United States

Raman spectroscopy has been one of the most helpful tools for analysis of two-dimensional (2D) materials\(^1-2\). While newly discovered materials should be probed using this technique, there have been just a few studies available for a large family of 2D transition metal carbides and nitrides known as MXenes\(^3-5\). To see which effects Raman spectroscopy can detect for MXenes we performed a systematic study of the mostly used MXene to date - Ti3C2Tx. By synthesizing material in different ways, we monitored changes in Raman spectra. we have synthesized Ti3C2 via MILD method, where HF is formed in-situ by mixing LiF and HCl, HF-HCl (mixture of two acids), and by using various concentration of HF: 5%, 10%, 20% and 30% solutions in water\(^3\). We collected Raman spectra from samples collected at different stages of MXene synthesis: from multilayer powders to delaminated flakes, in order to observe the effect of stacking. The whole spectrum of Ti3C2 is divided into 4 regions: a resonant peak, A1g out-of-plane vibrations of Ti, C and O, the surface group vibrations region and carbon vibrations region. Those regions change based on the synthesis method and flake surrounding. All those peaks are affected not only by surface functional groups\(^5\), but also by stacking of the flakes. Due to a plasmonic peak of Ti3C2Tx around 785 nm, resonant conditions\(^6\) are achieved enabling an extra peak at around 119-123 cm\(^{-1}\) when using a red diode laser. Lastly, we showed how photoluminescence, usually considered as an unwanted background of Raman spectra, can be used to detect the early stages of MXene degradation.

**S.NM09.10.01**

Controlling Defects in 2D GaS Continuous Films and Heterostructures for High Performance Wavelength-Tunable Photodetectors

Yang Lu and Jamie Warner; University of Oxford, United Kingdom

The rapid development of two-dimensional (2D) materials calls for the development of novel 2D semiconductors with large bandgap for applications in short-wavelength LEDs, type-I heterojunctions, etc. Gallium sulfide (GaS), a wide-bandgap semiconductor, fulfills these requirements but was not fully explored due to lack of controllable synthesis methods, unexplored layer-dependent properties and unanswered stability issues. Here, to answer these questions, we developed a CVD synthesis method of thickness-controlled (1–4L), uniform and continuous films of both defective GaS and defect-free GaS. A simple method for determination of thickness by Raman spectroscopy is developed. An enhanced stability of the defect-free GaS was demonstrated under laser and strong UV lights, and by controlling defects in GaS, the photoresponse range could be changed from vis-to-UV to UV-discriminating. The defect-free GaS is suitable for large-scale UV-sensitive high-performance photodetector arrays for information encoding under large vis-light noise, with short response time, excellent UV photoresponsivity and a 26-times increase of signal-to-noise ratio compared with small bandgap 2D semiconductors. By comprehensive characterizations from atomic-scale structures to large-scale device performances in 2D semiconductors, we provide insights into the role of defects, the importance of neglected material-quality control and how to enhance device performance. Finally, both layer-controlled defective and defect-free GaS prove to be promising platforms for study of novel phenomena and new applications in WS₂-GaS van der Waals heterojunctions.

**S.NM09.10.02**

Laser-Assisted Accelerated Synthesis of 2D Quantum Materials

Nurul Azam¹, Zabihollah Ahmadi¹, Salah Elafandi¹, Baha Yakupoglu¹, Mengkun Tian², Abdelaziz Boulesbaa³ and Masoud Mahjouri-Samani³; ¹Auburn University, United States; ²Georgia Institute of Technology, United States; ³California State University Northridge, United States

The firmly defined dimensionalities of two-dimensional (2D) layered materials including transition metal dichalcogenides (TMDCs) exposed numerous unusual properties that have been recently at the center of the quantum materials and information sciences research. In pursuit of the accelerated growth and discovery of 2D materials, many efforts have concentrated on developing new approaches including physical and chemical vapor deposition techniques. However, complex, uncontrolled gas-phase reactions, and flow dynamics have made the synthesis of these multi-component 2D crystals exceedingly challenging. This work demonstrates a novel laser-assisted synthesis technique (LAST), which significantly reduces the existing growth complexities and remarkably accelerates the growth of 2D materials. The uniqueness of this approach arises from the direct vaporization technique of stoichiometric powders by the laser heating process. We show that this directed laser heating permits pressure-independent decoupling of the growth and evaporation kinetics, enabling the use of stoichiometric powder as precursors for the growth of various high-quality 2D materials including MoS₂, MoSe₂, WSe₂, and WS₂.

Mr. Nurul Azam is currently a Ph.D. student in the Department of Electrical and Computer Engineering (ECE) at Auburn University (AU). His research in the Laser-Assisted Science and Engineering (LASE), Lab under the supervision of Prof. Mahjouri-Samani, focuses on investigating and developing novel approaches for the synthesis of 2D quantum materials and heterostructures.

**S.NM09.10.11**

Synthesis of Two-Dimensional, Semiconducting Quantum Materials via Chemical Vapor Deposition (CVD)

Daniel S. Choi¹, Evgeniya H. Lock² and Shashi P. Karna³; ¹National Research Council, United States; ²Naval Research Laboratory, United States; ³U.S. Army Research Laboratory, United States

In the past decade, there have been unprecedented advancements in research and development of materials for quantum applications such as ultrasensitive detection, quantum information processing, energy efficient ultrafast electronics, quantum light-emission, and many more that require a fundamental understanding of never-before observed physical and chemical phenomena in known materials. Of these new generation of materials, transition metal dichalcogenides (TMDs) have become attractive candidates for more extensive investigation due to their novel and non-classical behaviors observed at nanoscale as well as potential for their incorporation into devices and applications. For instance, nanoscale TMDs such as tungsten diselenide (WSe₂), tungsten disulfide (WS₂), and molybdenum disulfide (MoS₂) have been shown to exhibit highly localized, intense, quantum emission of single photons that have not been previously observed in their bulk counterparts. While understanding fundamental mechanism and origin, as well as the physical structure of these quantum materials and their properties are crucial, parallel efforts in developing large scale, controlled synthesis of these materials is just as imperative.
Currently, much of the studies on TMD materials for quantum applications have primarily been on larger flakes and crystals, or exfoliated films, which limits scalability of the material production as well as the need for transfer of the exfoliated material onto a suitable substrate.

In this work, we present a systematic synthesis of 2-dimensional, single- to few-layers of transition metal chalcogenides thin film directly on silicon substrate via chemical vapor deposition (CVD). Our approach not only sheds light into understanding the growth mechanism of 2-dimensional TMDs, but also provides optimal growth parameter for consistent, large scale production of these materials. The results presented will provide basis for synthesis of next-generation of 2-dimensional materials as well as shed light into bottom-up building approach of van der Waals heterostructures for quantum applications.

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S.NM09.10.12
Substrate-Mediated Hyperbolic Phonon Polaritons in MoO3 Jeffrey Schwartz1,2, Son T. Le2,3, Sergiy Krylyuk2, Albert Davydov2 and Andrea Centrone2; 1University of Maryland, United States; 2National Institute of Standards and Technology, United States; 3Theiss Research, United States

Hyperbolic phonon polaritons (HPhPs) are hybrid excitations of light and coherent charge oscillations that exist in strongly optically anisotropic 2D materials (e.g., MoO3). These polaritons propagate through the material’s volume with long lifetimes, enabling novel mid-infrared nanophotonic applications by compressing light to sub-diffraction dimensions. Here, the dispersion relations and HPhP lifetimes (up to ≈ 2 ps) in single-crystal α-MoO3 are determined by Fourier analysis of real-space, nanoscale-resolution polariton images obtained with the photothermal induced resonance (PTIR) technique. Measurements of MoO3 crystals deposited on periodic gratings showed longer HPhPs propagation lengths (≈ 2 ×) and lower optical compressions in suspended regions compared to regions in direct contact with the substrate. Additionally, PTIR data reveal polymeric contaminants, resulting from sample preparation, localized under parts of the MoO3 crystals. This work enhances the ability to engineer nanophotonic devices by leveraging substrate morphology to control polariton propagation.

S.NM09.10.13
Anion Charge Density Disturbance Induces In-Plane Instabilities within 2D Lateral Heterojunction of TMD—An Atomic View Bolong Huang; The Hong Kong Polytechnic University, Hong Kong

Two-dimensional (2D) heterostructure semiconductors are emerging as the potential candidates for broad applications, in which the transition-metal dichalcogenides (TMDs) have attracted the most attention due to their abundant advantages. TMDs have attracted tremendous interest due to the advantages of low-cost, earth-abundant, non-toxic, and environmentally friendly. Owing to the atomically thin structure, unique electronic and optical properties and rich diversity in chemical compositions, they have displayed considerable potential in the applications of integrated optoelectronic devices and systems such as p–n diodes, photodetectors, transistors, nanogenerators, and sensors as well as in catalysis. However, the investigations of these TMD heterostructure semiconductors usually only limit to the synthesis approach and opt-electronic properties, lacking the in-depth guidelines from the atomic exploration. Within the lateral heterojunction, the unique ripple effect has been identified as the consequence of the important interplay between different TMDs. Herein, the anion coupling induced charge disturbance within the WSe2/WS2 lateral heterojunction has been identified as the origin for the ripple structure induced by in-plane interfacial instability. Different scales of the first-principle simulations all verify the similar ripple phenomenon near the interfacial region of the WSe2/WS2 lateral heterojunction. Beyond the simple factor of lattice misfit, we confirm that the Se-S p-p coupling effect induced the uneven charge distribution is the intrinsic reason for such a unique structural phenomenon. By the introduction of the perturbation elastic entropy concept, we successfully predict the interfacial ripple scale in the WSe2/WS2 lateral heterojunction systems, supporting the simulation of experimental size. This work has compensated the knowledge gap between the theoretical investigation and experimental synthesis, which is essentially beneficial for the future fabrication of 2D heterostructure semiconductors with superior performance. The fundamentally general mechanism for the experimentally observed phenomenon is of pivotal significance in the further exploration in such 2D heterojunction semiconductor materials.

S.NM09.10.14
Materials for Resonant Passage of Isotopes Aleksey M. Bubenchikov; Tomsk State University, Russian Federation

The method of mathematical modelling is a good tool for constructing new materials [1]. The present work considers the problem which concerns quantum sifting of isotopes of gas components at cryogenic temperatures. The authors also focus on the task of constructing the membrane itself. The calculations show that the
membrane should have two identical ultrathin layers. By now, graphene nitride with regular pores has been synthesized using the double epitaxy method [2]. Mono-atomic layers of porous boron nitride [3] can also serve as the working layer of the membrane. Over the last decade, a group of new graphene-like mono-element 2D materials, such as germanene [4], silicene [5, 6], phosphorus [7], and stanene [8] have also been synthesized. In principle, all porous analogues of these materials are suitable for application as the working layer of the membrane. This appears to be possible since the result of resonant passage of one of the mixture components is largely determined by the distance between the plates.

The considered problem of particles passing through a composite barrier is a generalization of the well-known Landau problem of particles with a certain energy passing through a unitary barrier. When constructing an analytical solution to the generalized problem of wave dynamics, the authors proceeded from the Schrödinger integral equation. The solution was built as a result of dividing the functions containing a shift in the independent variable into a nonlinear differential operator and separated exponential functions of the parameter and the argument. Next, algebraic operations with differential operators were performed, and the resulting operator was applied to separated functions. The resulting solution for the wave function is completely determined by the spectrum of the composite barrier. Studying the asymptotic behaviour of the solution allowed for finding the zeros of the reflection coefficient. As a result, resonance modes of transmission of one of the components were found. These modes were determined by the sequence of resonant distances between the plates. Choosing the distance between the layers from this sequence it is possible to achieve a selectivity effect in which a particle with a mass of $m$ and energy of $E$ passes through a potential barrier consisting of two identical parts without reflection. In other words, one of the components shows complete passage, while the other component is characterized by partial passage only. This ensures operation of the membrane as a gas separator. The calculations show that, at certain temperatures, it is possible to achieve hyperselectivity of mixture separation.

References:

S.NM09.10.16
Synthesis and Study of 1H Structural Phase of Liquid-Exfoliated 2D Lead Iodide Nanodisks Using ADF-STEM Sapna Sinha$^1$, Taishan Zhu$^2$, Arthur France-Lanord$^2$, Yuwen Sheng$^1$, Jeffrey C. Grossman$^2$, Kyriakos Porfyarakis$^1$ and Jamie Warner$^1$; $^1$University of Oxford, United Kingdom; $^2$Massachusetts Institute of Technology, United States

Synthesis and study of new two-dimensional (2D) materials nanosheets is very important for both fundamental study of physical phenomenon as well as for new applications in nanoelectronics and optoelectronics. Lead iodide (PbI$_2$) has been reported to be an excellent candidate for applications in thin films, transistors and PbI$_2$ perovskites. However, not a lot of study has been carried out on easy and facile preparation of this material to produce scalable monolayer films. Liquid phase exfoliation (LPE) is considered to be an efficient method to obtain 2-dimensional nanosheets on a large scale. Based on previous findings on screening solvents for LPE, in this study, I will present results on obtaining several hundreds of >99% monolayer (PbI$_2$) using CHCl$_3$ as a solvent. We have then used atomic-resolution annular dark field scanning transmission electron microscopy (ADF-STEM) imaging to study the monolayer flakes of PbI$_2$. Here, I will report on a new structure of PbI$_2$ which has not been studied before. PbI$_2$, when suspended on graphene, converts into more energetically stable H-phase crystal structure compared to T-phase structure which was found to be more stable on lacy carbon TEM grid. I will also present results on the defects and edge structure of the monolayer PbI$_2$ and the unusually mobile atoms on the surface. The structural change of the PbI$_2$ depending on substrate, i.e. graphene, opens up the possibility to control and further study its properties by using other different kinds of substrates.

S.NM09.10.17
Chemical Vapor Deposition Synthesis of MoS2 Crystal Assisted by HSS/H2 Precursors—A Quantum Molecular Dynamics Study Sungwook Hong; California State University, Bakersfield, United States

Layered van der Waals Heterostructures such as MoS2 monolayers have attracted great attentions for the application in optoelectronic devices owing to their outstanding physical, chemical, and mechanical properties. Chemical vapor deposition (CVD) is commonly used for scalable growth of layered materials. During CVD synthesis, reactions of MoO3 and H2S reactants are essential reaction steps where MoO3 flakes are reduced and sulfurized, transferring to MoS2 crystals. Recent studies suggested that addition of H2 gas in this synthesis process could lead to synthesis of higher-quality MoS2 monolayers. However, effects of H2 partial pressure on synthesis of MoS2 still remain elusive. Here, we present quantum molecular dynamics (QMD) simulations for CVD synthesis of MoS2 layer using MoO3 flakes and H2S gas precursors with and without H2 gas. Our QMD simulations revealed that H2 molecules indeed act as effective reducing agents for the MoO3 flake. As such, our work provides a valuable input for the scalable growth of layered van der Waals Heterostructures.

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S.NM12.12.03
Imaging Spin-Filter (Au/Ir) for Momentum Microscopy Marten Patt1, Nils Weber2, Matthias Escher2, Timna-Joshua Kuehn2, Michael Merkel2 and Brandon Giles1; 1Scienta Omicron GmbH, Germany; 2FOCUS GmbH, Germany

Momentum Microscopy is a new technique in surface science, in which the momentum distribution of photoelectrons is projected onto an image plane. This image plane can be energy-filtered by a double-hemispherical electrostatic analyzer (NanoESCA) to achieve a monochromatic momentum distribution. Scanning the energy along the valence band is then used for band structure mapping which is a key technique to understand the electronic structure of novel materials. A new innovative method is to use the monochromatic electron distribution behind the double-hemispherical analyzer to retard it to the needed scattering energy of an Au/Ir (100) single crystal. This allows for spin-polarization dependent reflection, which enables a highly efficient imaging spin-filter technique [1].

We will show recent band-structure measurements of several TMDCs acquired with the NanoESCA and discuss the latest technical improvements of momentum microscopy with respect to 2D material characterization. First results of the imaging spin-filter installed at the ELI-Alps NanoESCA are shown, demonstrating its efficiency in real-space microscopy (e.g. imaging of magnetic domains) and in spin-resolved band-structure mapping.


SYMPOSIUM S.NM09

Layered van der Waals Heterostructures—Synthesis, Physical Phenomena and Devices
November 21 - November 30, 2020

Symposium Organizers
Zakaria Al Balushi, University of California, Berkeley
Monica Allen, University of California, San Diego
Deep Jariwala, University of Pennsylvania
Amalia Patane, University of Nottingham
SESSION S.NM09.08.02
Strong Magnetophonon Oscillations in Monolayer Graphene—A Spectroscopic Probe of Electron-Phonon Interactions
Mark T. Greenaway1,2, P Kumaravadivel3,3, D Perello3,3, A Berdyugin4, J Birkbeck3,3, J Wengraf3,4, S Liu5, J Edgar5, A Geim3,3, L Eaves2,3 and R Krishna Kumar3; 1Loughborough University, United Kingdom; 2The University of Nottingham, United Kingdom; 3University of Manchester, United Kingdom; 4University of Lancaster, United Kingdom; 5Kansas State University, United States

For more than 50 years, magnetophonon resonance (MPR) has proved to be a powerful tool for investigating electron-phonon interactions in a wide range of elemental and compound semiconductors and heterostructures. Its experimental signature is a series of oscillations in the magnetoresistance, periodic in inverse magnetic field, given by the equation,

\[ p \omega_c = \omega_p, \]

where \( p \) is an integer, \( \omega_c \) is the Landau level splitting and \( \omega_p \) is the phonon frequency. The successful observation of MPR in graphene has proved elusive due, in part, to the relative weak interaction of the massless Dirac Fermions with the lattice phonons.

Here we report the observation of large amplitude, temperature-dependent MPR oscillations in the magnetoresistance of large area, electrostatically gated Hall bars of exfoliated monolayer graphene encapsulated by hexagonal boron nitride (hBN) [1,2]. The oscillations are observed only in devices with a width which exceeds the ballistic carrier mean free path, 5 μm. We observe two distinct series of resonant peaks arising from inelastic scattering by transverse acoustic (TA) and longitudinal acoustic (LA) phonons. The LA phonon resonant amplitude is significantly weaker than that of the TA phonons. This is due, in part, to the carrier screening of the LA phonon modes. The magnetic field values of the resonant peaks are found to shift linearly with carrier sheet density from 10¹² to 10¹³ cm⁻². These experiments also allow us to measure the dispersion curves of the LA and TA phonons up to wavevectors of ~ 10⁹ m⁻¹. We model the experimental data to high accuracy using the Kubo formalism. We demonstrate that the LA and TA phonon speeds and the electron-phonon coupling strengths determined from the magnetophonon resonance measurements provide an excellent fit to the measured dependence of the resistivity at zero magnetic field over a temperature range of 4-150 K. Thus, MPR provides a spectroscopic tool for studying electron-phonon interaction in two-dimensional semiconductors.

Conventional metasurface designs use geometrically fixed structures, or materials with excessive propagation losses, thereby limiting their potential applications. Here demonstrate that this can be overcome through the realization of a reconfigurable hyperbolic metasurface comprising a heterostructure of isotopically enriched hexagonal boron nitride (hBN) in direct contact with the phase-change material (PCM), such as single-crystal vanadium dioxide (VO₂) or GST. Here, the metallic and dielectric domains in PCM provide spatially localized changes in the local dielectric environment that modify the polariton wavelength supported in hBN by a factor of 1.6. Using this platform, we demonstrate the first reduction to practice of in-plane HPPh refractive, and the means for launching, reflecting and transmitting of HPhPs at the PCM domain boundaries. Ultimately, this phenomenon can be used to create planar refractive optics, such as lenses or waveguides, but on length scales far below the diffraction limit. Further, my employing doped semiconductor materials with controllable plasma frequencies, such direct control of hyperbolic polaritons can also be obtained via modification of the free carrier density of the underlying semiconductor.

10:45 AM *S.NM09.03.05
Light Induced Phase Transitions in Halide Perovskites Aditya D. Mohite; Rice University, United States

Organic-inorganic (hybrid) perovskite have recently emerged as a new semiconductor platform for next generation optoelectronics devices. These perovskites solids feature weak bonds between their organic and inorganic building blocks, which results in an intrinsic softness and dynamics disorder of the lattice and an acute sensitivity to external stimuli. Here, we present comprehensive in-situ studies of light induced structural dynamics of in layered two-dimensional (2D) hybrid perovskites. We correlate the changes in the structure of the 2D perovskite to modification of both the physical properties and the figures of merit in solar cells and light emitting devices. We propose a new microscopic model to explain the evolution of the structure and optoelectronic properties under external stimuli. These results demonstrate the direct correlation between structural characterization of halide perovskites under external perturbation and intrinsic physical properties.

11:00 AM *S.NM09.07.04
Wafer-Scale Epitaxy of Transition Metal Dichalcogenides by Gas Source CVD Tanushree H. Choudhury, Mikhail Chubarov, Xiaotian Zhang and Joan M. Redwing; The Pennsylvania State University, United States

Novel electronic and optical properties of monolayer transition metal dichalcogenides (MX₂, M=W, Mo and X=S, Se) have garnered a lot of attention in the recent years. A major challenge to integrating these materials with existing device fabrication processes is the availability of epitaxial single-crystal monolayers over a wafer scale. Our approach focusses on synthesis of these monolayers using gas source precursors, like those used in traditional III-V semiconductor industry. These precursors are placed in temperature and pressure-controlled bubblers placed outside the chamber and can be metered independently into the growth zone with precision. Uniform epitaxial binary TMD monolayers including MoS₂, WS₂, WSe₂ and MoSe₂ have been deposited on 2” sapphire wafers in a cold-wall CVD reactor using metal hexacarbonyl and hydride chalcogen precursors. A multi-step growth process comprising of precursor modulation was developed for WSe₂ to independently control nucleation density and the lateral growth rate of monolayer domains on the sapphire substrate [1]. For the sulfides, additional temperature modulation was introduced to increase crystalline quality. Using this approach, uniform, coalesced monolayer and few-layer TMD films were obtained on 2” sapphire substrates. Deposition of these materials in the same reactor provides insight into the factors controlling their growth, which in essential for the growth of heterostructures and/or alloys. In-plane X-ray diffraction demonstrates that the films are epitaxially oriented with respect to sapphire with narrow X-ray full-width-at-half-maximum indicating minimal rotational misorientation of domains within the basal plane [2]. Transmission electron microscopy analysis of these materials revealed additional information about the coalesced film structure. For instance, ~95 % single oriented WS₂ domains were observed when the film growth rate was modulated. For WS₂, it was also confirmed that despite translational line defects present in the film, mirror boundaries were predominantly absent. WS₂ also showed no defect related photoluminescence peak at 80 K, indicating its high quality. In this talk the factors affecting the growth of TMDs (MX₂, M=W, Mo and X=S, Se) will be presented. The role of the substrate surface in the nucleation and growth of these TMDs will be discussed. In addition, the structural and optoelectronic characteristics for these films will also be presented.

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11:15 AM *S.NM09.07.01
Magnetic Transition Metal Dichalcogenides

Christopher Hinkle; University of Notre Dame, United States

The incorporation of magnetic dopants is a way to realize magnetism in semiconductors. The 2D material WSe₂ is a semiconductor with a bandgap of 1.3 eV, and Fe-doped WSe₂ is predicted to have room temperature, long-range ferromagnetism. Moreover, WSe₂ has been extensively studied for applications in electronic devices, and can be prepared by deposition methods that are compatible with semiconductor fabrication processes. 2D magnetic films are particularly intriguing in technologies that rely on exchange coupling since the efficiency of the exchange with the magnet is inversely proportional to the magnet thickness 1/\ell_{FM}. Chalcogenide-based TMD magnets can also have ideal interfaces with chalcogenide-based topological insulators (like Bi₂Se₃), enabling efficient spin torque devices and potentially realizing the quantum Hall effect without an external magnetic field.

Focusing on materials growth and integration techniques that utilize non-equilibrium, kinetically restricted strategies, coupled with in-situ characterization, enables the realization of atomic configurations and materials that are challenging to make but once attained, display enhanced and unique properties. In this work, we will highlight the growth of Fe-doped WSe₂ and report on its up to room temperature ferromagnetic properties. The evolution of Fe-doped WSe₂ films under different doping levels indicates that strain from the impurity atom itself coupled with strain imparted by the substrate can drive phase separation at high Fe concentrations. We find that suppressing that film strain helps promote more Fe incorporation (and higher Curie temperatures).

Cr₂O₃ has only 0.2% lattice mismatch with WSe₂ and is a magnetoelectric that can couple with ferromagnetic films. By using seed-layer techniques, we successfully prepared layered Fe-WSe₂ on Cr₂O₃ and demonstrate magnetic coupling between the two, a potentially promising route toward realizing electric field control of 2D magnets. Magnetic measurements show a clear hysteresis loop at 100 K in a 2 Tesla cooling field, from which a large negative bias field of 600 Oe is resolved. The bias field vs temperature measurements, where a negative bias field emerges below 250 K, indicates the existence of ferromagnetic exchange coupling in this heterostructure.

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11:30 AM *S.NM09.03.02
Moiré Heterostructure Quantum Emitter Arrays

Brian Gerardot; Heriot Watt University, United Kingdom

Van der Waals heterostructures present unique opportunities to synthesize artificial quantum materials. For example, a slight lattice mismatch or relative rotation between the constituent layers of a hetero-bilayer results in a long-range moiré superlattice which spatially modulates the electronic bandstructure. Single particle wavepackets can be trapped in the periodic potential pockets with three-fold symmetry to form an intrinsic quantum dot lattice. Here I will discuss the properties of such quantum emitter arrays. In a heterostructure of bilayer 2H-MoSe₂ and monolayer WSe₂, we observe two interlayer exciton (IX) species trapped in moiré potentials with distinct spin-layer-valley configurations. Due to the phenomenon of locked electron spin and layer pseudospin in bilayer 2H-MoSe₂, the IX species exhibit opposite valley magnetic moments. Further, we find the 2H-MoSe₂ stacking intrinsically locks the atomic registries of the spin-layer locked IX species together. I will also present photon antibunching of moiré trapped excitons to unambiguously prove their quantum nature. Finally, I will discuss the properties of the moiré quantum emitters under applied electric fields and changing chemical potential.

11:45 AM *S.NM09.08.03
Quantum Devices with 2D Materials

Klaus Ensslin; ETH Zurich, Switzerland

We demonstrate electronic constrictions on bilayer graphene that can be completely pinched off [1]. Split-gate devices in combination with a graphite backgates enable electronic tunability of the devices. The level spectrum of quantum point contacts in bilayer graphene has a peculiar magnetic field dependence quite different from what is known from semiconductors. We understand the details of this spectrum [2] based on the Berry curvature in bilayer graphene.

In few electron and hole quantum dots confined by p-n junctions [3] we investigate valley and spin splitting. Also many electron quantum dots with standard tunneling barriers as well as double and triple quantum dots [4] can be realized with an electronic quality comparable to the best dots fabricated in standard semiconductor environments. The spectrum of excited states in graphene dots is qualitatively different [5] compared to semiconductors because of the valley degree of freedom. These experiments open the door for using graphene quantum dots as spin qubits with potentially long coherence times.

We also discuss the properties of MoS₂ as a host material [6,7] for quantum dot-based qubits.


2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
References

12:00 PM *S.NM09.08.06
Strain Engineering of the Valley Magnetization and Berry Curvature Dipole in 2D Materials
Jieun Lee; Seoul National University, Korea (the Republic of)

The valley degree of freedom in two-dimensional (2D) honeycomb lattices has attracted much recent attention due to its non-trivial Berry curvature effects associated with two nonequivalent valleys. This feature gives rise to many interesting valley-dependent phenomena such as the valley optical selection rule and the valley Hall effect, each of which accessing the valley-dependent electron control using the optical and electrical means. The valley manipulation in these works, however, focus on the control of the electron occupation while the Berry curvature at the two valleys are remained constant. In this talk, we show the mechanical control of the valley degree of freedom which is enabled by the strain engineering of the Berry curvature. By fabricating flexible monolayer MoS2 devices, we reversibly control strain on monolayer MoS2 and demonstrate the generation of the current-induced valley magnetization due to the formation of the Berry curvature dipole. The measured valley magnetization is in excellent agreement with the calculated Berry curvature dipole, which depends on the magnitude and direction of strain. Our results show that the Berry curvature dipole acts as an effective magnetic field in current-carrying systems, providing a novel route to generate magnetization in 2D crystals.

SESSION S.NM09.12: Live Keynote II: Layered van der Waals Heterostructures—Synthesis, Physical Phenomena and Devices
Session Chairs: Monica Allen and Deep Jariwala
Monday Afternoon, November 30, 2020
S.NM09

7:30 PM *S.NM09.03.01
IV-VI van der Waals Materials and Their Properties
Jie Yao1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

Low-dimensional nanomaterials with properties distinctive from their bulk counterparts have been extensively investigated in recent years. Besides the widely explored graphene and transition metal chalcogenides (TMDCs), a new family of van der Waals (vdW) materials composed of group IV and VI elements, especially Ge/Sn monocalcogenides, have attracted great attention in recent years. They have shown strong in-plane anisotropy that is similar to phosphorene (black phosphorous layers), and a number of unique electrical, optical, thermal and mechanical properties. Here I would like to share some of our recent discoveries on this unique family of materials, including their valleytronic behaviors and Eshelby twist formation in crystal growth.

Unlike conventional valleytronic materials where cryogenic temperatures, strong electric or magnetic field are needed to differentiate the valleys, Tin sulfide (SnS) was expected to have non-degenerate valleys with selection rules that are fundamentally different. I will talk about our experimental demonstration of the valley effect in an ambient, and bias-free
model system of SnS and its alloys with other IV-VI materials. We elucidate the direct access and identification of different sets of valleys, based primarily on the selectivity in absorption and emission of linearly polarized light by optical reflection/transmission and photoluminescence measurements, and demonstrate strong optical dichroic anisotropy of up to 600% and nominal polarization degrees of up to 96% for the two valleys with band-gap values 1.28 and 1.48 eV, respectively; the ease of valley selection further manifested in their non-degenerate nature. In addition, the band gap values can be tuned effectively through alloying of SnS with similar materials such as SnSe. Such discovery enables a new platform for better access and control of valley polarization.

The IV-VI material family is also enabling new opportunities from twisting topology generation. Twisting of vdW layers has been shown to provide a new degree of freedom to tailor the electrical and optical properties of vdW crystals. I will talk about the first observation of Eshelby twist in Ge monochalcogenides that results in continuous twisting of multiple vdW layers. We exploit the screw dislocation driven growth of GeS nanowires, with growth direction perpendicular to the vdW layers. Results from comprehensive characterization on the helical vdW crystals agree well with Eshelby’s theory. Moreover, the planar growth of the vdW layers co-exists with the screw dislocation driven growth and leads to radial expansion of the nanowires, which results in discretized Eshelby twists resembling a helical assembly of nanoplates. We attribute the discretization to the change of twist rates of the nanowires in conjunction with a substrate pinning effect. We further show that the twisting topology can be tailored by controlling the radial size of the structure. In these helical crystals, atomically sharp interfaces with various twist angles are created, providing an intriguing tunable platform to explore various interlayer coupling effects in vdW materials.

7:45 PM *S.NM09.08.01
Orbital Magnetism and Quantized Anomalous Hall Effect in Twisted Bilayer Graphene Andrea Young; University of California, Santa Barbara, United States

In moire flat band systems, interlayer moire patterns can be used to engineer isolated superlattice bands in which the Coulomb interaction is comparable to the bandwidth. As in a Landau level, this leads to electron interaction dominated physics despite the low density of electrons, enabling full density control using electrostatic gates. Unlike Landau levels, however, moire flat bands occur under time reversal symmetric conditions. I will discuss experiments that observe the spontaneous breaking of time reversal symmetry, observed as magnetic hysteresis. Remarkably, hysteresis is accompanied by a quantized anomalous Hall effect, persisting to zero magnetic field and elevated temperatures. I will discuss the origins of this effect in the spontaneous orbital polarization of the electron system into a single, topological nontrivial superlattice band, and describe magnetic imaging data that confirms the orbital character of the magnetism.

8:00 PM *S.NM09.01.01
Magnetism and Topology in Graphene-Based Flat Minibands David Goldhaber-Gordon1,2; 1Stanford Univ, United States; 2SLAC National Accelerator Laboratory, United States

Until recently, flat bands were achieved as Landau levels at high magnetic field. Then, Pablo Jarillo-Herrero of MIT and coworkers demonstrated flat minibands in graphene-based superlattices, discovering correlated insulators and superconductors at different fillings. We have now discovered dramatic magnetic states in such systems. Specifically, in magic-angle twisted bilayer graphene also aligned with a hexagonal boron nitride (hBN) cladding layer, we observe a giant anomalous Hall effect and signs of chiral edge states. This all occurs at zero magnetic field, near 3 electrons per moire cell in the conduction miniband [1]. Remarkably, the magnetization of the sample can be reversed by applying a small DC current. Although the anomalous Hall resistance is not quantized, and dissipation is significant, we suggest that the system is an incipient Chern insulator, similar to an integer quantum Hall state. In a different superlattice system, ABC-trilayer graphene aligned with hBN, again near 3 electrons per moire cell a Chern insulator emerges [2]. A magnetic field of order 100 mT is needed to quantize the anomalous hall signal. This trilayer system can be tuned in-situ to display superconductivity instead of magnetism [3]. We will discuss possible magnetic states, and complementary probes to examine which state actually emerges as the ground state in each system.


This research was primarily supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, under contract DE-AC02-76SF00515.
Spontaneous symmetry breaking lies at the heart of the description of interacting phases of matter. Here we argue that a driven interacting system subject to a linearly polarized (achiral) driving field can spontaneously magnetize (acquire chirality). In particular, we find when a metal is driven close to its plasmon resonance, it hosts strong internal ac fields that enable Berryogenesis: the spontaneous generation of a self-induced Bloch band Berry flux, which supports and is sustained by a circulating plasmonic motion, even for a linear polarized driving field. This non-equilibrium phase transition occurs above a critical driving amplitude, and depending on system parameters, can enter the spontaneously magnetized state in either a discontinuous or continuous fashion. Berryogenesis relies on nontrivial interband coherences for electronic states near the Fermi energy generated by ac fields readily found in a wide variety of multiband systems. We anticipate that graphene devices, in particular, which can host high quality plasmons, provide a natural and easily available platform to achieve Berryogenesis and spontaneous non-equilibrium (plasmon-mediated) magnetization in present-day devices, e.g., those based on graphene plasmonics. If we have time, we will also discuss other manifestations of non-trivial quantum geometry in Dirac systems.

The prevalent von Neumann architecture in today’s processors involves memory and processing units to reside in physically separate locations. With memory speeds lagging behind the processor speeds, latency in accessing data from memory has resulted in the “von Neumann bottleneck”. To alleviate this issue, several alternative non-von Neumann architectures have been explored. Neuromorphic computing is one such non-von Neumann approach, inspired by the human brain’s ability of cognitive recognition. The brain operates through a network of neurons that are connected to each other by synapses. In 2008, after the discovery of memristors, the fourth circuit element, researchers have explored the idea of mimicking synaptic behavior with a single memristive device. Albeit significant advances, synaptic devices using phase change materials-based memristors and metal oxide-based resistive switching devices have some limitations. These devices exhibit high programming current in the range of µA to mA. Additionally, the synaptic weight update, i.e. the increase (decrease) of the synapse’s conductance with the application of a continuous stream of identical positive (negative) input voltage pulses, is non-linear. Non-linearity in weight update increases the complexity of using these devices for real-time unsupervised learning. So, it becomes necessary to employ a materials system which exhibits low programming current as well as a linear weight update.

Recently, two-dimensional (2D) materials are being largely explored to demonstrate their viability as electronic synapses and neurons. In this talk, we shall discuss the realization of a synaptic device using graphene/MoS2 heterostructures. In these devices, CVD-grown monolayer graphene acts as an electrode to CVD MoS2. These memristive devices exhibit low programming currents and a high dynamic range from 1 nA to 1 mA. In contrast with oxide-based or PCM-based synapses, these devices exhibit a gradual set and reset process when symmetric input voltage pulses are applied, resulting in a near-linear weight update. Linearity and symmetry in weight update is much desired for real-time learning applications. We shall also present the demonstration of an integrate-and-fire neuron using Ag/MoS2/Au vertical structures. These devices possess the four crucial features of neuron – all-or-nothing spiking, threshold-driven firing, post-firing refractory period and stimulus strength based frequency response. Realizing neurons and synapses using the same materials system allows the monolithic integration of the essential building blocks of neuromorphic hardware, and bears potential for a highly scalable spiking neural networks suitable for unsupervised learning applications.

An indirect exciton (IX), also known as an interlayer exciton, is a bound pair of an electron and a hole confined in spatially separated layers. Due to their long lifetimes, IXs can cool below the temperature of quantum degeneracy. This gives an opportunity to realize and study cold excitons.

We will overview studies of Bose-Einstein condensation of IXs. We will present direct measurements of spontaneous
coherence and condensation of IXs in GaAs heterostructures. We will present phenomena observed in the IX condensate, including the exciton density wave, spin textures, Pancharatnam-Berry phase and long-range coherent spin currents, and interference dislocations.

We will present van der Waals transition-metal dichalcogenide (TMD) heterostructures where IX condensation can be realized at high temperatures. We will present IXs at room temperature and indirect charged excitons, i.e. indirect trions, in van der Waals heterostructures.

SESSION S.NM09.02: Synthesis of van der Waals Heterostructures
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM09

5:00 AM *S.NM09.02.01
Tailoring the Synthesis and Assembly of 2D Materials for Monolayer and Bilayer Heterostructures Kai Xiao1, Yu-Chuan Lin1, Yiling Yu1, Hui Cai1, Xufan Li1, Kai Wang1, Chenze Liu2, Alexander Puretzky1, Gerd Duscher2, Mina Yoon1, Eva Zarkadoula1, Christopher Rouleau1 and David B. Geohegan1; 1Oak Ridge National Laboratory, United States; 2The University of Tennessee, Knoxville, United States

2D layered materials enable the construction of hybrid heterostructures with emergent electronic, optical, and quantum properties resulting from the interplay between the individual nanosheets. However, the synthesis of 2D heterostructures with
controlled twist angles and stackings is still a great challenge which currently limits their development. In this talk, I will discuss our recent work on the synthesis and assembly of 2D heterostructures through non-equilibrium synthesis and processing approaches including isoelectronic doping, atomic implantation, and van der Waals epitaxy. First, by tailoring isoelectronic doping of chalcogens and metals in 2D TMDs (e.g., MoSe₂, WS₂) during CVD synthesis, the uniform alloys, gradient alloys, and lateral heterostructures are controlled grown on substrates which exhibit many novel properties including tunable bandgaps, enhanced photoluminescence, modulated charge carriers, etc. Second, with well controlled kinetic energy of Se clusters impulsed laser deposition (PLD) plasmas, the CVD-synthesized 2D WS₂ crystals are precisely converted to monolayer Janus heterostructure and bilayer heterostructures by laser implantation. Last, I will briefly discuss the vdW epitaxial growth of GaSe/MoSe₂ heterostructures and corresponding gate-tunable photovoltaic properties. The interlayer stacking, interfacial structure and optical properties are characterized by atomic-resolution STEM, Raman and PL spectroscopy. The atomistic origins of the emerging properties of vdW heterostructures, including interlayer excitons, persistent photoconductivity, and gate-tunable photovoltaic response, will be discussed. Our results demonstrate that with nonequilibrium synthesis and processing approaches, 2D heterostructures can be precisely realized for future applications in atomically thin optoelectronics and quantum information science.

Research sponsored by the U.S. Dept. of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Div. (synthesis science) and Scientific User Facilities Div. (characterization science). Throughout the presentation, facilities available for collaboration at the Center for Nanophase Materials Sciences (CNMS) user facility will be presented.

5:15 AM S.NM09.02.02
Epitaxial Growth of Two-Dimensional WSe₂ on Highly Crystalline CVD Graphene Benjamin Huet, Xiaotian Zhang, Mikhail Chubarov, Tanushree H. Choudhury, David Snyder and Joan M. Redwing; The Pennsylvania State University, United States

Co-integrating graphene with other two-dimensional (2D) materials represents an important step toward the development of novel 2D material-based electronic and optoelectronic devices. In order to fully exploit the unique physical properties of graphene and the semiconducting transition metal dichalcogenides (TMDs) in functional applications, it is essential to control the crystallinity, the material sequence, the stacking order or twisting angle, and the interface cleanliness.

In this study, we investigate the direct growth of WSe₂ by gas source chemical vapor deposition (CVD) on top of CVD grown graphene. Isolated millimeter-size graphene crystals are first produced by CVD on Cu foils and then transferred onto fused silica or sapphire which are more compatible with the gas-source CVD process. This graphene template is used as the synthesis substrate for the high temperature growth of WSe₂ using tungsten hexacarbonyl (W(CO)₆) and hydrogen selenide (H₂Se) as precursors.

Using scanning electron microscopy (SEM) and atomic force microscopy (AFM), we compare the nucleation site density, size and shape of WSe₂ crystals grown on single layer graphene, bare C-plane sapphire and bare fused silica. WSe₂ crystals typically exhibit a triangular shape with a lateral size exceeding 1 micrometer.

The nucleation site density of WSe₂ crystals has also been studied as a function of the number of graphene layers and their relative twisting angle. The samples have been characterized by Kelvin probe force microscopy (KPFM), transmission electron microscopy (TEM), and Raman spectroscopy in order to better understand why single-layer graphene leads to a lower WSe₂ seeding density compared to twisted bi-/tri-layer graphene and an even lower density compared to AB stacked bi-/tri-layer.

WSe₂ crystals grown on graphene are found to follow 2 specific orientations rotated by a 60° angle. The alignment of the zigzag edges of the triangular WSe₂ crystals with the zigzag edges of the underlying hexagonal graphene domain is indicative of van der Waals epitaxy rather than remote epitaxy with the underlying substrate.

Finally, given that the graphene transfer process inherently leads to impurity intercalation, we investigate the impact of the transfer protocol and post-transfer annealing on the cleanliness of graphene/substrate and WSe₂/graphene interfaces. The cleanliness of the interface is mainly studied using photoluminescence (PL) and Raman spectroscopy.

5:25 AM *S.NM09.02.04
Synthesis and Properties of van der Waals Heterostacks with Controlled Angle Camilla Coletti; Istituto Italiano di Tecnologia, Italy
In this talk recent advances on the synthesis and application of large-scale highly-crystalline van der Waals heterostacks will be presented. The electronic performance of single-crystal graphene arrays obtained via patterned growth [1] will be discussed in terms of homogeneity and repeatability. Particular focus will be put in the heterostack obtained by directly synthetizing via chemical vapor deposition (CVD) graphene bilayers and few layers with controlled angle [2, 3]. Also, the synthesis of azimuthally aligned tungsten disulfide (WS2) on graphene will be presented [4, 5]. It will be shown via microstructural and electronic characterization that monolayer WS2 on graphene presents a remarkable spin-orbit splitting [5]. Nanomechanical properties such as superlubric sliding of WS2 flakes on graphene triggered by scanning probe microscopy will be discussed [6]. Furthermore, the fabrication and performance of an entirely scalable hybrid WS2/graphene photodetector will be presented [7]. Finally, the synthesis of transition metal dichalcogenide heterostructures with controlled angle via liquid phase CVD will be introduced.


Acknowledgement

The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement 785219 – GrapheneCore2.

5:40 AM S.NM09.02.05
Twisted Spirals of Layered Transition Metal Dichalcogenides
Yuzhou Zhao, Chenyu Zhang, Paul M. Voyles and Song Jin; University of Wisconsin-Madison, United States

Twisted moiré pattern introduces new phenomena to Van der Waals layered materials by periodically changing the local registry of atoms, making it a new degree of freedom in 2D material engineering. Conventional twisted structures are fabricated by mechanically stacking layers, however, it still remains challenging to get clean interfaces. Direct vapor phase growth may yield small fractions of twisted bilayers as a byproduct, there is no rational control over the twist angle. In this work, we demonstrate that continuously twisted structures beyond Eshelby twist can be realized starting with screw dislocation spirals of layered MX2 materials. Super twisted spirals of MX2 materials up to tens of microns in lateral size are grown, and the orientation of layers and moiré superlattices can be directly observed and measured using scanning transmission electron microscope. Our study provides a new strategy to the rational control of twist angle of 2D materials from direct growth, which could enable the study of twisted moiré superlattices.

5:50 AM *S.NM09.02.07
Modeling the Growth of 2D Crystals—Analytical, Phase-Field and Machine Learning Methods
Vivek B. Shenoy, Nathan Frey and Arkamita Bandyopadhyay; University of Pennsylvania, United States

Vertical stacking of monolayers via van der Waals (vdW) interaction opens promising routes toward engineering physical properties of two-dimensional (2D) materials and designing atomically thin devices. Increasingly, the bottleneck in this field is the controlled synthesis of these materials through methods such as chemical etching and chemical vapor deposition (CVD). In this talk, I will present insights into synthesis and growth of 2D materials developed from analytical, phase-field, and machine learning models. First, we adapt the state-of-the-art positive and unlabeled (PU) machine learning framework to predict which theoretically proposed 2D materials in the MXene family have the highest likelihood of being successfully synthesized. By considering both the MXenes and their precursors, we identify 18 MXene compounds that are highly promising candidates for synthesis. Next, we develop a general multiscale model for scalable CVD growth of layered materials and predict the necessary growth conditions for vertical (initial + subsequent layers) versus in-plane lateral (monolayer) growth. An analytic thermodynamic criterion is established for multilayer growth that depends on the sizes of both layers, the vdW interaction energies, and the edge energy of 2D layers. We connect the model to experimental controls.
and find that temperature and adatom flux from vapor are the primary criteria affecting the self-assembled growth. This model agrees with experimental observations of various monolayer and bilayer transition metal dichalcogenides grown by CVD. Finally, we consider CVD synthesizable transition metal dichalcogenide heterostructures as a robust platform for engineering quantum confinement of Dirac fermions using a multiscale model for electronic properties.

SESSION S.NM09.03: Optical Phenomena in van der Waals Materials
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM09

5:00 AM *S.NM09.03.01
IV-VI van der Waals Materials and Their Properties Jie Yao1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

Low-dimensional nanomaterials with properties distinctive from their bulk counterparts have been extensively investigated in recent years. Besides the widely explored graphene and transition metal chalcogenides (TMDCs), a new family of van der Waals (vdW) materials composed of group IV and VI elements, especially Ge/Sn monochalcogenides, have attracted great attention in recent years. They have shown strong in-plane anisotropy that is similar to phosphorene (black phosphorous layers), and a number of unique electrical, optical, thermal and mechanical properties. Here I would like to share some of our recent discoveries on this unique family of materials, including their valleytronic behaviors and Eshelby twist formation in crystal growth.

Unlike conventional valleytronic materials where cryogenic temperatures, strong electric or magnetic field are needed to differentiate the valleys, Tin sulfide (SnS) was expected to have non-degenerate valleys with selection rules that are fundamentally different. I will talk about our experimental demonstration of the valley effect in an ambient, and bias-free model system of SnS and its alloys with other IV-VI materials. We elucidate the direct access and identification of different sets of valleys, based primarily on the selectivity in absorption and emission of linearly polarized light by optical reflection/transmission and photoluminescence measurements, and demonstrate strong optical dichroic anisotropy of up to 600% and nominal polarization degrees of up to 96% for the two valleys with band-gap values 1.28 and 1.48 eV, respectively; the ease of valley selection further manifested in their non-degenerate nature. In addition, the band gap values can be tuned effectively through alloying of SnS with similar materials such as SnSe. Such discovery enables a new platform for better access and control of valley polarization.

The IV-VI material family is also enabling new opportunities from twisting topology generation. Twisting of vdW layers has been shown to provide a new degree of freedom to tailor the electrical and optical properties of vdW crystals. I will talk about the first observation of Eshelby twist in Ge monochalcogenides that results in continuous twisting of multiple vdW layers. We exploit the screw dislocation driven growth of GeS nanowires, with growth direction perpendicular to the vdW layers. Results from comprehensive characterization on the helical vdW crystals agree well with Eshelby’s theory. Moreover, the planar growth of the vdW layers co-exists with the screw dislocation driven growth and leads to radial expansion of the nanowires, which results in discretized Eshelby twists resembling a helical assembly of nanoplates. We attribute the discretization to the change of twist rates of the nanowires in conjunction with a substrate pinning effect. We further show that the twisting topology can be tailored by controlling the radial size of the structure. In these helical crystals, atomically sharp interfaces with various twist angles are created, providing an intriguing tunable platform to explore various interlayer coupling effects in vdW materials.

5:15 AM *S.NM09.03.02
Moiré Heterostructure Quantum Emitter Arrays Brian Gerardot; Heriot Watt University, United Kingdom

Van der Waals heterostructures present unique opportunities to synthesize artificial quantum materials. For example, a slight lattice mismatch or relative rotation between the constituent layers of a hetero-bilayer results in a long-range moiré superlattice which spatially modulates the electronic band-structure. Single particle wavepackets can be trapped in the periodic potential pockets with three-fold symmetry to form an intrinsic quantum dot lattice. Here I will discuss the properties of such quantum emitter arrays. In a heterostructure of bilayer 2H-MoSe2 and monolayer WSe2, we observe two interlayer exciton (IX) species trapped in moiré potentials with distinct spin-layer-valley configurations. Due to the
phenomenon of locked electron spin and layer pseudospin in bilayer 2H-MoSe2, the IX species exhibit opposite valley magnetic moments. Further, we find the 2H-MoSe2 stacking intrinsically locks the atomic registries of the spin-layer locked IX species together. I will also present photon antibunching of moiré trapped excitons to unambiguously prove their quantum nature. Finally, I will discuss the properties of the moiré quantum emitters under applied electric fields and changing chemical potential.

5:30 AM *S.NM09.03.03
Indirect Excitons Leonid Butov; University of California, San Diego, United States

An indirect exciton (IX), also known as an interlayer exciton, is a bound pair of an electron and a hole confined in spatially separated layers. Due to their long lifetimes, IXs can cool below the temperature of quantum degeneracy. This gives an opportunity to realize and study cold excitons.

We will overview studies of Bose-Einstein condensation of IXs. We will present direct measurements of spontaneous coherence and condensation of IXs in GaAs heterostructures. We will present phenomena observed in the IX condensate, including the exciton density wave, spin textures, Pancharatnam-Berry phase and long-range coherent spin currents, and interference dislocations.

We will present van der Waals transition-metal dichalcogenide (TMD) heterostructures where IX condensation can be realized at high temperatures. We will present IXs at room temperature and indirect charged excitons, i.e. indirect trions, in van der Waals heterostructures.

5:45 AM *S.NM09.03.04
Spontaneous Out-of-Equilibrium Correlated Phases in van der Waals Materials Plasmonics Justin Song1,2; 1Nanyang Technological University Singapore, Singapore; 2Institute of High Performance Computing, Singapore

Spontaneous symmetry breaking lies at the heart of the description of interacting phases of matter. Here we argue that a driven interacting system subject to a linearly polarized (achiral) driving field can spontaneously magnetize (acquire chirality). In particular, we find when a metal is driven close to its plasmon resonance, it hosts strong internal ac fields that enable Berryogenesis: the spontaneous generation of a self-induced Bloch band Berry flux, which supports and is sustained by a circulating plasmonic motion, even for a linear polarized driving field. This non-equilibrium phase transition occurs above a critical driving amplitude, and depending on system parameters, can enter the spontaneously magnetized state in either a discontinuous or continuous fashion. Berryogenesis relies on nontrivial interband coherences for electronic states near the Fermi energy generated by ac fields readily found in a wide variety of multiband systems. We anticipate that graphene devices, in particular, which can host high quality plasmons, provide a natural and easily available platform to achieve Berryogenesis and spontaneous non-equilibrium (plasmon-mediated) magnetization in present-day devices, e.g., those based on graphene plasmonics. If we have time, we will also discuss other manifestations of non-trivial quantum geometry in Dirac systems.

6:00 AM *S.NM09.03.05
Light Induced Phase Transitions in Halide Perovskites Aditya D. Mohite; Rice University, United States

Organic-inorganic (hybrid) perovskite have recently emerged as a new semiconductor platform for next generation optoelectronics devices. These perovskite solids feature weak bonds between their organic and inorganic building blocks, which results in an intrinsic softness and dynamics disorder of the lattice and an acute sensitivity to external stimuli. Here, we present comprehensive in-situ studies of light induced structural dynamics of in layered two-dimensional (2D) hybrid perovskites. We correlate the changes in the structure of the 2D perovskite to modification of both the physical properties and the figures of merit in solar cells and light emitting devices. We propose a new microscopic model to explain the evolution of the structure and optoelectronic properties under external stimuli. These results demonstrate the direct correlation between structural characterization of halide perovskites under external perturbation and intrinsic physical properties.

6:15 AM *S.NM09.03.06
Nano-Electronic and Photonic Devices Based on 2D Materials Miriam Serena Vitiello; NEST, National Research Council CNR-NANO and Scuola Normale Superiore, Italy

Bi-dimensional nano-materials and related heterostructures are establishing themselves as intriguing material systems for the development of a new class of electronic, photonic and plasmonic devices with ad hoc-properties, that can be engineered
“from scratch”. Huge potential can be envisaged in a variety of application fields, ranging from saturable absorbers to optical modulators, from optical communication modules to spintronics, from near-field components to photodetectors. Their peculiar band-structure and electron transport characteristics, which can be easily manipulated via layer thickness control, suggest they could also form the basis for a new generation of high-performance devices operating in the Terahertz frequency range (1-10 THz) of the electromagnetic spectrum. This talk will review latest achievements in the developments of active and passive THz photonic and nano-electronic devices exploiting 2D nano-materials and combined heterostructures and will discuss future perspectives of this rapidly developing research field.

SESSION S.NM09.04: Optoelectronics Based on 2D Materials
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM09

5:00 AM *S.NM09.04.01
Light-Matter Interactions of 2D Materials and Their Novel Sensing Applications Shengxi Huang; The Pennsylvania State University, United States

Emerging quantum materials, such as novel two-dimensional (2D) materials and topologically nontrivial materials, have gained increasing attention due to their unique electronic and photonic properties. The realization of the optoelectronic applications of these materials still faces several challenges. For example, it is critical to gain clear understandings of (1) the fundamental light-matter interactions, which govern many of the key material properties, and (2) the coupling with other nanostructures, which is a required structure for devices and systems. This talk introduces new discoveries and pioneering works using optical spectroscopic techniques on these critical challenges, and novel applications of 2D materials in chemical and biological sensing. The first part of this talk presents the essential material properties investigated using spectroscopy, including interlayer coupling of Moiré patterns of 2D materials, anisotropic light-matter interactions of 2D quantum materials, and quantum optical emission properties of nanoengineered 2D layers. The spectroscopic techniques, including low-frequency Raman spectroscopy and polarization-and time-resolved spectroscopy, can also be widely used in other material systems such as semiconductor superlattices. The second part of this talk focuses on the interaction of 2D materials with other nanostructures and related applications. The interactions of 2D materials and selected organic molecules revealed novel enhancement effect of Raman signals for molecules on 2D surface, which offers a new paradigm in biochemical sensing. However, there is a selection rule regarding the 2D material substrates for molecules, which is critical for the design of biochemical molecular sensing platform and has been revealed recently. Overall, the works presented in this talk are significant in fundamental nanoscience, and offer important guidelines for practical applications in optoelectronics, sensing, and quantum technologies. The methodologies used here also provide a framework for the future study of many new low-dimensional and quantum materials.

5:15 AM S.NM09.04.02
Ring-Integrated Photodetectors for Silicon Photonics Based on Photo-Thermoelectric Effect in hBN/SLG/hBN
Heterostructures Jakob Muench1, Simone Schuler1,2, Dries Van Thourhout1, Alfonso Ruocco1, Kenji Watanabe3, Takashi Taniguchi4, Alberto Montanaro5, Simone Marconi5, Vito Sorianello5, Marco Romagnoli5, Andrea C. Ferrari1 and Thomas Mueller2; 1Cambridge Graphene Centre, University of Cambridge, United Kingdom; 2Technische Universität Wien, Austria; 3Ghent University, Belgium; 4National Institute for Material Science, Japan; 5Consorzio Nazionale per le Telecomunicazioni, Italy

Graphene is ideally suited for next generation communication systems [1], due to its unique optoelectronic properties [2] and CMOS compatibility [1]. Here, we present a graphene-based photodetector (GPD) for telecom wavelengths, combining an on-chip Si ring-cavity with high-mobility (> 10,000 cm²/Vs) single layer graphene (SLG) encapsulated in hBN. The constructive interference inside the ring results in a ~100% absorption of the guided light. Dual-gate electrodes on the active layer generate a p-n-junction in SLG, enabling a response due to the photo-thermoelectric (PTE) effect [3]. At optical input power levels ~ 0.1mW, comparable to those required by receivers used in 100 Gbs⁻¹ links [1], the GPD reaches a responsivity ~ 90 V/W, one order of magnitude higher than the highest reported to date for integrated PTE based GPDs [4], an electrical 3-dB cut-off frequency ~ 11 GHz, and a noise-equivalent power ~ 40 pW/√Hz. For higher input powers (~ 1mW), the strong light-matter interaction inside the Si ring results in electronic temperature increases of the photo-excited carriers ~ 100 K, and the transition to the ‘strong heating’ regime, characterized by sublinear scaling between photovoltage...
and input power [5]. Our devices can thus provide a route to studying strongly heated hot electrons in photo-excited SLG under continuous-wave illumination.


5:25 AM S.NM09.04.05
Scalable MoS2/WS2-Heterostructure Photodetectors Fabricated by a Transfer-Free Approach Tilmar Kuemmell1, Ulrike Hutten1, Leon Daniel1, Annika Grundmann2, Michael Heuken2,3, Holger Kalisch2, Andrei Vescan2 and Gerd Bacher1; 1Universität Duisburg-Essen, Germany; 2RWTH Aachen University, Germany; 3Aixtron SE, Germany

2D semiconductors based on TMDCs are highly promising materials for ultrathin, flexible and large-area photodetectors due to their thickness in the nm range and their effective absorption. The high exciton binding energy in these materials leads to a fast recombination and poor charge carrier separation, which represents an inherent drawback of such devices. To overcome this challenge, 2D heterostructures have been developed, separating optically generated charge carriers and thus increasing photoresponsivity. However, up to now, such heterostructure devices have been fabricated by stacking exfoliated flakes [1] or by transferring CVD-synthesized layers on top of each other [2]. These approaches suffer from process-induced defects and contaminations, and are hardly suited for industrially relevant fabrication routes.

We realized photodetectors based on TMDC heterostructures that are directly grown by MOCVD on a sapphire substrate [3], without any change between systems and without delicate transfer steps that bear the risk of uncontrolled contamination. The 1 mm² active area of the devices consists of a MoS2/WS2-heterobilayer, and interdigital contact patterns have been defined by electron beam lithography and metallization with Ti/Au. As a reference, devices based on MoS2 and WS2 monolayers, respectively, have been fabricated.

The photocurrent of the devices is analyzed under illumination with a defocussed laser (λ = 442 nm). Using either MoS2 or WS2 monolayers for light detection, only very low responsivities - far below 1 mA/W - are obtained. Obviously, low carrier mobilities and fast recombination rates are detrimental for the photosensitivity in monolayer devices. The situation is completely different for the directly grown MoS2/WS2-heterostructures: A several orders of magnitude enhanced responsivity of up to 16 A/W is achieved under an illumination of 45 mW/cm², corresponding to absolute photocurrents in the mA range. We attribute the large gain not only to an effective charge carrier separation, but also to an efficient hole trapping, leading to an enhanced electron flow in the heterostructure. This interpretation is consistent with the observation of a reduced responsivity for higher excitation densities, where these trap states become saturated.


5:35 AM *S.NM09.04.06
Refractive Index Control of Highly Anisotropic 2D Materials Joshua D. Caldwell; Vanderbilt University, United States

Two-dimensional materials are inherently anisotropic – with strong bonding in-plane and weak bonding out-of-plane. Consequently, their optical properties are birefringent, particularly at frequencies of the optically active infrared phonons. At these frequencies, the strong optical anisotropy results in hyperbolicity, where the permittivity tensor along at least one axis is negative, while at least one is positive. Hexagonal boron nitride (hBN) is an exemplary material in this regard. Materials which exhibit hyperbolicity can support volume-confined polaritonic modes, which have a wavelength much shorter than that of light in free space. Such spatially compressed modes have important implications for IR technologies, as they may be utilized to create planar meta-optics that are much more compact than the current state of the art. In particular, 2D materials can be used to realize metasurfaces, capable of shaping both nearfield- and far field light waves for a broad range of applications.

Conventional metasurface designs use geometrically fixed structures, or materials with excessive propagation losses, thereby limiting their potential applications. Here demonstrate that this can be overcome through the realization of a reconfigurable hyperbolic metasurface comprising a heterostructure of isotopically enriched hexagonal boron nitride (hBN) in direct contact with the phase-change material (PCM), such as single-crystal vanadium dioxide (VO2) or GST. Here, the metallic and
dielectric domains in PCM provide spatially localized changes in the local dielectric environment that modify the polariton wavelength supported in hBN by a factor of 1.6. Using this platform, we demonstrate the first reduction to practice of in-plane HPhP refraction, and the means for launching, reflecting and transmitting of HPhPs at the PCM domain boundaries. Ultimately, this phenomenon can be used to create planar refractive optics, such as lenses or waveguides, but on length scales far below the diffraction limit. Further, my employing doped semiconductor materials with controllable plasma frequencies, such direct control of hyperbolic polaritons can also be obtained via modification of the free carrier density of the underlying semiconductor.

SESSION S.NM09.05/S.NM07.06: Keynote Session: Strong Correlation in Low-Dimensional Materials of TMPS3
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM09

5:00 AM *S.NM09.05/S.NM07.06.01
Strong Correlation in Low-Dimensional Materials of TMPS3 Je-Geun Park1,2; 1Institute for Basic Science (IBS), Korea (the Republic of); 2Seoul National University, Korea (the Republic of)

One of the most pressing questions in condensed matter physics is how electron correlations play out on two-dimension. For this question, the newly emerged magnetic van der Waals material can be helpful. In particular, TMPS3 with TM=transition metal elements have attracted significant attention as it exhibits all three fundamental magnetic models of magnetism; Ising (FePS3), XY (NiPS3) and Heisenberg (MnPS3) Hamiltonian. Using these materials, we have studied some of the fundamental theorems of modern magnetism: Onsager solution for the Ising model, The Berezinskii–Kosterlitz–Thouless transition for the XY model, and Mermin-Wagner theorem for the Heisenberg model. Besides, we have also investigated how correlation physics plays a role in optical spectroscopy data. In this talk, I will demonstrate how we can use this unique magnetic property of these materials to learn of the old physics.

SESSION S.NM09.06: Microscopic Studies of 2D Materials and Heterostructures
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
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5:00 AM S.NM09.06.01
Understanding Local Spatially Varying Photoconductivity across Nanoscale Interfaces in Two-Dimensional MoS2/Ws2Lateral Heterostructures Sanjini Nanayakkara1, Samuel Berweger2, Hanyu Zhang1, Prasana Sahoo3, Dmitry Voronine3, Pavel Kabos2, Andrew Ferguson1, Jeffrey Blackburn1 and Elisa Miller-Link1; 1National Renewable Energy Laboratory, United States; 2National Institute of Standards and Technology, United States; 3University of South Florida, United States

Heterostructuring of 2D materials, through the formation of vertical or lateral structures, may provide access to a multitude of novel photo-physical and electronic properties than can be tailored through a wide breath of available 2D materials. In this research, we will focus on chemical vapor deposition grown lateral heterostructures of MoS2/WS2 with a goal of measuring and understanding the local carrier distribution and conductivity across the atomically precise material interfaces. We have used advanced atomic force microscopy methods, including scanning microwave microscopy to elucidate the local, spatially varying carrier distribution in 2D MoS2/WS under dark conditions as well as under illumination with photon energy-resolved narrowband illumination. Our results show that strong spatial variations in the photoconductive response exists, even within individual flakes that were imaged. We corroborate our analysis with spatially resolved photoluminescence mapping and discuss our results in terms of the dynamics of long-lived photo generated carriers.

5:10 AM S.NM09.06.02
Direct Visualisation of Non-Equilibrium Structural Transformations in Atomically-Thin Chalcogenides Pawan Kumar, James P. Horwath, Alexandre C. Foucher, Natalia Aacero, Eric A. Stach and Deep M. Jariwala; University of Pennsylvania, United States
Two-dimensional (2D) transition metal dichalcogenides have been the subject of sustained research interest due to their extraordinary electronic and optical properties. At the same time, they are also a very rich system from the perspective of structural phases and phase transitions. Thus far, transformation from 2H semiconducting to 1T metallic phase in MoS$_2$ has been well demonstrated. Likewise, thermally induced defect creation, etching and oxidation have also been well studied. However, one aspect of structural properties of semiconducting TMDCs that has been understudied is the structural transformation in a highly non-equilibrium or far out of equilibrium thermodynamic conditions. In this talk, we will discuss our recent progress in studying disintegration and phase evolution of atomically thin MoS$_2$ under varying temperatures (upto 700 C) and heating rates (25 C/sec). We probe these transformations at the atomic scale using aberration corrected scanning transmission electron microscope (AC-STEM) while heating the samples in-situ. We observe strong dependence of the resulting structures and phases on the heating rates and temperatures. In particular, for fast heating rates (~25 C/sec), we observe abrupt melting of the few layer regions into high ordered and crystalline, hexagonal islands of sizes < 20 nm. Importantly, we also find, lateral heterostructures of 2H and 3R phases including presence of ordered, intermediate phases and sharp boundaries. For slower heating rates (~25 C/min) ex-situ in a furnace, this transformation occurs via sulphur sublimation resulting in formation of etch pits to nanocrystalline and amorphous regions that are sub-stoichiometric. We further use Electron Energy Loss Spectroscopy (EELS) to distinguish atomic level electronic structure information. The use of non-equilibrium heating rates to achieve highly crystalline and quantum confined features from 2D atomic layers opens new avenues for fundamental materials engineering and applications in confined dimensions.

SESSION S.NM09.07: New Approaches to Synthesis of van der Waals Materials
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
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5:00 AM *S.NM09.07.01
Magnetic Transition Metal Dichalcogenides Christopher Hinkle; University of Notre Dame, United States

The incorporation of magnetic dopants is a way to realize magnetism in semiconductors. The 2D material WSe$_2$ is a semiconductor with a bandgap of 1.3 eV, and Fe-doped WSe$_2$ is predicted to have room temperature, long-range ferromagnetism. Moreover, WSe$_2$ has been extensively studied for applications in electronic devices, and can be prepared by deposition methods that are compatible with semiconductor fabrication processes. 2D magnetic films are particularly intriguing in technologies that rely on exchange coupling since the efficiency of the exchange with the magnet is inversely proportional to the magnet thickness $1/\ell_{FM}$. Chalcogenide-based TMD magnets can also have ideal interfaces with chalcogenide-based topological insulators (like Bi$_2$Se$_3$), enabling efficient spin torque devices and potentially realizing the quantum Hall effect without an external magnetic field.

Focusing on materials growth and integration techniques that utilize non-equilibrium, kinetically restricted strategies, coupled with in-situ characterization, enables the realization of atomic configurations and materials that are challenging to make but once attained, display enhanced and unique properties. In this work, we will highlight the growth of Fe-doped WSe$_2$ and report on its up to room temperature ferromagnetic properties. The evolution of Fe-doped WSe$_2$ films under different doping levels indicates that strain from the impurity atom itself coupled with strain imparted by the substrate can drive phase separation at high Fe concentrations. We find that suppressing that film strain helps promote more Fe incorporation (and higher Curie temperatures).

Cr$_2$O$_3$ has only 0.2% lattice mismatch with WSe$_2$ and is a magnetoelectric that can couple with ferromagnetic films. By using seed-layer techniques, we successfully prepared layered Fe-WSe$_2$ on Cr$_2$O$_3$ and demonstrate magnetic coupling between the two, a potentially promising route toward realizing electric field control of 2D magnets. Magnetic measurements show a clear hysteresis loop at 100 K in a 2 Tesla cooling field, from which a large negative bias field of 600 Oe is resolved. The bias field vs temperature measurements, where a negative bias field emerges below 250 K, indicates the existence of ferromagnetic exchange coupling in this heterostructure.

This work is supported in part by NEWLIMITS, a center in nCORE, a Semiconductor Research Corporation (SRC) program sponsored by NIST through award number 70NANB17H041. This work is also supported by the National Science Foundation under awards 1917025 and 1921818.

5:15 AM *S.NM09.07.04
Wafer-Scale Epitaxy of Transition Metal Dichalcogenides by Gas Source CVD Tanushree H. Choudhury, Mikhail
Novel electronic and optical properties of monolayer transition metal dichalcogenides (MX₂, M=W, Mo and X=S, Se) have garnered a lot of attention in the recent years. A major challenge to integrating these materials with existing device fabrication processes is the availability of epitaxial single-crystal monolayers over a wafer scale. Our approach focuses on synthesis of these monolayers using gas source precursors, like those used in traditional III-V semiconductor industry. These precursors are fed into the growth chamber independently into the growth zone with precision. Uniform epitaxial binary TMD monolayers including MoS₂, WS₂, WSe₂, and MoSe₂ have been deposited on 2” sapphire substrates in a cold-wall CVD reactor using metal hexacarbonyl and hydride chalcogen precursors. A multi-step growth process comprising of precursor modulation was developed for WSe₂ to independently control nucleation density and the lateral growth rate of monolayer domains on the sapphire substrate [1]. For the sulfides, additional temperature modulation was introduced to increase crystalline quality. Using this approach, uniform, coalesced monolayer and few-layer TMD films were obtained on 2” sapphire substrates. Deposition of these materials in the same reactor provides insight into the factors controlling their growth, which in essential for the growth of heterostructures and/or alloys. In-plane X-ray diffraction demonstrates that the films are epitaxially oriented with respect to sapphire with narrow X-ray full-width-at-half-maximum indicating minimal rotational misorientation of domains within the basal plane [2]. Transmission electron microscopy analysis of these materials revealed additional information about the coalesced film structure. For instance, ~95 % single oriented WS₂ domains were observed when the film growth rate was modulated. For WS₂, it was also confirmed that despite translational line defects present in the film, mirror boundaries were predominantly absent. WS₂ also showed no defect related photoluminescence peak at 80 K, indicating its high quality. In this talk the factors affecting the growth of TMDs (MX₂, M=W, Mo and X=S, Se) will be presented. The role of the substrate surface in the nucleation and growth of these TMDs will be discussed. In addition, the structural and optoelectronic characteristics for these films will also be presented.

The authors acknowledge financial support of the U.S. National Science Foundation through the Penn State 2D Crystal Consortium – Materials Innovation Platform (2DCC-MIP) under NSF cooperative agreement DMR-1539916 and EFRI 2-DARE Grant EFRI-1433378.


5:30 AM *S.NM09.07.05
Synthesis and Characterization of Two-Dimensional Metal Carbides Otitoaleke Akinola, Suyogya Karki, Vivian Rogers, Deji Akinwande and Jean Anne Incorvia; The University of Texas at Austin, United States

MXenes (formula Mₓ₊₁Xₓₙ), are a class of two-dimensional (2D) materials, which are derived from a MAX crystal structure MₓAlₓAXₙ where the M represents early transition metals (Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta), the X is for C and/or N, and the A elements include Al, Si, P, and others. The MAX phase is structured with the A atoms sandwiched between the M and X layers from which MXene monolayer sheets can be derived by selectively etching out the A atoms from the bulk MAX crystal. While MXenes have been extensively explored theoretically, they are just starting to be made in experiment due to the difficulty in having to chemically etch to separate the layers, compared to van der Walls [1]. Hence, it is important to make progress in the chemical exfoliation in order to study them experimentally and understand how their behavior matches theory.

Extensive work has been done predicting intrinsic 2D ferromagnetic and antiferromagnetic materials with high Curie temperature T_C (or Neel temperature) [2] coupled with recent discoveries of low-dimensional materials with intrinsic long-range magnetic ordering [3]. But still few low-dimensional magnetic materials have been even synthesized. In addition to great electronic properties such as tunable bandgap with tensile strain or electric field, and mechanical properties [4], MXenes can have exciting magnetic properties [5]. For example, from theory pristine Ti₂C and Ti₂N are nearly half-metallic ferromagnets, Cr₂N is antiferromagnetic, and Cr₂C is a half-metallic ferromagnet which can undergo ferromagnetic metallic to anti-ferromagnetic insulating state transitions using appropriate surface functionalization with F, OH, H, or Cl groups [5]. These spintronic and manipulatable magnetic/electronic properties give MXenes an edge over the more popular graphene material [1].

Here we show our work on synthesizing chromium carbide (Cr₂C) nanosheets from the parent bulk chromium aluminum carbide (2:1:1 Cr₂:Al:C atomic %) MAX phase powder through wet etching. We show the processes that has been developed to successfully exfoliate the material to reduce it to low-dimensional flakes using HCl+LiF, and HCl+NaF chemical etching. We also show how we have been able to reduce the etch time from 96 hours to 48 hours. After the etch, the samples are dried. Using the scanning electron microscope, a clear accordion structure is seen as is expected for MXenes, showing sheets of Cr₂C after the Al is etched away. We find a large number of accordion structures, with sheet lengths 5-10 μm in
size, similar to mechanically exfoliated sizes of commonly studied 2D materials. We will show our results separating the accordion structures into low-dimensional flakes using mechanical exfoliation following the chemical exfoliation and will show energy-dispersive x-ray spectroscopy results showing that the Al content has been significantly reduced by our etching procedure. Lastly, we will show characterization of the structural, electronic, and magnetic properties of the Cr$_2$C flakes.

References

SESSION S.NM09.08: Quantum Electronic Devices Based on 2D Materials
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM09

5:00 AM *S.NM09.08.01
Orbital Magnetism and Quantized Anomalous Hall Effect in Twisted Bilayer Graphene Andrea Young; University of California, Santa Barbara, United States

In moire flat band systems, interlayer moire patterns can be used to engineer isolated superlattice bands in which the Coulomb interaction is comparable to the bandwidth. As in a Landau level, this leads to electron interaction dominated physics despite the low density of electrons, enabling full density control using electrostatic gates. Unlike Landau levels, however, moire flat bands occur under time reversal symmetric conditions. I will discuss experiments that observe the spontaneous breaking of time reversal symmetry, observed as magnetic hysteresis. Remarkably, hysteresis is accompanied by a quantized anomalous Hall effect, persisting to zero magnetic field and elevated temperatures. I will discuss the origins of this effect in the spontaneous orbital polarization of the electron system into a single, topological nontrivial superlattice band, and describe magnetic imaging data that confirms the orbital character of the magnetism.

5:15 AM *S.NM09.08.02
Strong Magnetophonon Oscillations in Monolayer Graphene—A Spectroscopic Probe of Electron-Phonon Interactions Mark T. Greenaway1,2, P Kumaravadivel1,3, D Perello1,3, A Berdyugin1, J Birkbeck3,3, J Wengraf6,4, S Liu5, J Edgar5, A Geim13, L Eaves23 and R Krishna Kumar3; 1Loughborough University, United Kingdom; 2The University of Nottingham, United Kingdom; 3University of Manchester, United Kingdom; 4University of Lancaster, United Kingdom; 5Kansas State University, United States

For more than 50 years, magnetophonon resonance (MPR) has proved to be a powerful tool for investigating electron-phonon interactions in a wide range of elemental and compound semiconductors and heterostructures. Its experimental signature is a series of oscillations in the magnetoresistance, periodic in inverse magnetic field, given by the equation, $p \omega_c = \omega_p$, where $p$ is an integer, $\omega_c$ is the Landau level splitting and $\omega_p$ is the phonon frequency. The successful observation of MPR in graphene has proved elusive due, in part, to the relative weak interaction of the massless Dirac Fermions with the lattice phonons.

Here we report the observation of large amplitude, temperature-dependent MPR oscillations in the magnetoresistance of large area, electrostatically gated Hall bars of exfoliated monolayer graphene encapsulated by hexagonal boron nitride (hBN) [1,2]. The oscillations are observed only in devices with a width which exceeds the ballistic carrier mean free path, 5 μm. We observe two distinct series of resonant peaks arising from inelastic scattering by transverse acoustic (TA) and longitudinal acoustic (LA) phonons. The LA phonon resonant amplitude is significantly weaker than that of the TA phonons. This is due, in part, to the carrier screening of the LA phonon modes. The magnetic field values of the resonant peaks are found to shift linearly with carrier sheet density from $10^{12}$ to $10^{13}$ cm$^{-2}$. These experiments also allow us to measure the dispersion curves of
the LA and TA phonons up to wavevectors of \( \sim 10^9 \text{ m}^{-1} \). We model the experimental data to high accuracy using the Kubo formalism. We demonstrate that the LA and TA phonon speeds and the electron-phonon coupling strengths determined from the magnetophonon resonance measurements provide an excellent fit to the measured dependence of the resistivity at zero magnetic field over a temperature range of 4-150 K. Thus, MPR provides a spectroscopic tool for studying electron-phonon interaction in two-dimensional semiconductors.


5:30 AM *S.NM09.08.03
**Quantum Devices with 2D Materials** Klaus Ensslin; ETH Zurich, Switzerland

We demonstrate electronic constrictions on bilayer graphene that can be completely pinched off [1]. Split-gate devices in combination with a graphite backgates enable electronic tunability of the devices. The level spectrum of quantum point contacts in bilayer graphene has a peculiar magnetic field dependence quite different from what is known from semiconductors. We understand the details of this spectrum [2] based on the Berry curvature in bilayer graphene. In few electron and hole quantum dots confined by p-n junctions [3] we investigate valley and spin splitting. Also many electron quantum dots with standard tunneling barriers as well as double and triple quantum dots [4] can be realized with an electronic quality comparable to the best dots fabricated in standard semiconductor environments. The spectrum of excited states in graphene dots is qualitatively different [5] compared to semiconductors because of the valley degree of freedom. These experiments open the door for using graphene quantum dots as spin qubits with potentially long coherence times. We also discuss the properties of MoS_2 as a host material [6,7] for quantum dot-based qubits.


References

5:45 AM *S.NM09.08.04
**Engineering 2D Materials with a Twist** Cory R. Dean; Columbia University, United States

Atomically thin crystals such as graphene, boron nitride and the transition metal dichalcogenides continue to attract enormous interest. Encompassing a wide range of properties, including single-particle, topological and correlated phenomenon, these 2D materials represent a rich class of materials in which to explore both novel physical phenomenon and new technological pursuits. By integrating these materials with one another, an exciting new opportunity has emerged in which entirely new layered heterostructures can be fabricated with emergent properties beyond those of the constituent materials. In this talk I will discuss some of our recent efforts where, by tuning the geometry of these heterostructures at the nanoscale, we are able to realize yet a new level of control over their electronic properties. In particular I will discuss the significant role played by the rotational alignment between adjacent layers and the approach we are taking towards manipulating this degree of freedom to dynamically tune device properties in ways that are not possible with conventional materials.

6:00 AM *S.NM09.08.05
Thermoelectricity in Twisted Bilayer Graphene

Arindam Ghosh, Phanibhusan Mahapatra, Bhaskar Ghawri, U. Chandni and Manjari Garg; Indian Institute of Science, India

Twisted bilayer graphene (TBLG) is a new and versatile platform to realize effects of strong electron-electron interaction as the mis-orientation angle (theta) between the graphene lattices profoundly affects the electronic structure of the combined system. While the layers behave independently at large theta (> 3 degree), new electronic bands emerge when theta is decreased, including nearly flat bands at the magic angle of 1.1 degree that has been shown the harbor superconductivity and magnetism. In addition of direct electrical transport, thermoelectric properties are also highly sensitive to electronic correlations, and often manifest in departure from the well-established Mott semiclassical framework. Here we present the results of measurement of thermoelectric power in TBLG over a wide range of theta. We have shown that thermoelectricity in TBL at large theta (> 2 - 3 degree) is expectedly determined by independent excitations in the two graphene layers, and can be described by the Mott relation [1,2]. At low theta (< 2 degree), however, we observed a strong departure from the semi-classical description, which is most pronounced at the half-filling of the underlying Moire lattice, and persists up to temperatures as high as 40 K [3]. In accordance with the strong enhancement in the electronic interactions at half filling, our experiments suggest the possibility of a novel interaction-driven thermoelectricity in TBLG.

[3] B. Ghawri et al. (To be submitted, 2019)

6:15 AM *S.NM09.08.06
Strain Engineering of the Valley Magnetization and Berry Curvature Dipole in 2D Materials

Jieun Lee; Seoul National University, Korea (the Republic of)

The valley degree of freedom in two-dimensional (2D) honeycomb lattices has attracted much recent attention due to its non-trivial Berry curvature effects associated with two nonequivalent valleys. This feature gives rise to many interesting valley-dependent phenomena such as the valley optical selection rule and the valley Hall effect, each of which accessing the valley-dependent electron control using the optical and electrical means. The valley manipulation in these works, however, focus on the control of the electron occupation while the Berry curvature at the two valleys are remained constant. In this talk, we show the mechanical control of the valley degree of freedom which is enabled by the strain engineering of the Berry curvature. By fabricating flexible monolayer MoS2 devices, we reversibly control strain on monolayer MoS2 and demonstrate the generation of the current-induced valley magnetization due to the formation of the Berry curvature dipole. The measured valley magnetization is in excellent agreement with the calculated Berry curvature dipole, which depends on the magnitude and direction of strain. Our results show that the Berry curvature dipole acts as an effective magnetic field in current-carrying systems, providing a novel route to generate magnetization in 2D crystals.

SESSION S.NM09.09: Next-Generation Electronics Based on Heterostructures of 2D Materials
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
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5:00 AM S.NM09.09.02
High-Speed Two-Dimensional Solid-State Non-Volatile Memory Based on Electric Double Layer Gating with a Monolayer Electrolyte

Shubham Sukumar Awate1, Jierui Liang1, Ke Xu1, Benjamin Hunt2 and Susan Fullerton1, 1University of Pittsburgh, United States; 2Carnegie Mellon University, United States

A high-speed, two-dimensional, solid-state, non-volatile memory has been demonstrated using electric double layer (EDL) gating of two-dimensional (2D) field effect transistors (FETs) with nanosecond scale switching speeds. The “monolayer electrolyte” FET (i.e., MEFET) consists of cobalt crown ether phthalocyanine (CoCrPc) and lithium ions deposited as a monolayer on the surface a 2D semiconductor by drop casting and annealing. CoCrPc is an electrically insulating (band gap ~ 1.34 eV) and the four crown ethers each solvate a Li+ ion. In response to an applied electric field, Li+ ions diffuse through the crown ether cavity and are positioned either near or away from the channel resulting in on and off states, respectively. We have previously shown switching behavior on 2D FETs using this material with potential application in non-volatile memory. Achieving well-ordered monolayers of CoCrPc and complete solvation of Li+ into the crown ethers are critical for device
operation because the location and orientation of the molecules governs the device mechanism. Here we will show how the quality of the drop-casted CoCrPc/LiClO₄ depends on concentration and annealing temperature. When the well-ordered electrolyte layer deposited on a WSe₂ FET is capped with h-BN, the off-state is stabilized (as confirmed by density functional theory (DFT)) and 50 nanosecond switching speeds (limit of the instrument) are demonstrated with an on-off current ratio > 10⁵. The device is stable for at least 1000 cycles (max. measured) after programming with 50 ns pulse and the retention of each state persists for at least 28 hours (max. measured). Top-gated MEFETs are currently being fabricated to reduce the program/erase voltages.

5:10 AM S.NM09.09.04
Cross-Plane Thermal Conductance Modulation in van der Waals Heterojunctions Charles A. Sievers¹, Aditya Sood², Eric Pop² and Davide Donadio¹; ¹University of California, Davis, United States; ²Stanford University, United States

Van der Waals heterostructures have been shown to exhibit a multitude of quantum electronic transport phenomena, such as superconductivity and integer quantum Hall effects, which entail great promise for new nanoscale devices.¹ Alongside exceptional electronic properties, two-dimensional van der Waals materials present intriguing heat transport properties, such as ultra-high thermal conductivity.² Here, we use elastic scattering lattice dynamics³ calculations to investigate cross-plane thermal conductance across twisted and untwisted heterojunctions composed of graphene, molybdenum disulfide, and hexagonal boron nitride sheets. We found large degrees of cross-plane thermal conductance modulation through phonon filtering and localization based on heterojunction composition and twisting angle.

1. Novoselov K, Mishchenko A, Carvalho A, and Catro-Neto A 2016 2D Materials and van der Waals heterostructures Science 29, 353

5:20 AM *S.NM09.09.05
Novel Infrared Photodetectors Based on Layered van der Waals Heterostructures Jinshui Miao, Fang Wang, Peng Wang and Weida Hu; Chinese Academy of Sciences, China

Infrared photodetectors based on traditional thin-film semiconductors such as InGaAs, InSb, HgCdTe, Si BIB, and QWIP as well as novel type-II superlattice exhibit highly sensitive detection capability. However, these devices always need to work at low temperature, resulting in an additional large and expensive cooling system. Recently, two dimensional (2D) materials and their van der Waals heterostructures have attracted tremendous attention owing to their optoelectronic tunability and potential optoelectronic applications. Nevertheless, as a photoconductive detector, the signal-to-noise ratio could be very low without the suppression of dark current. Meanwhile, the performance of the photodetectors, which are based on 2D materials and layered van der Waals Heterostructures, including phototransistors, photoconductors with photogating, and photodiodes, is strongly affected by surface/interface and in-plane trap states resulting in the restricted electron-hole separation efficiency and low speed, and intrinsic ultrathin absorption thickness for 2D photodetectors suffers the low quantum efficiency. Here we report the progress on novel uncooled infrared photodetectors based on 2D materials and their van der Waals heterostructures manipulated by localized fields. We fully exploit the detection ability of 2D materials and their van der Waals heterostructures by introducing localized-field, including ferroelectric filed, vertical heterojunction field, p-n junction photovoltaic field and so forth. With a strong induced localized-field, high performance infrared photodetectors based on Graphene, TMDs, Pd (Pt) Se, Black phosphorus, Black arsenic-phosphorus etc. may lead to a disruptive revolution in prospective low dimensional electronic/optoelectronic devices. Our study opens a new avenue for the controllable fabrication of built-in localized-field in 2D devices, which is a prominent challenge in low dimensional material researches. Feng Wu, Qing Li, Peng Wang*, Hui Xia, Zhen Wang, Yang Wang, Man Luo, Long Chen, Fansheng Chen, Jinshui Miao, Xiaoshuang Chen, Wei Lu, Chongxin Shan, Anliian Pan, Xing Wu*, Wencai Ren, Deep Jariwala and Weida Hu*, High efficiency and fast van der Waals hetero-photodiodes with a unilateral depletion region, Nature Communications, 10, 4664 (2019).


Mingsheng Long, Anyuan Gao, Peng Wang, Hui Xia, Claudia Ott, Chen Pan, Yajun Fu, Erfu Liu, Xiaoshuang Chen, Wei Lu, Tom Nilges, Jianbin Xu, Xiaomu Wang*, Weida Hu*, Feng Miao*, Room-temperature high detectivity mid-infrared...
Cognitive computing and artificial intelligence are rapidly emerging fields. The brain operates through a network of neurons that are connected to each other by synapses. In 2008, the prevalent von Neumann architecture in today’s processors involves memory and processing units to reside in physically separate locations. With memory speeds lagging behind the processor speeds, latency in accessing data from memory has resulted in the “von Neumann bottleneck”. To alleviate this issue, several alternative non-von Neumann architectures have been explored. Neuromorphic computing is one such non-von Neumann approach, inspired by the human brain’s ability of cognitive recognition. The brain operates through a network of neurons that are connected to each other by synapses. In 2008, after the discovery of memristors, the fourth circuit element, researchers have explored the idea of mimicking synaptic behavior with a single memristive device. Albeit significant advances, synaptic devices using phase change materials-based memristors and metal oxide-based resistive switching devices have some limitations. These devices exhibit high non-linearity in weight update, i.e. the increase (decrease) of the synapse’s conductance with the application of a continuous stream of identical positive (negative) input voltage pulses, is non-linear. Non-linearity in weight update increases the complexity of using these devices for real-time unsupervised learning. So, it becomes necessary to employ a materials system which exhibits low programming current as well as a linear weight update. Recently, two-dimensional (2D) materials are being largely explored to demonstrate their viability as electronic synapses and neurons. In this talk, we shall discuss the realization of a synaptic device using graphene/MoS2 heterostructures. These memristive devices exhibit low programming currents and a high dynamic range from 1 nA to 1 mA. In contrast with oxide-based or PCM-based synapses, these devices exhibit a gradual set and reset process when symmetric input voltage pulses are applied, resulting in a near-linear weight update. Linearity and symmetry in weight update is much desired for real-time learning applications. We shall also present the demonstration of an integrate-and-fire neuron using Ag/MoS2/Au vertical structures. These devices possess the four crucial features of neuron – all-or-nothing spiking, threshold-driven firing, post-firing refractory period and stimulus strength based frequency response. Realizing neurons and synapses using the same materials system allows the monolithic integration of the essential building blocks of neuromorphic hardware, and bears potential for a highly scalable spiking neural networks suitable for unsupervised learning applications.

5:50 AM *S.NM09.09.08
Photo-Defined In-Plane Heterostructures in Two-Dimensional In2Se3 John Igo, Matthew Gabel, Zhi-Gang Yu, Liangliang Yang and Yi Gu; Washington State University, United States

Two-dimensional (2D) van der Waals materials and related heterostructures have shown a wide variety of novel electronic and opto-electronic properties. However, a key challenge in fully realizing their potential is a general lack of manufacturing techniques capable of producing desired heterostructures at a large scale. Here, we demonstrate a highly scalable direct-laser-writing approach to fabricating in-plane heterostructures in two-dimensional In2Se3 layers. This approach derives from an optically activated solid-solid phase transition that leads to significant changes in local properties (semiconducting vs. metal-like), while preserving the single crystallinity of the local lattice, leading to well-defined heterointerfaces and demonstrating a scalable path to large-area device manufacturing. Carrier transport across in-plane heterojunction nanoscale devices fabricated by this technique exhibits asymmetric diode behaviors supported by the presence of interface energy barriers as revealed by Kelvin probe force microscopy. Scanning photocurrent microscopy shows short-circuit photocurrent in these devices, demonstrating their potential applications in efficient photodetection and photovoltaics. Our numerical modeling of the device characteristics reveals space-charge-limited and injection-limited conduction as the carrier transport mechanisms,
in contrast to the standard diode model.

SESSION S.NM09.10: Poster Session: Layered van der Waals Heterostructures—Synthesis, Physical Phenomena and Devices
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
5:00 AM - 8:00 AM
S-NM09

S.NM09.10.01
Controlling Defects in 2D GaS Continuous Films and Heterostructures for High Performance Wavelength-Tunable Photodetectors Yang Lu and Jamie Warner; University of Oxford, United Kingdom

The rapid development of two-dimensional (2D) materials calls for the development of novel 2D semiconductors with large bandgap for applications in short-wavelength LEDs, type-I heterojunctions, etc. Gallium sulfide (GaS), a wide-bandgap semiconductor, fulfills these requirements but was not fully explored due to lack of controllable synthesis methods, unexplored layer-dependent properties and unanswered stability issues. Here, to answer these questions, we developed a CVD synthesis method of thickness-controlled (1–4L), uniform and continuous films of both defective GaS and defect-free GaS. A simple method for determination of thickness by Raman spectroscopy is developed. An enhanced stability of the defect-free GaS was demonstrated under laser and strong UV lights, and by controlling defects in GaS, the photoresponse range could be changed from vis-to-UV to UV-discriminating. The defect-free GaS is suitable for large-scale UV-sensitive high-performance photodetector arrays for information encoding under large vis-light noise, with short response time, excellent UV photoresponsivity and a 26-times increase of signal-to-noise ratio compared with small bandgap 2D semiconductors. By comprehensive characterizations from atomic-scale structures to large-scale device performances in 2D semiconductors, we provide insights into the role of defects, the importance of neglected material-quality control and how to enhance device performance. Finally, both layer-controlled defective and defect-free GaS prove to be promising platforms for study of novel phenomena and new applications in WS₂-GaS van der Waals heterojunctions.

S.NM09.10.02
Laser-Assisted Accelerated Synthesis of 2D Quantum Materials Nurul Azam1, Zabihollah Ahmadi1, Salah Elafandi1, Baha Yakupoglu1, Mengkun Tian2, Abdelaziz Boulesbaa3 and Masoud Mahjouri-Samani1; 1Auburn University, United States; 2Georgia Institute of Technology, United States; 3California State University Northridge, United States

The firmly defined dimensionalities of two-dimensional (2D) layered materials including transition metal dichalcogenides (TMDs) exposed numerous unusual properties that have been recently at the center of the quantum materials and information sciences research. In pursuit of the accelerated growth and discovery of 2D materials, many efforts have concentrated on developing new approaches including physical and chemical vapor deposition techniques. However, complex, uncontrolled gas-phase reactions, and flow dynamics have made the synthesis of these multi-component 2D crystals exceedingly challenging. This work demonstrates a novel laser-assisted synthesis technique (LAST), which significantly reduces the existing growth complexities and remarkably accelerates the growth of 2D materials. The uniqueness of this approach arises from the direct vaporization technique of stoichiometric powders by the laser heating process. We show that this directed laser heating permits pressure-independent decoupling of the growth and evaporation kinetics, enabling the use of stoichiometric powder as precursors for the growth of various high-quality 2D materials including MoS₂, MoSe₂, WSe₂, and WS₂.

Mr. Nurul Azam is currently a Ph.D. student in the Department of Electrical and Computer Engineering (ECE) at Auburn University (AU). His research in the Laser-Assisted Science and Engineering (LASE), Lab under the supervision of Prof. Mahjouri-Samani, focuses on investigating and developing novel approaches for the synthesis of 2D quantum materials and heterostructures.

S.NM09.10.11
Synthesis of Two-Dimensional, Semiconducting Quantum Materials via Chemical Vapor Deposition (CVD) Daniel S. Choi1, Evgeniya H. Lock2 and Shashi P. Karna3; 1National Research Council, United States; 2Naval Research Laboratory,
In the past decade, there have been unprecedented advancements in research and development of materials for quantum applications such as ultrasensitive detection, quantum information processing, energy efficient ultrafast electronics, quantum light-emission, and many more that require a fundamental understanding of never-before observed physical and chemical phenomena in known materials. Of these new generation of materials, transition metal dichalcogenides (TMDs) have become attractive candidates for more extensive investigation due to their novel and non-classical behaviors observed at nanoscale as well as potential for their incorporation into devices and applications. For instance, nanoscale TMDs such as tungsten diselenide (WSe$_2$), tungsten disulfide (WS$_2$), and molybdenum disulfide (MoS$_2$) have been shown to exhibit highly localized, intense, quantum emission of single photons that have not been previously observed in their bulk counterparts. While understanding fundamental mechanism and origin, as well as the physical structure of these quantum materials and their properties are crucial, parallel efforts in developing large scale, controlled synthesis of these materials is just as imperative. Currently, much of the studies on TMD materials for quantum applications have primarily been on larger flakes and crystals, or exfoliated films, which limits scalability of the material production as well as the need for transfer of the exfoliated material onto a suitable substrate.

In this work, we present a systematic synthesis of 2-dimensional, single- to few-layers of transition metal chalcogenides thin film directly on silicon substrate via chemical vapor deposition (CVD). Our approach not only sheds light into understanding the growth mechanism of 2-dimensional TMDs, but also provides optimal growth parameter for consistent, large scale production of these materials. The results presented will provide basis for synthesis of next-generation of 2-dimensional materials as well as shed light into bottom-up building approach of van der Waals heterostructures for quantum applications.

*This work was partially supported by the Office of Naval Research through Naval Research Laboratory Base Program.

**S.NM09.10.12**

**Substrate-Mediated Hyperbolic Phonon Polaritons in MoO$_3** J. Schwartz$^{1,2}$, Son T. Le$^{2,3}$, Sergiy Krylyuk$^2$, Albert Davydov$^2$ and Andrea Centrone$^2$; $^1$University of Maryland, United States; $^2$National Institute of Standards and Technology, United States; $^3$Theiss Research, United States

Hyperbolic phonon polaritons (HPhPs) are hybrid excitations of light and coherent charge oscillations that exist in strongly optically anisotropic 2D materials (e.g., MoO$_3$). These polaritons propagate through the material’s volume with long lifetimes, enabling novel mid-infrared nanophotonic applications by compressing light to sub-diffraction dimensions. Here, the dispersion relations and HPhP lifetimes (up to $\approx 2$ ps) in single-crystal $\alpha$-MoO$_3$ are determined by Fourier analysis of real-space, nanoscale-resolution polariton images obtained with the photothermal induced resonance (PTIR) technique. Measurements of MoO$_3$ crystals deposited on periodic gratings showed longer HPhPs propagation lengths ($\approx 2 \times$) and lower optical compressions in suspended regions compared to regions in direct contact with the substrate. Additionally, PTIR data reveal polymeric contaminants, resulting from sample preparation, localized under parts of the MoO$_3$ crystals. This work enhances the ability to engineer nanophotonic devices by leveraging substrate morphology to control polariton propagation.

**S.NM09.10.13**

**Anion Charge Density Disturbance Induces In-Plane Instabilities within 2D Lateral Heterojunction of TMD—An Atomic View** Bolong Huang; The Hong Kong Polytechnic University, Hong Kong

Two-dimensional (2D) heterostructure semiconductors are emerging as the potential candidates for broad applications, in which the transition-metal dichalcogenides (TMDs) have attracted the most attention due to their abundant advantages. TMDs have attracted tremendous interest due to the advantages of low-cost, earth-abundant, non-toxic, and environmentally friendly. Owing to the atomically thin structure, unique electronic and optical properties and rich diversity in chemical compositions, they have displayed considerable potential in the applications of integrated optoelectronic devices and systems such as p–n diodes, photodetectors, transistors, nanogenerators, and sensors as well as in catalysis. However, the investigations of these TMD heterostructure semiconductors usually only limit to the synthesis approach and opt-electronic properties, lacking the in-depth guidelines from the atomic exploration. Within the lateral heterojunction, the unique ripple effect has been identified as the consequence of the important interplay between different TMDs. Herein, the anion coupling induced charge disturbance within the WSe$_2$/WS$_2$ lateral heterojunction has been identified as the origin for the ripple structure induced by in-plane interfacial instability. Different scales of the first-principle simulations all verify the similar ripple phenomenon near the interfacial region of the WSe$_2$/WS$_2$ lateral heterojunction. Beyond the simple factor of lattice misfit, we confirm that the Se-S P-p coupling effect induced the uneven charge distribution is the intrinsic reason for such a unique structural phenomenon. By the introduction of the perturbation elastic entropy concept, we successfully predict the
interfacial ripple scale in the WSe2/WS2 lateral heterojunction systems, supporting the simulation of experimental size. This work has compensated the knowledge gap between the theoretical investigation and experimental synthesis, which is essentially beneficial for the future fabrication of 2D heterostructure semiconductors with superior performance. The fundamentally general mechanism for the experimentally observed phenomenon is of pivotal significance in the further exploration in such 2D heterojunction semiconductor materials.

S.NM09.10.14
Materials for Resonant Passage of Isotopes Aleksey M. Bubenchikov; Tomsk State University, Russian Federation

The method of mathematical modelling is a good tool for constructing new materials [1]. The present work considers the problem which concerns quantum sifting of isotopes of gas components at cryogenic temperatures. The authors also focus on the task of constructing the membrane itself. The calculations show that the membrane should have two identical ultrathin layers. By now, graphene nitride with regular pores has been synthesized using the double epitaxy method [2]. Mono-atomic layers of porous boron nitride [3] can also serve as the working layer of the membrane. Over the last decade, a group of new graphene-like mono-element 2D materials, such as germanene [4], silicene [5, 6], phosphorus [7], and stanene [8] have also been synthesized. In principle, all porous analogues of these materials are suitable for application as the working layer of the membrane. This appears to be possible since the result of resonant passage of one of the mixture components is largely determined by the distance between the plates.

The considered problem of particles passing through a composite barrier is a generalization of the well-known Landau problem of particles with a certain energy passing through a unitary barrier. When constructing an analytical solution to the generalized problem of wave dynamics, the authors proceeded from the Schrödinger integral equation. The solution was built as a result of dividing the functions containing a shift in the independent variable into a nonlinear differential operator and separated exponential functions of the parameter and the argument. Next, algebraic operations with differential operators were performed, and the resulting operator was applied to separated functions. The resulting solution for the wave function is completely determined by the spectrum of the composite barrier. Studying the asymptotic behaviour of the solution allowed for finding the zeros of the reflection coefficient. As a result, resonance modes of transmission of one of the components were found. These modes were determined by the sequence of resonant distances between the plates. Choosing the distance between the layers from this sequence it is possible to achieve a selectivity effect in which a particle with a mass of \( m \) and energy of \( E \) passes through a potential barrier consisting of two identical parts without reflection. In other words, one of the components shows complete passage, while the other component is characterized by partial passage only. This ensures operation of the membrane as a gas separator. The calculations show that, at certain temperatures, it is possible to achieve hyperselectivity of mixture separation.

References:

S.NM09.10.16
Synthesis and Study of 1H Structural Phase of Liquid-Exfoliated 2D Lead Iodide Nanodisks Using ADF-STEM Sapna Sinha1, Taishan Zhu2, Arthur France-Lanord2, Yuwen Sheng1; Jeffrey C. Grossman2, Kyriakos Poryfrakis1 and Jamie Warner1; 1University of Oxford, United Kingdom; 2Massachusetts Institute of Technology, United States

Synthesis and study of new two-dimensional (2D) materials nanosheets is very important for both fundamental study of
physical phenomenon as well as for new applications in nanoelectronics and optoelectronics. Lead Iodide (PbI₂) has been
reported to be an excellent candidate for applications in thin films, transistors and PbI₂ perovskites. However, not a lot of
study has been carried out on easy and facile preparation of this material to produce scalable monolayer films. Liquid phase
exfoliation (LPE) is considered to be an efficient method to obtain 2-dimensional nanosheets on a large scale. Based on
previous findings on screening solvents for LPE, in this study, I will present results on obtaining several hundreds of >99%
monolayer (PbI₂) using CHCl₃ as a solvent. We have then used atomic-resolution annular dark field scanning transmission
electron microscopy (ADF-STEM) imaging to study the monolayer flakes of PbI₂. Here, I will report on a new structure of
PbI₂ which has not been studied before. PbI₂, when suspended on graphene, converts into more energetically stable H-phase
crystal structure compared to T-phase structure which was found to be more stable on lacy carbon TEM grid. I will also
present results on the defects and edge structure of the monolayer PbI₂ and the unusually mobile atoms on the surface. The
structural change of the PbI₂ depending on substrate, i.e. graphene, opens up the possibility to control and further study its
properties by using other different kinds of substrates.

Structure and Defect Dynamics of 2D Monolayer Lead Iodide Nanodisks with Epitaxial Alignment on Graphene, (accepted,
in press, Nature Comms.)

S.NM09.10.17
Chemical Vapor Deposition Synthesis of MoS2 Crystal Assisted by HSS/H2 Precursors—A Quantum Molecular
Dynamics Study Sungwook Hong; California State University, Bakersfield, United States

Layered van der Waals Heterostructures such as MoS₂ monolayers have attracted great attentions for the application in
optoelectronic devices owing to their outstanding physical, chemical, and mechanical properties. Chemical vapor deposition
(CVD) is commonly used for scalable growth of layered materials. During CVD synthesis, reactions of MoO₃ and H₂S
reactants are essential reaction steps where MoO₃ flakes are reduced and sulfurized, transferring to MoS₂ crystals. Recent
studies suggested that addition of H₂ gas in this synthesis process could lead to synthesis of higher-quality MoS₂ monolayers.
However, effects of H₂ partial pressure on synthesis of MoS₂ still remain elusive. Here, we present quantum molecular
dynamics (QMD) simulations for CVD synthesis of MoS₂ layer using MoO₃ flakes and H₂S gas precursors with and without
H₂ gas. Our QMD simulations revealed that H₂ molecules indeed act as effective reducing agents for the MoO₃ flake. As
such, our work provides a valuable input for the scalable growth of layered van der Waals Heterostructures.
This work was supported as part of the Computational Materials Sciences Program funded by the U.S. Department of
Energy, Office of Science, Basic Energy Sciences, under Award Number DE-SC00014607.

SYMPOTIUM S.NM10

Synthesis, Properties and Applications of 2D MXenes
November 21 - December 1, 2020

Symposium Organizers
Majid Beidaghi, Auburn University
Johanna Rosen, Linkoping University
Susan Sinnott, The Pennsylvania State University
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SESSION S.NM10.06: Live Panel Session: Young Investigators Talks: Synthesis, Properties and Applications of 2D MXenes
Session Chair: Majid Beidaghi
Sunday Morning, November 29, 2020
S.NM10

8:00 AM EFFECT OF PRE-INTERCALATION ON THE PERFORMANCE OF MULTI-LAYERS MXENE—MICHAEL NAGUIB, TULANE UNIVERSITY

9:00 AM 2D MULTI-PRINCIPAL ELEMENT CARBIDES MXENES—BABAK ANASORI, INDIANA UNIVERSITY-Purdue University

SESSION S.NM10.08: Live Keynote: Synthesis, Properties and Applications of 2D MXenes
Session Chair: Majid Beidaghi
Tuesday Afternoon, December 1, 2020
S.NM10

5:15 PM MXENE HYDROGELS AND THEIR APPLICATIONS—HUSAM N. ALSHAREEF, KING ABDULLAH UNIVERSITY OF SCIENCE & TECHNOLOGY (KAUST)

5:55 PM THE VARIETY OF COLORS—OPTICAL PROPERTIES OF MXENES—YURY GOGOTSI, DREXEL UNIVERSITY

6:35 PM THE INTERLAYER SPACE, CATIONS AND WATER IN MULTILAYERED MXENES—MICHEL BARSOUM, DREXEL UNIVERSITY

SESSION S.NM10.01: Electronic, Optical and Magnetic Properties
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM10

5:00 AM *S.NM10.01.01
The Variety of Colors—Optical Properties of MXenes Kathleen A. Maleski and Yury Gogotsi; Drexel University, United States

The largest family of 2D materials, known as transition metal carbides and/or nitrides (MXenes), have a chemical formula of M_{n+1}X_nT_x, where M represents a transition metal (Ti, Mo, Nb, V, Cr, etc.), X is either carbon and/or nitrogen, and T_x represents surface terminations. The diversity in composition (~30 MXenes synthesized so far), availability of solid solutions on M and X sites, and control of surface terminations offers a plethora of structures and chemistries to investigate. The first discovered and most studied MXene, titanium carbide (Ti_3C_2T_x), has shown interaction with a wide range of the electromagnetic spectrum, including visible light transparency (>97% visible light transmittance per nanometer), a transverse surface plasmon in the near-infrared range (750-800 nm), and to capability to perform as an electromagnetic shield or dipole antenna in microwave or radio frequencies. Combining the optical properties with ease in processing, high electronic conductivity and mechanical strength, MXenes have the characteristics necessary to develop as optical materials. This talk will provide insight into the optical properties and potential applications of MXenes as well as spectroscopic information which can be applied to designing photonic and optoelectronic devices, such as electron transport layers for solar cells, optical sensors, random or femtosecond lasers, electrochromic devices, photonic diodes, metamaterials, photothermal therapy.
2D magnetic materials have received tremendous attention recently due to their fundamentally unique properties from their bulk counterparts and promises in data storage, sensing, and magneto-opto-electronic applications. Following the discovery of 2D ferromagnetic ordering of monolayer CrI3 and ultrathin Cr2Ge2Te6, several 2D magnetic materials including halides, chalcogenides, and sulphides, have been reported. MXenes are 2D transition metal carbides, carbonitrides, and nitrides with a general formula M_{n-1}X_{n}T_{x}, where M is early transition metal (such as Ti, Cr, Mn), X is C and/or N, n = 1-3, and T, represents surface terminations (such as O and F). Although there are several DFT calculations that suggest magnetic ordering in 2D MXene flakes, there is no experimental report on magnetic ordering of MXenes. In this talk, magnetic and electronic properties of Cr2TiC2T MXenes (Ti2CT, Mo2TiC2T), a double-metal ordered transition metal carbide MXene will be presented and discussed. We used a combination of vibrating sample magnetometry (VSM) and synchrotron X-ray magnetic linear dichroism (XMLD) to obtain evidence of antiferromagnetic order below 40 K in a free-standing film and a single flake of this MXene. Moreover, the temperature-dependence of resistivity and angular-dependent magnetoresistance measurements reveal distinct changes below 40 K, suggesting a coupling between the magnetic order and electronic transport.

MXenes are a rapidly-expanding family of 2D transition metal carbides and nitrides that have attracted attention due to their suitability for solution processing, hydrophilic surfaces, metallic conduction, and versatility in hosting a range of intercalant agents, and more.

References


Hantanasirisakul, K.; Gogotsi, Y. Adv Mater 2018, 30 (52), e1804779.
The Interlayer Space, Cations and Water in Multilayered MXenes

Michel W. Barsoum; Drexel Univ, United States

Discovered in 2011, the 2D early transition metal carbides known as MXenes - obtained by etching the A-layers from the MAX phases - have generated substantial interest in the scientific community because of their potential in an ever-expanding host of applications. Whether during etching or use, it is critical to understand what happens in the interlayerspace. In most applications, the first step is to etch and wash MXene multilayers, MLs, until they disperse. Using primarily XRD diffraction, the relationship between etchant used and washing protocols and the swelling of the interlayer space of Ti3C2Tx MLs is elucidated. How changing the intercalant cations can change the spacing, and even the nature of Ti3C2Tx MLs from hydrophilic to hydrophobic, is discussed. How to render MXenes oxidation resistant in aqueous solutions is described. Lastly, the similarities of MXenes and clays are overviewed.

5:50 AM S.NM10.01.06
Raman Spectroscopy of Transition Metal Carbides and Nitrides (MXenes) Asia Sarycheva and Yury Gogotsi; Drexel University, United States

Raman spectroscopy is known as a fast and non-invasive tool to characterize materials, in particular their atomic bonding. In the recent years, it was widely used in the field of 2D materials, including graphene1, transition metal dichalcogenides2, boron nitride3 and others4. It has also been used to evaluate the composition and defects in the structure of those materials. Moreover, Raman spectra could be collected even from a monolayer of 2D material. This impact on the field shows that Raman spectroscopy can give a lot of information about 2D materials, therefore is an essential tool for studying the new families of 2D materials. One of those families are MXenes, 2-dimensional transition metal carbides and nitrides, discovered at Drexel University at 20115, which gained already a lot of interest in a variety of applications. There is a limited number of Raman spectroscopy studies of MXenes studies6-10, therefore a database for quick assessment of a MXene is needed. We obtained Raman spectra and assigned peaks for M2X members of the family: Nb2C, Mo2C, V2C and Ti2C, as well as M2X3: Ti3C2, Mo2TiC2 and M2X4: Cr3Ti2C2 and Nb4C3, Mo2Ti2C4, covering the most widely used MXenes. We showed the difference between multilayer form (powder), delaminated form (deposited thin film or filtrated free-standing film). In the collected library of Raman spectra of MXenes we showed the change in the atomic vibrations with changing or substituting M element(s).


6:00 AM S.NM10.01.08
MXenes for Plasmonic Photodetection
Jehad K. El-Demellawi; King Abdullah University of Science and Technology, Saudi Arabia

MXenes have recently shown impressive optical and plasmonic properties associated with its ultrathin atomic layer structure.1 However, their use in photonic and plasmonic devices is still marginally explored. Herein, we have fabricated various flexible photodetectors made of different MXenes, i.e., Mo2CTx, Ti3C2Tx, Nb2CTx, T2CT2 and V2CT2. The surface chemistry and the optoelectronic properties of the mechanically flexible arrays of two-terminal, parallel-type photodetectors deposited on paper substrates are thoroughly investigated. Amongst the five studied MXenes, Mo2CT have exhibited the best...
performance owing to its relative stability against oxidation, moderately high free carrier density and electrical conductivity,[2] though not as high as that of Ti3C2Tx.[1,3,4]

The Mo2CTx flexible devices have exhibited broad photosresponse in the range of 400-800 nm with high responsivity (R, up to 9 A W-1), detectivity (D*, ~5x1011 Jones) and reliable photoswitching characteristics at a wavelength of 660 nm. It is worth mentioning that despite being the first demonstration of MXene-based photodetection, the performance of Mo2CTx thin films considering their R and D* is surpassing the majority of previously reported visible-band photodetectors based on solution-processed 2D materials. In particular, the responsivity of Mo2CTx devices were found to be ~18000 and ~1200 times higher than that of the first reported graphene[5] and MoS2[6] photodetectors, respectively. In addition to their attractive performance and solution processability, we have revealed that our MXene-based devices possess an additional set of advantages including full visible spectrum coverage, highly stable operation and mechanical flexibility. Furthermore, micro-Raman spectroscopy conducted on bare and on gold-coated Mo2CTx films allowing for surface-enhanced Raman scattering demonstrated a surface chemistry and a specific low-frequency band that we have related to the vibrational modes of the single Mo2CTx nanosheets.

The photodetection mechanism of our devices was unveiled using spatially-resolved STEM-EELS and ultrafast femtosecond transient absorption spectroscopy. We show that the photoresponse is dominated by the intrinsic plasmon-assisted hot carrier generation. The demonstrated ability of coupling with light and dephasing of surface plasmons with a short lifetime, without the need of integration with other metallic plasmonic structures, as previously demonstrated with several 2D materials,[7] have led to a photoresponse outperforming that of photoelectron-based devices.

Our findings shed light on the knowledge of photocurrent generation mechanisms in MXenes, making them much more viable for many photonic and plasmonic device applications. Moreover, the specific ability to detect and excite individual surface plasmon modes, provide a viable platform for various MXene-based optoelectronic applications.

6:10 AM *S.NM10.01.09
Rational Design of 2D Magnetic Materials Vivek B. Shenoy, Nathan Frey and Arkamita Bandyopadhyay; University of Pennsylvania, United States

Recent experimental success in the realization of two-dimensional (2D) magnetism has invigorated the search for low-dimensional material systems with tunable magnetic anisotropy that exhibit intrinsic long-range ferromagnetic order. In this talk, I will present a rational design approach for studying and engineering magnetism in MXenes. I will also discuss a recently developed model for applying machine learning to accelerate MXene synthesis. Using a crystal field theory model and first-principles simulations, we demonstrate intrinsic ferromagnetism, high magnetic moments, high Curie temperatures, and intrinsic semiconducting and half-metallic transport behavior in nitride and ordered double-transition-metal MXenes. We report that modifying the surface termination and transition metal in monolayer M2NTx nitride MXenes gives rise to a rich diversity of noncollinear spin structures and finely tunable magnetic anisotropy. We predict that manipulating the strength of the spin-orbit interaction and electron localization via the chemical degrees of freedom can induce sufficient anisotropy to counteract thermal fluctuations that suppress long-range magnetic order. Further, surface engineering and applied electric fields enable robust switching and stabilization of magnetic behavior in MXenes. We extend this approach to study recently synthesized non-van der Waals 2D transition metal oxide materials, showing an observable net magnetic moment in 2D iron and chromium oxides. Our work suggests that MXenes and transition metal oxides offer a promising avenue for achieving practical solid-state devices with 2D magnetic materials.

SESSION S.NM10.02: Synthesis, Characterization and Surface Chemistry
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM10

5:00 AM *S.NM10.02.01
The Role of “X” in MXenes—Titanium Carbonitride as a Model System Michael Naguib; Tulane University, United States

MXenes is a large family of two-dimensional (2D) transition metal carbides and nitrides of composition M(n+1)XnTz; M is an early transition metal (e.g. Ti, V, Nb, Mo), X is carbon or nitrogen, n =1-3 and Tz stands for mixture of surface terminations (e.g. O, OH, F). With more than two dozen of MXene reported in the recent years, MXenes has expanded significantly the chemical space of 2D materials. Most of studies on MXenes focused on the first reported MXene viz. Ti3C2Tx, much smaller
number of studies focused on other transition metals including ordered double transition metal and solid solutions at the M sites in MXenes. While nitrogen doping nanomaterials including transition metal carbides and oxides are known to be a very promising approach for altering materials properties and performance, very limited number of studies focused on carbonitride MXene. Herein, we use the titanium carbonitride as a model system to highlight the importance of studying the role of "X" in MXene. The characteristic differences between Ti$_3$C$_2$T$_z$ and Ti$_3$CNTz MXenes from both structure and surface chemistries points of views are discussed based on experimental results obtained using multiple techniques and theoretical calculations. Also, the performances of Ti$_3$CNTz as electrode materials for electrochemical energy storage electrocatalysis in addition to their performance as catalysts will be discussed and compared to that of Ti$_3$C$_2$T$_z$.

5:15 AM S.NM10.02.03
Computational Investigation of the Structure-Property Relationships of MXenes Susan B. Sinnott; The Pennsylvania State University, United States

Material modeling methods are now widely applied to investigate and design new materials. This is especially helpful in cases where different compositions are possible and structure-property relationships need to be predicted. This presentation will discuss the application of material modeling methods to MXenes. The methods used include density functional theory calculations and atomic-scale simulations with reactive force fields.

5:25 AM *S.NM10.02.04
MXene Surface Chemistry Per O. Persson; Linköping University, Sweden

Since their discovery in 2011 [1], MXenes have outperformed existing materials for a range of applications such as energy storage [2], water filtering [3], electromagnetic shielding [4], as catalysts for H$_2$ evolution from water [5] and as astonishingly effective materials for capturing CO$_2$ [6] to name but a few examples. Their outstanding performance is accredited to a range of properties, e.g. hydrophilic and conductive, that can be attributed to a rich transition metal chemistry. Ultimately, the range of properties are dictated by the tailoring potential of the MXenes. In this respect, MXenes stand out in stark contrast to commonly employed 2-dimensional structures.

The general formula to describe MXenes, M$_{n+1}$TX$_x$, identifies that the tailoring potential in the MXene family is vast. In addition to choice of thickness (n) and X element, for instance, M can be a range of single transition metal elements, or an extensive set of combinations between multiple M elements in an ordered or disordered condition. Similarly, the range and corresponding potential mix of terminating elements or molecules is an apparent key in determining the final MXene properties. On top of this, the surfaces may be further decorated by functional elements.

The present contribution primarily adopts advanced electron microscopy methods to reveal the state of the art available tailoring of the MXene structure and chemistry, owing to recent advances in tuning of surface terminations, surface decoration and corresponding properties.

5:40 AM *S.NM10.02.05
MXene Chemistry—Fundamentals and Applications Vadym Mochalin; Missouri University of Science and Technology, United States

A large family of two-dimensional transition metal carbides and nitrides (MXenes) raises interest for many applications due to their high electrical conductivity, mechanical properties [1], potentially tunable electronic structure [2], nonlinear optical properties [3], and the ability to be manufactured in the thin film state [4]. However, their chemistry that is key to development of these applications, still remains largely terra incognita [5]. In this presentation we will discuss recent progress in understanding fundamental MXene chemistry and harnessing it for development of applications.

For example, during delamination and storage in ambient air environment, spontaneous oxidation of MXene flakes leads to formation of titanium oxide, a process that can be harnessed for simple, inexpensive, and environmentally benign manufacturing MXene–titania composites for optoelectronics, sensing, and other applications [6]. We show that partially oxidized MXene thin films containing the in situ formed phase of titanium oxide have a significant photoresponse in the UV region of the spectrum. The relaxation process of photoexcited charge carriers, which takes a long time (~24 h), can be accelerated in the presence of oxygen and water vapor in the atmosphere. These properties of spontaneously formed MXene-titania thin films make them attractive materials for photodetectors with memory effect and sensitivity to the environment, as well as many other photo- and environment-sensing applications.

Other selected examples illustrating connections between understanding MXene chemistry and development of their applications will also be considered.
References
1. Y. Li, S. Huang, C. Wei, C. Wu, V. N. Mochalin, Nature Communications, 10, 3014 (2019)

5:55 AM S.NM10.02.06
Scalable Synthesis of Ti3C2Tx MXene Christopher E. Shuck1, Asia Sarycheva1, Mark Anayee1, Ariana S. Levitt1, Yuanzhe Zhu1, Simge Uzun1, Vitaliy Balitskiy2, Veronika Zahorodna2, Oleksiy Gogotsi2 and Yury Gogotsi1; 1Drexel University, United States; 2Materials Research Center, Ukraine
Scaling the production of synthetic two-dimensional (2D) materials to industrial quantities has faced significant challenges due to synthesis bottlenecks whereby few have been produced in large volumes. These challenges typically stem from bottom-up approaches limiting the production to the substrate size or precursor availability for chemical synthesis and/or exfoliation. MXenes are a large family of 2D carbides and/or nitrides that have applications in electrochemical energy storage, electromagnetic interface shielding, electrocatalysis, gas sensing, electrochromic devices, and many others. In contrast to other 2D materials, MXenes are produced via a top-down synthesis approach. The selective wet etching process does not have similar synthesis constraints as some other 2D materials. The reaction occurs in the whole volume; therefore the process can be readily scaled with reactor volume. In this study, the synthesis of 2D titanium carbide MXene (Ti3C2Tx) was studied in two batch sizes, 1 and 50 g, to determine if large-volume synthesis affects the resultant structure or composition of MXene flakes. Characterization of the morphology and properties of the produced MXene using scanning electron microscopy, X-ray diffraction (XRD), dynamic light scattering (DLS), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), UV-visible spectroscopy, and conductivity measurements showed that the materials produced in both batch sizes are essentially identical. This illustrates that MXenes experience no change in structure or properties when scaling synthesis, making them viable for further scale-up and commercialization.

6:05 AM S.NM10.02.08
Composition-Dependent Oxidation Stability of 2D Transition Metal Carbides (MXenes) Mikhail Shekhirev1,2, Zein Alali1,2 and Yury Gogotsi1,2; 1Drexel University, United States; 2A.J. Drexel Nanomaterials Institute, United States
Transition metal carbides, carbonitrides and nitrides, also known as MXenes, attract significant attention due to their unique combination of properties. In addition to interest from scientific community, MXenes hold a great promise for multiple applications, such as energy storage, electromagnetic interference shielding, water purification and others. In order to transition from the lab bench to industrial scale applications, however, it becomes increasingly important to understand how stable MXenes are under different conditions and to find approaches to optimize shelf life of the material. That is why a number of recent reports focused on oxidation stability of titanium carbide (Ti3C2Tx, where T is termination, such as -OH, =O, -F) as the most studied member of MXene family, suggesting different strategies to inhibit its degradation. Despite the recent advances in improving of Ti3C2Tx stability, understanding degradation process for other members of MXene family remains elusive. With the wide variety of MXene compositions available (>30 reported, about 100 of possible stoichiometric compositions and infinite number of solid solutions) it is critical to investigate how MXenes other than Ti3C2Tx behave and how their chemical composition affects stability.
In this presentation we report on our studies on stability of MXenes against hydrolysis and oxidation in aqueous solutions. We evaluate different approaches suggested in literature and numerically compare their efficiency. For instance, efficiency of different additives, such as antioxidants and edge capping agents, will be discussed using Ti3C2Tx MXene as a model system, as well as other MXene compositions. Significant attention will be paid to effect of synthesis method and surface groups on MXene stability. Finally, the effect of M element in MXene will be discussed using the M2CTx MXene family (M=Ti, Nb or V) as an example.

6:15 AM S.NM10.02.10
2D Multi-Principal Element Carbides MXenes Babak Anasori; Purdue School of Engineering, Indiana University-Purdue University, United States
The family of two-dimensional (2D) transition metal carbides and nitrides, MXenes, is one of the largest families of 2D materials with more than thirty synthesized compositions (e.g., Ti2C, Ti3C2, Nb2C, Mo2C) and several more that are predicted to exist. MXenes with two transition metals exist in either random solid solutions or ordered forms. The latter MXenes are called ordered double-transition metals carbides, in which two transition metals form either in-plane or out-of-plane atomic ordering, such as in Mo1.33Y0.66C, Cr2TiC2, and Mo2Ti2C3. In the ordered double-transition metal carbides (MXenes), physical, electrochemical, and mechanical properties can be tuned by controlling the transition metals ordered chemistry. Here, by combining two relatively new fields of double-transition metal MXenes and high entropy alloys and ceramics, a new area in the MXenes field has emerged as multi-principal element MXenes. In these MXenes, four transition metals are combined in the form of solid-solutions in the 2D atomic planes of MXenes. In this talk, the rationale behind high entropy MXenes, their synthesis conditions, and their properties will be discussed.

6:30 AM S.NM10.02.11
Self-Assembly of Recombinant Silk Fibroin on Ti3C2 MXene Surface Michelle Krecker1, Daria Bukharina1, Christine B. Hatter2, Yury Gogotsi2 and Vladimir Tsukruk1; 1Georgia Institute of Technology, United States; 2Drexel University, United States

Here we show that MXene flakes can be uniformly coated with amorphous recombinant silk fibroin in aqueous solution under ambient conditions. X-ray photoelectron spectroscopy has revealed a reduction of TiO2 formation by half on modified flakes after 21 days in water, suggesting the silk coating provides some protection against oxidation of the MXene surface, a common issue of MXene dispersions. High resolution atomic force microscopy was used to map the morphological changes of these modified flakes over time and showed silk fibril formation on flake surfaces. This spontaneous reorganization of recombinant silk, a material that typically has difficulty reorganizing after the harsh chemical treatment used to solubilize spun fibers, suggesting some chemical reduction provided by the MXene flake.

SESSION S.NM10.03: Electrochemical Properties and Energy Storage Applications
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM10

5:00 AM S.NM10.03.01
Dense Charge Accumulation in MXene with a Hydrate-Melt Electrolyte Masashi Okubo and Atsuo Yamada; The University of Tokyo, Japan

Renewable energy systems are in urgent demand; however, integration of renewable energy into electrical grids requires rapid load-leveling of abrupt power spikes/drops and a wide distribution of high-power energy storage devices represents the most promising solution. However, current electrochemical energy storage devices do not meet all the requirements for grid-scale use, particularly because of slow charge/discharge rates caused by limited ion transport. Supercapacitors have rapid operation owing to the formation of an electric double-layer (EDL) at the electrode surface, which contributes to a higher power density and longer cycle lifetime than achievable in conventional batteries. In particular, supercapacitors based on aqueous electrolytes are attractive because of their low cost, high ion conductivity, non-flammability, and eco-friendliness. However, the energy density of such devices is severely limited by the narrow potential window of water (1.23 V). To overcome this obstacle, we focus on a highly-concentrated aqueous electrolyte known as a hydrate melt (Li(TFSI)0.7(BETI)0.3/2H2O, TFSI: bis(trifluoromethanesulfonyl)imide, BETI: bis(pentafluoroethanesulfonyl)imide). Owing to the unique local coordination structure of water, hydrate melts show an exceptionally wide electrochemical potential window (> 3 V) as electrolytes, which far exceeds the thermodynamic hydrogen/oxygen evolution limits of water (1.23 V). Aqueous supercapacitors based on hydrate-melt electrolytes are expected to realize much higher voltage operation and hence much higher energy densities with an appropriate choice of electrode materials. As an electrode material that can maximize use of the wide electrochemical window provided by hydrate-melt electrolytes, we used transition-metal carbidies MXene. Because MXenes are reported to provide a large specific capacitance greater than 300 F/g in conventional aqueous electrolytes, their combination with a hydrate-melt electrolyte should realize a much higher energy density. Here, we demonstrate the high-voltage operation of an aqueous supercapacitor consisting of an MXene Ti2CTx electrode and
a hydrate melt electrolyte.

5:15 AM S.NM10.03.02
3D Printing of Additive-Free MXene Ink for Fabrication of Micro-Supercapacitors with Ultra-High Energy Densities Jafar Orangi, Fatima Hamade, Virginia A. Davis and Majid Beidaghi; Auburn University, United States

Small scale energy storage devices are expected to play a significant role in the future advances of portable electronics, wireless sensors, and multifunctional micro/nanosystems. A crucial requirement for the fabrication of energy storage devices with high energy and power densities is using electrode materials with superior electrochemical properties. Another important requirement is the assembly of the electrode materials into structures that promote high ionic and electronic conductivities. In this talk, we report a scalable printing method for fabrication of on-chip three-dimensional (3D) micro-supercapacitors based on a class of 2D transition metal carbides called MXenes as electrode materials. MXenes offer high electronic conductivity and high specific capacitance and therefore, have attracted much interest as high-performance electrode materials for supercapacitors. In our work, the fabrication of MXene electrodes and device assembly is achieved using an extrusion-based 3D printing process that uses viscoelastic water-based MXene ink. A programmable printing machine was used in the printing process which involved layer-by-layer deposition of the MXene ink to fabricate the 3D electrodes. The developed printing method allows rapid fabrication of micro-supercapacitors on a variety of substrates, while electrode height can be controlled by the number of deposited layers. All-solid-state devices printed on flexible substrates showed excellent electrochemical performances under different bending conditions and delivered extremely high areal capacitances (over 800 mF cm-2). Our study suggests that due to its high electronic conductivity and electrochemical properties, MXene is an excellent electrode material for the fabrication of 3D energy storage devices.

5:25 AM S.NM10.03.03
d-Spacing Effect on the Electrochemical Performance of MXene in Organic and Room Temperature Ionic Liquids Kun Liang1, Naresh Osti2, Eugene Mamontov2, Bishnu Thapaliya1, Sheng Dai1 and Michael Naguib1; 1Tulane University, United States; 2Oak Ridge National Laboratory, United States; 3The University of Tennessee, Knoxville, United States

MXenes exhibit excellent capacitance at high rates in aqueous electrolytes, especially in H₂SO₄ aqueous electrolyte, but in a narrow potential window, which limits the energy density. Moreover, oxidation of Ti₃C₂ under high anodic potentials in aqueous electrolytes further limits its use to cathodes of asymmetric devices. Organic electrolyte and room temperature ionic liquids (RTIL) can provide a higher potential window, leading to higher energy density and open circuit potential. While they can host other ions beyond protons, the rate capability of MXenes is not at the same level as what has been achieved in aqueous electrolytes. We hypothesis that there should be an optimum d-spacing that can allow for fast ions (beyond protons) for high power with high energy considering the larger voltage window offered by both organic and RTIL electrolytes. To test this hypothesis, we are studying the effect of interlayer spacing on the overall electrochemical performance of the electrodes to define. The specific capacitances from intercalated Ti₃C₂Tz for both Li⁺ and EMI⁺ were higher than those from non-intercalated Ti₃C₂Tz. The intercalated MXene shows a higher specific capacitance of 137 and 98 F g⁻¹ in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-TFSI) and EMI-TFSI/AN electrolyte, respectively. The diffusion coefficient of EMI⁺ in intercalated Ti₃C₂Tz was higher than that from non-intercalated Ti₃C₂Tz, and the larger d-spacing, the higher the diffusion coefficient. Moreover, quasi-elastic neutron scattering was used to study MXene with different d-spacing, and it showed high mobile EMI⁺ confined in-between the layers of MXene with large d-spacing.

5:40 AM *S.NM10.03.04
Capacitive Energy Storage in MXenes—Termination Dependence and Ion Specific Intercalation Processes Paul Kent; Oak Ridge National Laboratory, United States

The capacitive properties of MXenes are high tunable based on their composition, terminal groups, electrolyte, choice of intercalated ions, and nanoscale confinement. To enhance the energy stored and power that can be delivered in these materials requires a significantly improved understanding of the MXene properties, intercalation chemistry, and determining the relevant processes. I will first describe a first-principles computational study focused on predicting the achievable capacitance in different MXenes with a simplified model aqueous electrolyte. Second, I will describe a highly integrated and high fidelity study between experimental and modeling approaches to investigate the intercalation processes for aqueous Li⁺, Na⁺, K⁺, Cs⁺, Mg²⁺ into Ti₃C₂ MXenes. Experiments include microcalorimetry, atomic force microscopy and cyclic voltammetry whose results are directly linked to the results of detailed first-principles modeling. Our integrated analysis allows us to understand the energy storage processes and highlights the importance of the dynamics of cations and...
positionings and their role in capacitive energy storage properties. These findings will expedite the evolutions of energy
related functional devices by enabling improved design of higher-performing membranes and two-dimensional materials.

This work was supported as part of the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy
Frontier Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences.

5:55 AM S.NM10.03.06
Energy Storage Devices in Textiles by Knitting MXene Yarns Ariana S. Levitt, Genevieve Dion and Yury Gogotsi;
Drexel University, United States

Textile devices integrate exciting functionalities into clothing, including the ability to sense, actuate, monitor health signals,
and communicate with nearby electronics. These devices require power to function, motivating researchers to develop energy
storage devices that can be seamlessly integrated into textiles. In the last ten years, several works have been published on the
development of fiber- and yarn-based supercapacitors using various carbon-based active materials such as activated carbon,
graphene, and intrinsically conducting polymers. These devices demonstrate high energy density below ~4 cm in length but
suffer from high resistance at longer lengths leading to reduced performance. For this reason, new active materials with
higher conductivity and advanced device architectures are needed to improve the capacitance and rate performance of textile
supercapacitors.

We pioneer the incorporation of Ti$_3$C$_2$Tx, a two-dimensional carbide and member of the MXene family, into commercial
natural and synthetic fibers to develop highly conductive and electrochemically active yarn electrodes. The outstanding
electrical and electrochemical performance of these yarns produced by several techniques, from electrospinning to
infiltration, can be attributed to the high conductivity (10,000 S cm$^{-1}$ as a thin film) and high capacitance of Ti$_3$C$_2$T$_x$ (1500 F
cm$^{-3}$) due to redox reactions of surface titanium atoms. These yarns were knitted into a new architecture of textile energy
storage devices, 3D knitted supercapacitors, using industrial knitting machines. Unlike fiber- and yarn-based supercapacitors,
knitted supercapacitors consist of interconnected loops of fiber/yarn electrodes, providing multiple pathways for electron
transport and reducing resistance relative to a freestanding fiber/yarn. By tuning the knit structure and geometry, such as
stitch density and fabric dimensionality, the spacing between electrodes reduced 4-fold, increasing the areal capacitance from
402 mF cm$^{-2}$ to 707 mF cm$^{-2}$ at 2 mV s$^{-1}$. This is the first work to study industrially relevant knitting parameters in designing
textile-based supercapacitors and their effects on electrochemical performance. The ability to rapidly fabricate meters of
electrochemically active yarns and energy storing textiles enables the design and study of fully integrated textile circuits that
could one day be developed into garments capable of sensing and computing.

6:05 AM S.NM10.03.08
Supercapacitor Yarns Based on Graphene-Oxide and MXene Flakes—Size Effect and More Wei Gao; North Carolina
State University, United States

We will discuss our recent progress on direct fiber extrusion from graphene-oxide (GO) and MXene dispersions in water, and
the corresponding fiber performance as supercapacitor electrodes in supercapacitor yarns. The flake sizes of these 2D sheets
turn out to impact the resulted fiber properties and performance to a great extent.
Supercapacitors are known to have superior power densities over batteries due to their surface-centered charge-discharge
processes. Recently, increasing attention has been attracted to yarn-shaped supercapacitor systems, mainly due to their high
flexibility and pliable nature, leading to potential applications in wearable electronics, microrobots, medical implants, and
smart textiles. However, one of the major limitations that occurs when supercapacitors are made into fiber/yarn shapes, is the
increased equivalent series resistance (ESR) due to the fibrous geometry adopted here. For instance, even the best
supercapacitor yarns reported will exhibit a few hundred ohms of resistance at one-meter length, which is usually neglected
by researchers in their publication. To directly tackle this issue, here we report our strategies of using a metallic core filament
in the yarn supercapacitors developed in our lab. With detailed materials and process engineering, we can boost the power
density by one order of magnitude.

6:15 AM *S.NM10.03.10
Theoretical Exploration of the Potential of MXenes as Electrode Materials in Batteries Jun Fan; City University of
Hong Kong, Hong Kong

MXenes, a class of two-dimensional transition metal carbides, nitrides and carbonitrides, have been extensively studied since
their discovery. Because of their superior conductivity, large specific surface area and tunable physic-chemical properties,
MXenes have been demonstrated to be promising electrode materials for various batteries such as: Li ion batteries, Na ion
batteries and Lithium-sulfur batteries etc. So far, more than thirty different kinds of MXenes have been successfully synthesized in experiment and at the same time more members were predicted to exist by theoretical calculations. Since MXenes possess rich chemical compositions and their family are still growing, it is meaningful to further exploit more high-performance MXenes-based electrode materials for various batteries. In this talk, some strategies including changing the functional groups and transition metals of MXenes for designing high-capacity anode materials in Na ion batteries will be discussed. Specifically, the structural, electronic, adsorption and diffusion properties of Ti3C2, Ti3C2S2 and Zr-based MXenes as anode materials for Na ion batteries by using density functional theory (DFT) calculations will be included. More importantly, a correlation between charge transfer, lattice mismatch and the capacity of MXenes were identified, which will be useful for designing other 2D anode materials for Na ion batteries [1-2]. At the meantime, the potential of a series of MXenes as anchoring materials for Lithium-sulfur batteries and structure-properties correlation will also be presented [3]. Moreover, the strain effects on electronic properties of MXenes with a focus on lithium adsorption and structural transformation will also be discussed [4].


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SESSION S.NM10.04: Electronic, Electrochemical and Emerging Applications of MXenes
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM10

5:00 AM *S.NM10.04.01
MXenes Thin Film for Lightweight Electromagnetic Interference Shielding Chong Min Koo1,2; 1Korea Institute of Science and Technology, Korea (the Republic of); 2Korea University, Korea (the Republic of) MXenes, 2D transition metal carbides, has emerged as a light-weight, ultrathin electromagnetic shielding materials for mobile telecommunication devices and advanced 5G smart electronics, since it offers an attractive combination of high electronic conductivity (~5000 S/cm), low density, hydrophilicity, and processability. In this presentation, we demonstrate that MXene is an ideal candidate for light-weight shielding with minimal thickness. The MXene thin film shows the extraordinary EMI shielding behavior due to its large electrical conductivity and 2D nano structure. These unique experimental results will be understood by theoretical calculations. Additionally, this presentation demonstrates that the simple post-treatment of MXene thin film deduces an unusual strong interaction with electromagnetic wave, resulting in strong absorption-induced attenuation.

5:15 AM S.NM10.04.03
Mechanical and Electrical Properties of Ti3C2T, MXene Single Flakes Alexey Lipatov1, Mohamed Alhabeb2, Haidong Lu1, Babak Anasori2, Alexei Gruverman1, Yury Gogotsi2 and Alexander Sinitskii2; 1University of Nebraska–Lincoln, United States; 2Drexel University, United States Two-dimensional (2D) transition metal carbides and nitrides, known as MXenes, are a large class of materials that are finding numerous applications ranging from energy storage and electromagnetic interference shielding to water purification and antibacterial coatings. However, while bulk applications of MXenes are rapidly developing, their intrinsic physical property characterization through single-flake measurements remains a largely unexplored area of research. Here, we report the elastic properties of monolayers and bilayers of the most important MXene material to date, Ti3C2T, (T stands for surface termination) measured using nanoindentation with the tip of an atomic force microscope. The effective Young’s modulus of a
single layer of Ti$_3$C$_2$Tx was found to be 0.33 ± 0.03 TPa, which is the highest among the reported values for solution-processed 2D materials, including graphene oxide. Individual Ti$_3$C$_2$Tx flakes also exhibit a high conductivity of 4600±1100 S/cm and field-effect electron mobility of 2.6±0.7 cm$^2$/Vs. We found that the resistivity of individual flakes is only one order of magnitude lower than the resistivity of multilayer Ti$_3$C$_2$Tx films, which indicates a surprisingly good electron transport through the surface terminations of different flakes, unlike in many other 2D materials.

5:25 AM S.NM10.04.04
Scalable, Highly Conductive and Micro-Patternable MXene Films Jason Lipton$^1$, Jason A. Röhr$^1$, Vi Dang$^1$, Adam Z. Goad$^2$, Kathleen A. Maleski$^2$, Yury Gogotsi$^2$ and André D. Taylor$^1$; $^1$New York University, United States; $^2$A.J. Drexel Nanomaterials Institute, United States

2D transition metal carbides and nitrides (MXenes) have accumulated tremendous interest recently as a result of their high conductivity, aspect ratio, and excellent figures of merit in numerous application areas. Freestanding films of MXenes are important for versatility in their incorporation into roll-to-roll production to allow for large-scale fabrication. Vacuum assisted filtration is currently the state-of-the-art for fabrication of freestanding MXene films, but this method does not project well for large-scale production due to limitations on film areas and thicknesses as well as the required use of a vacuum system. Aqueous-based solution casting onto hydrophilic substrates is a useful way to make MXene coatings but they cannot be delaminated from the substrate to yield a freestanding film. In this work, we show that it is possible to fabricate Ti$_3$C$_2$ MXene freestanding films through simple drop-casting onto hydrophobic substrates. MXene films prepared using this technique have greater alignment of MXene flakes due to repulsive interactions between the substrate and the Ti$_3$C$_2$ MXenes and allows for facile delamination of the film from the substrate. We show that freestanding drop-cast MXene films can be fabricated in large areas (125 cm$^2$) and thicknesses (23.2 µm), have high electronic conductivity and smooth surfaces as a result of improved flake alignment. Drop-cast MXene films can also be micropatterned in three dimensions simply by using commercially available microstructured plastics as substrates. The results presented here suggest a new scalable path towards creating MXene freestanding films for novel prototypes and industrialization.

5:35 AM S.NM10.04.05
MXene Family of Materials for Electromagnetic Interference Shielding Meikang Han$^1$, Christopher E. Shuck$^1$, Roman Rakhmanov$^1$, David Parchment$^1$, Babak Anasori$^2$, Chong Min Koo$^2$, Gary Friedman$^1$ and Yury Gogotsi$^2$; $^1$Drexel University, United States; $^2$Indiana University–Purdue University Indianapolis, United States; $^3$Korea Institute of Science and Technology, Korea (the Republic of)

New ultrathin and multifunctional electromagnetic interference (EMI) shielding materials are required for protecting electronics against electromagnetic pollution in the fifth-generation (5G) era. Micrometer-thin films built of 2D Ti$_3$C$_2$T$_x$ MXene nanosheets have shown extraordinary promise for EMI shielding. Yet, EMI shielding properties of other MXenes have not been explored, despite the fact that more than 30 different stoichiometric MXenes have been reported and many more are possible, including an infinite number of solid solutions. We report on a systematic study of EMI shielding properties of 16 single-metal, ordered double-metal and random solid solution MXenes. Films with thickness ranging from nanometers to micrometers were produced by spin-casting, spray-coating and vacuum filtration. EMI shielding effectiveness of the sprayed Ti$_3$C$_2$T$_x$ film with a thickness of ~40 nm reaches 21 dB (shielding >99% EM wave). Adjustable EMI shielding properties were achieved in solid solution MXenes with different ratios of elements. This work opens a pathway for designing ultrathin, flexible and multifunctional MXene films with outstanding EMI shielding performance coupled with other specific characteristics of particular MXenes.

5:45 AM S.NM10.04.07
Effect of Cation Pre-Intercalation on the Electrochemical Performance of Multilayer Ti$_3$C$_2$ MXene in Aqueous Electrolyte Kaitlyn E. Prenger$^1$, Ameer Al-Temimy$^{2,3}$, Kun Liang$^1$, Simone Raoux$^{2,4}$, Tristan Petit$^2$ and Michael Naguib$^1$; $^1$Tulane University, United States; $^2$Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany; $^3$Freie Universität Berlin, Germany; $^4$Humboldt-Universität zu Berlin, Germany

Electrically conductive 2D transition metal carbides and nitrides known as MXenes, discovered in 2011, have already shown an enormous potential in the field of electrochemical energy storage, due to their capabilities to host ions and protons in addition to their high electrical conductivity. MXenes are synthesized by selective etching of atomically thin metal layers from layered ceramics called MAX phases. The as synthesized MXene is in the form of multilayers held together by hydrogen and van der Waals bonds. The multilayers can be delaminated via intercalation followed by mechanical agitation to separate the layers from each other forming colloidal solution that can then be filtered forming freestanding MXene paper. While delaminated Ti$_3$C$_2$ MXene has shown high capacitance, multilayer Ti$_3$C$_2$ has shown more modest values. One
limitation for using the free-standing MXene paper is the thickness, which results in low areal capacitance.

Herein, we will present on the electrochemical performance of multilayer MXene that was pre-intercalated with metal cations (Na\(^+\), K\(^+\), Mg\(^{2+}\)) in between layers of Ti\(_3\)C\(_2\) in H\(_2\)SO\(_4\) aqueous electrolyte. At 5 A/g a gravimetric capacitance of 325 F/g was achieved, and it was stable over thousands of cycles. This is comparable to electrochemical performance of freestanding MXene paper but much higher than what can be achieved for conventional multilayer MXene without pre-intercalation. More interestingly, an areal capacitance up to 3 F/cm\(^2\) was achieved for cation pre-intercalated multilayer Ti\(_3\)C\(_2\). This simple modification of Ti\(_3\)C\(_2\) MXene in its multilayer form yielded an easier avenue for making Ti\(_3\)C\(_2\) supercapacitor electrodes with high areal capacitance. X-ray absorption spectroscopy (XAS) shows that changing cations in-between the layers alters the oxidation state of the titanium atoms in Ti\(_3\)C\(_2\) MXene, whereas dispersing MXene in an H\(_2\)SO\(_4\) environment resulted in reducing the surface titanium atoms of MXene. These results also encourage further investigation on the effects of intercalation and other modifications to Ti\(_3\)C\(_2\) interlayer chemistry.

**5:55 AM S.NM10.04.10 Two-Dimensional MXene Ti3C2Tx Membrane-Based Osmotic Power Generator** Seunghyun Hong\(^1\), Fangwang Ming\(^1\), Yifeng Shi\(^1\), Renyuan Li\(^1\), In S. Kim\(^2\), Chuyang Y. Tang\(^1\), Peng Wang\(^1,4\) and Husam N. Alshareef\(^3\); \(^1\)King Abdullah University of Science and Technology, Saudi Arabia; \(^2\)Gwangju Institute of Science and Technology, Korea (the Republic of); \(^3\)The University of Hong Kong, Hong Kong; \(^4\)The Hong Kong Polytechnic University, Hong Kong

Salinity-gradient is emerging as one of promising clean and renewable sources of energy, but its energy efficiency is severely limited by unsatisfactory performance of available semipermeable membranes [1]. Most recently, nanoconfined two-dimensional channels, as fluidic conduits for harnessing the Gibbs free energy of mixing under salinity gradient, have exhibited their superior energy conversion performance to conventional technologies [2]. Here, the lamellar Ti\(_3\)C\(_2\)Tx MXene membrane is presented as a high-performance salinity battery, directly converting the stored chemical potential energy to electricity [3]. Subnanometer 2D channels in the MXene Ti\(_3\)C\(_2\)Tx membranes enable cation-selective passage, assisted with tailored surface functional groups, under salinity gradient, and consequently produce diffusion potential. A record-high output power density of 21 W-m\(^{-2}\) at room temperature with an energy conversion efficiency of up to 40.6 % is achieved by controlled surface charges at a 1000-fold salinity gradient. Furthermore, thermal control of surface charges and ionic mobility yields a power density of up to 54 W-m\(^{-2}\). Our findings advance the fundamental understanding of nanoionic transport through MXene 2D channels and thus offer a new opportunity to develop MXene membranes as a promising platform for the high-performance salinity battery.


**6:05 AM S.NM10.04.11 Biological Activities and In Vitro Toxicological Features of the MXenes** Agnieszka M. Jastrzebska\(^1\), Aleksandra Szuplewska\(^a\) and Anita Rozmysłowska-Wojciechowska\(^1\); \(^1\)Warsaw University of Technology, Faculty of Materials Science and Engineering, Poland; \(^2\)Warsaw University of Technology, Poland

The past few years have witnessed significant development in the chemistry and potential biological applications of two-dimensional (2D) materials. Innovative 2D carbides, nitrides and carbonitrides of early transition metals, called MXenes, have been also extensively studied for several years on the applications in human health protection. The recent advances include biotechnological and biomedical applications such as anticancer treatment, photothermal therapy, drug delivery platforms, or nano-drugs without any additional modification. These can be combined with bioimaging, magnetic resonance or photoacoustic techniques. It is currently accepted that the specific functionalities of the MXenes can result in wide spectrum of bio-activities. In this context, MXenes are currently being carefully studied, with strong attention to mechanisms of action and biocompatibility features. We already know that MXenes exhibit different cellular effects which can be additionally induced by multiple external or internal factors. These effects are in turn strictly dependent on MXenes structure, chemical composition, and surface characteristics which positively support their interesting potential in nano-therapies. In fact, MXenes are promising anticancer agents, which can not only inhibit proliferation of cancer cells but also induce oxidative stress, and even influence the cell functioning and cell cycle through inducing programmed cellular death (apoptosis). On the other hand, such a wide range of bio-activities may inevitably cause unexpected toxicological effects that require a broader understanding. The obtained results clearly indicate that in this respect, the surface chemistry of MXenes has a significant impact on their biological properties. This is closely related to the synthesis methods and also oxidizing properties, leading to the occurrence of potentially toxic superficial metal oxides. In the case of MXenes, the challenge now relates not only to obtain the needed biological properties but above all, to understand and maintain (stabilize) them in the
desired environment. The presented studies will shed some light on the issues raised above and also outline new directions in toxicology of the MXene phases. They are focused on elucidating antiproliferative, pro-oxidative, and pro-apoptotic mechanisms of action. The specific features of MXenes such as a high degree of morphological anisotropy, specific chemical functionalities, surface oxides, and unique surface charges undoubtedly define their biological properties.

6:15 AM S.NM10.04.12
Photosensitizer and Anticancer Drug-Loaded 2D Nanosheet—Preparation, Stability and Anticancer Property Gang Liu1,2 and Naoki Komatsu3; 1Wuhan Institute of Technology, China; 2Kyoto Univ, Japan

Cancer phototherapy (PT) including photodynamic therapy (PDT) and photothermal therapy (PTT) has attracted extensive interest due to its non-invasive and region-specific nature. In order to enhance the efficacy, we have fabricated various nanocomposites consisting of a photosensitizer (chlorin e6 (Ce6), pheophorbide a (Pa) or bacteriopheophorbide a (bPa)) for PDT and a two-dimensional nanosheet (graphene or MoS2) for PTT by a one-pot protocol through liquid phase exfoliation. In addition, an anticancer drug (doxorubicin (DOX) or irinotecan (Ir)) was loaded on the nanosheet in the same way. All the nanocomposites were stably dispersed in water except for MoS2-Ir. Among the nanocomposites, MoS2-Ce6 killed cancer cells more than ten times more effective than Ce6 loaded other nanomaterials [1].


6:25 AM S.NM10.04.13
2D MXene Heterostructures as Electrodes for High-Rate Supercapacitors Armin VahidMohammadi1,2, Wentao Liang3, Mehrnaz Mojtabavi3, Meni Wanunu3 and Majid Beidaghi1; 1Auburn University, United States; 2University of Connecticut, United States; 3Northeastern University, United States

Two-dimensional (2D) transition metal carbides (called MXenes) are among the most promising candidates for supercapacitor electrodes because of their ability to intercalate a variety of cations and high rate pseudocapacitive properties in acidic and neutral electrolytes. However, the research on 2D MXenes is just at its early stages, and out of ~30 MXene compositions that are experimentally made, only Ti3C2Tx MXene has been extensively studied. A few reports have also shown the promise of other MXenes, such as 2D V2CTx in aqueous supercapacitors. Recently, we have shown high rate pseudocapacitance and exceptional (electro)chemical stability of cation-pillared delaminated V2CTx in neutral aqueous electrolytes as well as highly acidic electrolytes with capacitances as high as ~ 1300 F cm−3 (obtained in 3M H2SO4).[2] Despite these promising properties, the peak capacitance of Ti3C2Tx and V2CTx in 3M H2SO4 can only be achieved in certain potentials (~−0.3 V vs. Ag/AgCl for Ti3C2Tx and ~0 V vs. Ag/AgCl for V2CTx). In addition, the cycle life of V2CTx electrodes in the highly acidic sulfuric acid electrolyte is not on par with the Ti3C2Tx. Also, similar to the other 2D materials, the self-restacking of MXenes and their lower capacitances compared to other pseudocapacitive materials have hindered their further development. Controlled pillaring of 2D materials into multilayers and vertical stacking of different 2D layers into heterostructures have shown to be effective methods to avoid their self-restacking and overcome drawbacks of individual 2D materials.[1] Such pillared 2D multilayers or superlattice heterostructures built by sequential stacking of multiple 2D layers can display new and improved electrochemical responses and offer the combination of their building blocks’ best properties. In this talk, we argue that combining different delaminated MXenes into stacked heterostructures can result in new electrode structures that have superior properties in supercapacitors. We demonstrated this by fabricating all MXene heterostructures from delaminated Ti3C2Tx and V2CTx, which showed new features in their cyclic voltammetry profiles and could deliver the highest volumetric capacitance of ~1470 F cm−3 in 3M H2SO4 electrolyte. This study paves the way for the preparation of high-performance hetero-layered MXene structures for electrochemical energy storage applications and beyond.

References

6:35 AM S.NM10.04.15
Achieving Superlubricity with 2D Transition Metal Carbides (MXenes) and MXene/Graphene Coatings Shuohan Huang1, Kalyan Mutyala2, Anirudha Sumant2 and Vadym Mochalin1; 1Missouri University of Science and Technology, United States; 2Argonne National Laboratory, United States

Two-dimensional (2D) materials have demonstrated unique friction and wear properties compared with their bulk (3D) counterparts. Some of the well-known 2D materials such as graphene, MoS2 and h-BN have shown outstanding tribological
properties as additives to solvents, nanofillers in composite materials, and solid lubricants. A relatively new, large and quickly growing family of two-dimensional (2D) early transition metal carbides and nitrides (MXenes) [1] possess a unique combination of high electrical conductivity and hydrophilicity [2], which offers great potential in different applications such as energy generation [3] and storage, sensors [4], composites, and biomedical applications.

There is an increased interest to mechanical properties of MXenes [5]. However, their tribological behavior has not been sufficiently studied yet. Here we investigate the tribological properties of Ti$_3$C$_2$ MXene with different flake sizes deposited on SiO$_2$ coated Si substrates subjected to wear by sliding against a diamond-like carbon (DLC) coated steel-ball using a ball-on-disc type tribometer operating in dry nitrogen and in ambient air environments. We have observed that the friction is reduced to superlubric regime in dry nitrogen environment. Moreover, a combination of MXene and graphene has also been studied and the results show that with the addition of graphene, the abrasion was further reduced while the superlubricity behavior was maintained. This work opens new opportunities for exploring the potential of MXenes and MXene/graphene coatings as novel solid lubricants for various applications.

References


SESSION S.NM10.05: Poster Session: Synthesis, Properties and Applications of 2D MXenes

On Demand Abstracts Available for Viewing Starting Saturday, November 21, 2020

Morning, November 21, 2020

5:00 AM - 8:00 AM

S-NM10

S.NM10.05.02

High Temperature Synthesis of a Crystalline MXene with Ordered Surface Terminations Jacob Pawlik and Daniel Druffel; University of North Carolina, United States

In this work, a new MXene is experimentally described which exhibits uniform functionality on MX layers (-Cl), contrary to the mixed functionality (-F, -O, -OH) of traditional MXenes. Most MXenes contain random surface terminations, arising from the vigorous etching process of the MAX phase with acids such as HF. However, the present MXene Y$_2$CCl$_2$ is synthesized by a direct high temperature method followed by liquid exfoliation, which results in highly crystalline 2D flakes. This MXene has well-defined properties due to single moiety surface terminations, allowing for construction of simple computational models. Previous research in the field highlights the difficulty of predicting properties such as band gap and surface energy due to the unpredictable arrangement of surface terminations and complexity of computational models. A crystalline MXene with ordered terminations offers an easily synthesizable target with properties that can be predictably tuned.

First, Y$_2$CCl$_2$ was directly synthesized by heating a pellet composed of Y, C, and YCl$_3$ in a sealed tantalum tube at 950°C for 5 days according to literature procedures. Next, density functional theory (DFT) calculations were performed to predict the energy required to exfoliate Y$_2$CCl$_2$ into an MXene. The binding energy of Y$_2$CCl$_2$ (0.14 J/m$^2$) is less than half the binding energy of graphite, indicating that Y$_2$CCl$_2$ should be easier to exfoliate than graphite. A common method for exfoliating graphite is sonication in a liquid with similar surface properties, so the material was sonicated in the polar aprotic solvent propylene carbonate. The mixture quickly forms a well-dispersed solution of 2D Y$_2$CCl$_2$ flakes. Transmission electron microscopy (TEM) shows flakes with lateral sizes of 2-5 µm, and electron diffraction confirms retention of the crystalline Y$_2$CCl$_2$ structure. The optical properties were evaluated by UV-Vis spectroscopy, which reveals an absorption peak at 1.64
eV that is close to the expected band gap of 1.56 eV, calculated using the HSE06 functional. Furthermore, X-ray photoelectron spectroscopy measurements reveal unusual oxidation states associated with yttrium (2+) and carbon (2-), suggesting interesting electrical properties.

This material has several attractive features that may be utilized. Y₂CCl₂ is easily exfoliated in mild conditions, avoiding the hazards of corrosive media such as HF and HCl. Also, the material absorbs light in the visible, making Y₂CCl₂ potentially useful for light harvesting and photocatalytic applications. More broadly, Y₂CCl₂ is part of a larger class of metal carbide halide materials with the stoichiometry M₂CX₂ (M = Y, Sc, Gd; X = F, Cl, Br, I) that share similar structure and properties. Through preliminary calculations, we predict that other metal carbide halides may be exfoliable and contain similar properties to Y₂CCl₂. Overall, Y₂CCl₂ and other similar metal carbide halides offer a new class of MXenes with ordered surface terminations.

S.NM10.05.04
Investigating Chemical Reactivity of MXenes Using Gas Chromatography Shuohan Huang, Gabriel Huliiung and Vadym Mochalin; Missouri University of Science and Technology, United States

MXenes are a new family of two-dimensional (2D) materials discovered in 2011. Because of their 2D structure and many outstanding properties [1], MXenes have raised significant interest for various applications, such as batteries, optoelectronic devices [2], supercapacitors, lasers [3,4], sensors [5], etc. It was found that titanium carbide MXene flakes in aqueous solutions spontaneously transform into TiO₂ and recently, it has been demonstrated that water plays the main role in the reactions leading to this chemical transformation [6]. Thus, studying MXene reactivity is important for prolonged shelf life of MXene colloidal solutions, as well as for robust performance of MXene based devices. In this work, we demonstrate the use of gas chromatography technique to study reactivity of MXenes. Several hypotheses have been put forward to explain the degradation of MXenes in aqueous environments. However, no studies of the gaseous products of this reaction have been reported. The analysis of gases produced during MXene degradation, using gas chromatography, allows for a better understanding of the degradation process. The chemical reactivity of MXenes with different monolayer thickness was also investigated at different pH and temperatures. Our results have led to new, important conclusions about the chemical reactivity of MXenes in aqueous solutions. This knowledge will have significant impacts on the development of MXenes and other 2D materials for many applications.

References

S.NM10.05.10
Raman Spectroscopy Reveals the Effect of Synthesis Conditions on Ti₃C₂: Asia Sarycheva and Yury Gogotsi; Drexel University, United States

Raman spectroscopy has been one of the most helpful tools for analysis of two-dimensional (2D) materials1-2. While newly discovered materials should be probed using this technique, there have been just a few studies available for a large family of 2D transition metal carbides and nitrides known as MXenes3-5. To see which effects Raman spectroscopy can detect for MXenes we performed a systematic study of the mostly used MXene to date - Ti₃C₂Tx. By synthesizing material in different ways, we monitored changes in Raman spectra. we have synthesized Ti₃C₂ via MILD method, where HF is formed in-situ by mixing LiF and HCl, HF-HCl (mixture of two acids), and by using various concentration of HF: 5%, 10%, 20% and 30% solutions in water3. We collected Raman spectra from samples collected at different stages of MXene synthesis: from multilayer powders to delaminated flakes, in order to observe the effect of stacking. The whole spectrum of Ti₃C₂ is divided into 4 regions: a resonant peak, A₁₈ out-of-plane vibrations of Ti, C and O, the surface group vibrations region and carbon
vibrations region. Those regions change based on the synthesis method and flake surrounding. All those peaks are affected not only by surface functional groups\textsuperscript{5}, but also by stacking of the flakes. Due to a plasmonic peak of Ti\textsubscript{3}C\textsubscript{2}Tx around 785 nm, resonant conditions\textsuperscript{6} are achieved enabling an extra peak at around 119-123 cm\textsuperscript{-1} when using a red diode laser. Lastly, we showed how photoluminescence, usually considered as an unwanted background of Raman spectra, can be used to detect the early stages of MXene degradation.

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**S.NM10.05.14**

**MXene-Based Composite Functional Inks for 3D Printed Lithium-Ion Batteries**

Jafar Orangi and Majid Beidaghi;
Auburn University, United States

In a broad range of applications, including energy storage, flexible electronics, and sensors, additive manufacturing is considered as a promising device fabrication technique due to its potential for the development of complex architectures and using a variety of materials. Extrusion-based three-dimensional (3D) printing is a low-cost and straightforward method that offers rapid and precise fabrication of “on-chip” batteries and supercapacitors with 3D architectures. In this presentation, we report on our recent research on the development of functional nanocomposite inks based on two-dimensional (2D) MXenes, with the application in lithium-ion storage. MXenes are a new class of 2D materials with high electronic conductivity and hydrophilicity and have gained interest as high-performance electrode materials for electrochemical energy storage. The developed nanocomposite inks are incorporated with the MXene sheet as a conductive additive that can also provide the rheological properties required for extrusion-based 3D printing without the need for any other additive or binder. The inks were prepared by mixing lithium iron phosphate and lithium titanate nanoparticles with a highly concentrated water-based MXene ink and were directly used for printing of the cathode and the anode of a microbattery, respectively. A programmable printing machine was used in the fabrication process that follows the layer-by-layer deposition of the nanocomposite ink. The developed inks and printing methodologies facilitate the rapid fabrication of microbatteries on a variety of substrates, while the loading of active material per area of the device can be controlled by the number of deposited layers. The electrochemical test results show the excellent performance of 3D printed batteries.

**SYMPOSIUM S.NM11**

Topological and Quantum Phenomena in Oxides and Oxide Heterostructures
November 21 - November 21, 2020

Symposium Organizers
Aiping Chen, Los Alamos National Laboratory
John Heron, University of Michigan
Xia Hong, University of Nebraska-Lincoln
Jorge Iniguez, Luxembourg Institute of Science and Technology

* Invited Paper
SESSION S.NM11.01: Emerging Phenomena in Ferroelectric and Multiferroic Materials
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

S-NM11

5:00 AM *S.NM11.01.02

Characterization of Novel Topological Phases in Ferroelectric Materials Javier Junquera1, Fernando Gómez-Ortiz1, Pablo García-Fernández1, Nauro A. Pererira Gonçalves2,3 and Jorge Íñiguez2,3; 1Universidad de Cantabria, Spain; 2Luxembourg Institute of Science and Technology (LIST), Luxembourg; 3University of Luxembourg, Luxembourg

Complex topological configurations are a fertile area to explore novel emergent phenomena and exotic phases in Condensed-Matter Physics. The discovery of magnetic skyrmions one decade ago [1] have triggered a flurry of research on these particle-like nanometer-sized topologically protected spin textures, mostly motivated by their potential use in spintronic devices such as race track memories [2]. Since then, researchers have long wondered whether ferroelectrics may present topological textures akin to magnetic skyrmions and chiral bubbles. In this quest, the side by side advances in experimental growth and characterization techniques, and the development of new modelling tools are of paramount importance. In this respect, the emerging field of second-principles simulations [3-4], where an effective model is constructed by a judicious choice of the essential physics, and the parameters of the model are extracted by fitting to Density Functional Theory, are proving increasingly valuable in the study of large systems, overlapping in size with those that can be currently grown by atomic layer deposition methods. As a result of this continuous feedback between theory and experiment, the recent discovery of polarization vortices [5] and their associated complex-phase coexistence and response under applied fields in superlattices of (PbTiO3)n/(SrTiO3)n [6] suggests the presence of a complex, multi-dimensional system capable of emergent physical responses, such as a chirality [7]. In this talk, I shall describe the latest developments to create, tune, and characterize topological textures in ferroelectrics [8,9]. Polar structures with a well-defined topological charge and chirality will be presented. The stabilization of such non-uniform polarization topology results in highly enhanced susceptibilities, and also provides a pathway for engineering novel functionalities previously inaccessible, such as regions with negative capacitance [10].

Financial support from the Spanish Ministry of Economy and Competitiveness through Grant PGC2018-096955-B-C41

References

5:15 AM S.NM11.01.04

Photoinduced Topotactic Reduction of Colloidal Iron Oxide Nanocrystals Hankyeol Jung and Alina Schimpf; University of California, San Diego, United States

Photoinduced topotactic reduction of colloidal iron oxide nanocrystals

Magnetite (Fe3O4) and maghemite (γ-Fe2O3) nanocrystals have been extensively studied due to their superparamagnetic behavior that potentiates their application in magnetic storage devices, catalysis, and medical diagnosis and treatment. As the ratio of Fe3+/Fe2+ determines the phase and magnetic properties of iron oxide nanocrystals, controlling the oxidation state of Fe is critical for such applications. Oxidation of Fe3O4 to γ-Fe2O3 has been thoroughly studied and is known to occur slowly in air or more rapidly with heat or additional oxidants. Reduction of γ-Fe2O3 to Fe3O4, however, is less well understood. We report reduction of colloidal γ-Fe2O3 nanocrystals by UV irradiation in the presence of a sacrificial reductant. Specifically, anaerobic irradiation in the presence of ethanol reduces Fe3+ to Fe2+, yielding a topotactic reduction of γ-Fe2O3 to Fe3O4. The properties of the nanocrystals upon photoreduction are monitored by UV/visible/near-IR electronic absorption spectroscopy, superconducting quantum interference device magnetometry and powder X-ray diffraction. Factors influencing the photoreduction, such as the type of hole quencher and nanocrystal size will be discussed. Our findings demonstrate a new
Controlling topological properties by varying external parameters is the quintessential step for developing next-generation devices with topological materials. Correlated topological phases (CTPs) can be induced by the interplay of electron correlation and spin-orbit coupling. They are the promising candidates whose band topology can be engineered by breaking the intricate balance between different energy scales. Pyrochlore iridate films belong to a family of cubic 5d transition metal oxides. They are representative systems where various CTPs can be studied by manipulating magnetism with lattice strain. However, their in-situ epitaxial growth has been known to be notoriously difficult. We recently succeeded in developing a new technique to grow in-situ fully strained Nd2Ir2O7 thin films. A fully strained film with antiferromagnetism shows an anomalous Hall conductivity which is an order of magnitude larger than that in the bulk or the relaxed film. Moreover, we observed the large spontaneous Hall conductivity which comes from the strain-induced magnetic T1-octupole. Our work demonstrates that topological properties can be engineered by manipulating magnetism with strain in oxide heterostructures.

References:
Domain walls naturally arise whenever a symmetry is spontaneously broken. They interconnect regions with different realizations of the broken symmetry, promoting structure formation from cosmological length scales to the atomic level. In my talk, I will present topological 1D spin textures and domain walls with intriguing physical properties, which emerge in spin-spiral multiferroics and chiral magnets and which hold great promise for nanoelectronics and spintronics applications. In particular, I will discuss that a wide variety of new domain walls occurs in the presence of spatially modulated domain states. In contrast to domain walls in conventional ferroics, such domain walls exhibit a well-defined inner structure, which—analogous to cholesteric liquid crystals—consists of topological disclination and dislocation defects. Similar to the magnetic skyrmions, the domain walls can carry a finite topological charge, permitting an efficient coupling to spin currents and contributions to a topological Hall effect. Our studies establish domain walls in chiral magnets as functional nano-objects with non-trivial topology, opening the door to innovative device concepts in information and communication nanotechnology.

SESSION S.NM11.03: Emerging Phenomena at Oxide Heterostructures and Interfaces
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM11

5:00 AM S.NM11.03.05
Experimental Realization of Intrinsic Strain-Induced Ferroelectricity in SrMnO3 Films via Selective Oxygen Annealing
Hyunji An1, Jeong-Kyu Kim3, Sangmoo Kim3, Jiwoong Yang3, Hojoong Choi3, Chung Wung Bark3, Bong-Joong Kim3, Kyung-Tae Ko4, and Sanghan Lee1; 1Gwangju Institute of Science and Technology (GIST), Korea (the Republic of); 3POSTECH, Korea (the Republic of); 4Gachon University, Korea (the Republic of); 3Korea Basic Science Institute, Korea (the Republic of)

SrMnO3 (SMO) has recently aroused enormous interest because theoretical studies predicted the paraelectric-antiferromagnetic system in its bulk state can be transformed into a new multiferroic system via strain-engineering. However, experimental verification is still inadequate due to high-leakage current density (180 A/cm²) and surface cracks, which are derived from oxygen deficiency of strained SMO thin films. Hence, we devised a selective oxygen annealing (SOA) method effectively filling the oxygen vacancies while protecting the surface of the SMO. By applying this method, clean surface and insulating behavior (current density: 3.8 x 10⁻⁶ A/cm² and dielectric loss <0.1) are successfully achieved in a 1.7% tensile-strained SMO thin film. This SOA method not only allows direct investigation of the intrinsic multiferroicity of strained SMO but also device application without leakage issues. Based on the obtained insulating behaviors, the SMO thin film shows the room-temperature ferroelectric polarization loop (Pₑ: 1 μC/cm²) and the dielectric constant (εᵣ: 138.1). Moreover, a significant reduction of the dielectric constant from 138.1 to 6.7 is observed by systematically releasing the epitaxial strain. These findings can be important experimental evidence of phase transition from paraelectric to ferroelectric phase via strain-engineering as theoretically predicted. Furthermore, since SMO can be optionally a low-k or high-k material, it can be applied to a wide range of capacitors or memory devices. We also believe that our SOA method will be an important key to open the next-step of multiferroic SMO by enabling us to directly investigate its intrinsic characteristics.

SESSION S.NM11.04: Search for Quantum Materials and States
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM11

5:00 AM *S.NM11.04.01
Tunable Resistivity Exponents in the Metallic Phase of Epitaxial Nickelates
Beatriz Noheda1,1, Qikai Guo1, Saeedeh Farokhipoor1, Cesar Magen2, and Francisco Rivadulla3; 1University of Groningen, Netherlands; 2Universidad de Zaragoza, Spain; 3Universidade de Santiago de Compostela, Spain

The tunable resistivity of materials undergoing a metal-insulator transitions (MIT) holds great promise for resistive switching applications, such as adaptable electronics and cognitive computing. However, a complete understanding of the metallic
phase in these strongly correlated electron systems is still one of the central open problems in condensed matter physics. Here we will present a detailed analysis of the electrical resistivity exponent of thin films of NdNiO$_3$ as a function of epitaxial strain. Strain-free thin-films show a linear dependence of the resistivity versus temperature, consistent with a classical Fermi gas ruled by electron-phonon interactions. In addition, the apparent temperature exponent, $n$, can be tuned with the epitaxial strain between $n = 1$ and $n = 3$. We discuss the critical role played by quenched random disorder in the value of $n$. Our work shows that the assignment of Fermi/Non-Fermi liquid behaviour based on experimentally obtained resistivity exponents requires an in-depth analysis of the degree of disorder in the material.

This work is being considered for publication as Qikai Guo, Saeedeh Farokhipoor, Cesar Magen, Francisco Rivadulla and Beatriz Noheda, “Tunable resistivity exponents in the metallic phase of epitaxial nickelates” and it can be found at https://nature-research-under-consideration.nature.com/users/37265-nature-communications/posts/53928-tunable-resistivity-exponents-in-the-metallic-phase-of-epitaxial-nickelates, and at https://arxiv.org/abs/1909.06256

5:15 AM *S.NM11.04.02
Majorana Zero Mode for Topological Quantum Computing Jinfeng Jia; Shanghai Jiao Tong University, China

Majorana zero mode (MZM) can be used in fault-tolerant quantum computation relying on their non-Abelian braiding statistics, therefore, lots of efforts have been made to find them. Signatures of the MZMs have been reported as zero energy modes in various systems. As predicted, MZM in the vortex of topological superconductor appears as a zero energy mode with a cone like spatial distribution. Also, MZM can induce spin selective Andreev reflection (SSAR), a novel magnetic property which can be used to detect the MZMs. Here, I will show you that the Bi$_2$Te$_3$/NbSe$_2$ hetero-structure is an artificial topological superconductor and all the three features are observed for the MZMs inside the vortices on the Bi$_2$Te$_3$/NbSe$_2$. Especially, by using spin-polarized scanning tunneling microscopy/spectroscopy (STM/STS), we observed the spin dependent tunneling effect, which is a direct evidence for the SSAR from MZMs, and fully supported by theoretical analyses. More importantly, all evidences are self-consistent. Our work provides definitive evidences of MFs and will stimulate the MZMs research on their novel physical properties, hence a step towards their statistics and application in quantum computing. Finally, the possible application in topological quantum computing is discussed.

References

5:30 AM *S.NM11.04.03
Temperature Promoted Topological Order in PbO$_2$: Bartomeu Monserrat, Bo Peng, Ivona Bravić and Judith L. MacManus-Driscoll; University of Cambridge, United Kingdom

Topological materials host exotic properties such as dissipationless spin and charge currents or Majorana fermions that could find numerous technological applications, for example in low-power electronics and spintronics or in quantum computers. However, most topological properties are currently restricted to extremely low temperatures, precluding applications.

In this talk, we will describe our first principles quantum mechanical calculations to understand the microscopic origin of the interplay between temperature and topological order in materials. Our work reveals that this interplay is dominated by a combination of thermal expansion and electron-phonon coupling, and that increasing temperature should destroy topological order in most materials, in agreement with all available experimental reports. Interestingly, our results also suggest avenues for designing materials with the opposite behaviour, and we present a polymorph of PbO$_2$ as the first example of a material in which increasing temperature promotes rather than destroys topological order.
Morning, November 21, 2020
S-NM11

5:00 AM *S.NM11.05/S.NM12.05.02
Topological Quantum Phenomena in Correlated Oxide Heterostructures Ho Nyung Lee; Oak Ridge National Laboratory, United States

Many physical phenomena in condensed matter arise from strong correlation and spin-orbit coupling (SOC), and their proper control is important for creating novel quantum materials (QMs), such as Mott insulators, quantum spin liquids, topological insulators, Weyl semimetals, etc. to name a few. As the importance of quantum information science emerges, there is an increased attention to QMs to address the need for new materials for addressing challenges in quantum computing and sensing. Among many classes of QMs, complex oxides offer a rich playground to exploit both correlations of Coulombic interactions between electrons often found in 3d transition metal oxides (TMOs) and SOC from heavy metal based 5d TMOs, such as SrIrO3 and Na2IrO3, leading to many intriguing physical properties. Hybrid materials with a proper balancing of the correlation and SOC offer unique opportunities to discover new properties, and heterostructuring or combining dissimilar materials is a great approach to harnessing the complex interplay between quantum wavefunctions and various control parameters, such as proximity, dimensionality, topology, and symmetry. In this talk, I will review recent progresses in topological quantum materials and present our recent work on topological Hall effect from chiral magnetism and its control via interfacial symmetry control. Furthermore, an effort to combine topology and correlation to develop correlated topological materials and an approach to develop novel Berry phase engineered heterostructures will be presented.

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.

SESSION S.NM11.06: Spin-Orbit Coupling Driven Quantum Phenomena

On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM11

5:00 AM *S.NM11.06.03
LaTiO3/ SrTiO3 Interfaces—From Giant Rashba Spin Splitting to Edge State Conduction Michael Veit1, Xin Yu Zheng1, Remi Arras2, Brad Ramshaw2, Mun Chan4, Di Yi1, Rossitza Pentcheva3 and Yuri Suzuki1; 1Stanford University, United States; 2University of Toulouse, France; 3Cornell University, United States; 4Los Alamos National Laboratory, United States; 5University of Duisberg-Essen, Germany

The Mott insulator/ band insulator interface of LaTiO3/ SrTiO3 was first shown to exhibit metallicity due to electronic reconstruction by Ohtomo and Hwang in 2002. This work led to significant research activity exploring emergent metallicity at complex oxide interfaces – most notably at the LaAlO3/SrTiO3 interface. However there has been comparably less study of the LaTiO3/ SrTiO3 interface versus the LaAlO3/ SrTiO3 interface. We have recently found that the metallic behavior at the LaTiO3/ SrTiO3 interface is accompanied by giant Rashba spin-orbit coupling. Evidence for this giant Rashba spin splitting is manifest in two sets of Shubnikov-de Haas oscillations associated with an inner and outer Fermi surface, Berry phase of π, substantial anisotropic magnetoresistance and a weak anti-localization correction to the magnetoconductivity. Together these results indicate a giant Rashba coupling which is an order of magnitude larger than other complex oxide interfaces such as LaAlO3/SrTiO3. By gating the samples with an electric field, we observe (i) quantized resistance peaks which are independent of sample dimensions in a conventional 6-terminal Hall bar geometry, (ii) a strong negative magnetoresistance near the quantized peaks in resistance, and (iii) nonlocal transport in a 4-terminal geometry. All of these observations are consistent with edge state conduction and the quantum spin Hall effect.

†This work was funded by the Vannevar Bush Fellowship of the Department of Defense under Contract No. N00014-15-1-0045.
SrTiO₃/FeSe Superlattice for Robust Interface Enhanced Superconductivity

Kamron L. Kopecky, Sumner B. Harris and Renato P. Camata, The University of Alabama at Birmingham, United States

The unconventional, iron-based superconductor FeSe has a low Tc in bulk form at 8 K but sees a massive enhancement up to as high as ~109 K when monolayers are interfaced with the complex oxide SrTiO₃. The origin of this Tc enhancement is due to both electron transfer from SrTiO₃ to FeSe as well as interfacial electron-phonon interactions. Since FeSe monolayers are highly unstable in air, protective layers must be grown on top to enable ex-situ study or application. These capping layers limit the Tc enhancement to ~30 K. In order to preserve the high Tc as well as environmentally stabilize the FeSe layers, we have explored the growth of novel SrTiO₃/FeSe superlattice heterostructures by pulsed laser deposition (PLD). Starting with TiO₂ terminated SrTiO₃ single crystals as the growth substrate, alternating FeSe and SrTiO₃ layers are grown in a reducing, high vacuum environment. Typically, SrTiO₃ growth takes place in an oxygen background, but here we have achieved low to zero defect SrTiO₃ layers by controlling the kinetic energy of the laser-generated plasma plume by monitoring the plasma properties in-situ with planar and cylindrical Langmuir probes. The kinetic energy cut-off for both the SrTiO₃ and FeSe plume is kept below ~30 eV by balancing the laser energy and spot size on the ablation targets. Adjusting the kinetic energy allows control over the oxygen defects, which dope electrons into the FeSe, while the superlattice structure enables double-sided interfacial electron-phonon interactions between SrTiO₃ and FeSe. We report on both in-situ and separate, extensive plasma measurements during PLD conditions used for superlattice growth. The plasma density can be fine-tuned over orders of magnitude between 1×10¹⁸-1×10²⁰ m⁻³ by changing the spot size on the target while utilizing the same laser fluence, which changes the growth rate. The kinetic energy distribution of the plasma plume constituents is also highly tunable below the plasma absorption threshold. Ions and neutrals can be easily generated with kinetic energies as high as 150 eV if large laser spot sizes greater than ~6 mm² are used. However, it is by decreasing the spot size down to 3.5 mm² or less, and thereby reducing the high-energy tail of the kinetic energy distribution, that layers with significantly fewer defects are produced. We also report on x-ray diffraction and x-ray photoelectron characterization of the superlattices.

SYMPOSIUM S.NM12

Synthesis and Control of Dirac or Topological Materials
November 21 - November 30, 2020

Symposium Organizers
Matthew Brahlek, Oak Ridge National Laboratory
Yue Cao, Argonne National Laboratory
Joseph Checkelsky, Massachusetts Institute of Technology
Phil King, University of St Andrews

Symposium Support
Bronze
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* Invited Paper
SESSION S.NM12.13: Live Keynote I: Synthesis and Control of Dirac or Topological Materials
Session Chairs: Yue Cao and Phil King
Sunday Morning, November 29, 2020
S.NM12

10:15 AM INTRODUCTION AND ANNOUNCEMENTS

10:17 AM *S.NM12.05.03
Magnetic Weyl Semimetals Claudia Felser and Jacob Gayles; Max Planck Institute, Germany

Topology a mathematical concept became recently a hot topic in condensed matter physics and materials science. One important criteria for the identification of the topological material is in the language of chemistry the inert pair effect of the s-electrons in heavy elements and the symmetry of the crystal structure [1]. Beside of Weyl and Dirac new fermions can be identified compounds via linear and quadratic 3-, 6- and 8- band crossings stabilized by space group symmetries [2]. In magnetic materials the Berry curvature and the classical AHE helps to identify interesting candidates. Magnetic Heusler compounds were already identified as Weyl semimetals such as Co2YZ [3-6] (Y=Ti, Mn; Z=Ge, Sn, Ga, Al), in Mn3Z [7-9] (Z=Ge, Sn). Co3Sn2S2 is a 2D Weyl semimetal with edge states [8-10].


10:47 AM *S.NM12.07.02
Controlling Quantum Materials by Nonlinear Phononics Michael Först; Max Planck Institute for the Structure and Dynamics of Matter, Germany

Irradiation with light is able to dynamically push quantum materials away from equilibrium, driving them into states with transiently perturbed magnetic and electronic properties. This field has become a rich playground for fundamental research but may also be relevant for technical applications that require ultrafast switching capabilities.

In this talk, I will focus on our use of intense terahertz and mid-infrared light fields to control quantum solids by resonant excitation of crystal lattice vibrations. This approach has been demonstrated to switch between different phases and reveal hidden states not accessible at equilibrium. Examples are the control of insulator-metal transitions[1][2][3], magnetism[4][5] and ferroelectricity[6][7], as well as the enhancement of superconducting coherence[8].

Anharmonicities in the crystal lattice dynamics, like rectification[9][10], parametric amplification[11] and harmonic generation[12] of optical phonons, are an important ingredient of the microscopic physics underlying these phenomena. I will present the fundamentals of these nonlinear physics and discuss how they connect to the manipulation of the magnetic and electronic phases.

In the presence of strong interactions, the fluid of mobile electrons in a metal can spontaneously break the point group symmetries of its underlying host lattice, forming an electronic analogue of a classical liquid crystal. The experimental discovery of 2D electronic liquid crystals (ELCs) was first made nearly 20 years ago in semiconductor heterostructures and has since been reported in several other systems including the copper- and iron-based high-temperature superconductors. However whether or not a 3D version of an ELC can exist has remained unclear. In this talk, I will present signatures of a 3D ELC in the strongly spin-orbit coupled metallic pyrochore Cd$_2$Re$_2$O$_7$ detected using ultrafast coherent phonon spectroscopy and a recently developed spatially-resolved nonlinear optical polarimetry technique. I will discuss implications for the possible topological superconducting phase that has been reported to emerge in Cd$_2$Re$_2$O$_7$ under pressure.
Quantum Transport Properties of Cadmium Arsenide Films Grown by Molecular Beam Epitaxy

Susanne Stemmer, David Kealhofer, Luca Galletti, Timo Schumann, Manik Goyal and Honggyu Kim; University of California, Santa Barbara, United States

Interfaces and heterostructures with topological semimetals offer new opportunities to control and manipulate their unique electronic states and a wealth of associated phenomena, for example, via electric field effect, strain, or symmetry breaking. In this presentation, we will discuss recent progress in heterostructures of a prototype three-dimensional Dirac semimetal, cadmium arsenide (Cd₃As₂), which are grown by molecular beam epitaxy. We show that high-mobility, epitaxial Cd₃As₂ films can be grown in different crystallographic orientations. The easy cleavage plane of single crystals, the tetragonal (112) plane, is also the most common growth surface. In this orientation, the bulk Dirac nodes project on two points in the surface Brillouin zone. The (001) plane differs from the (112) plane and indeed all others in that the two bulk nodes project onto one point, rather than two, of the surface Brillouin zone. Here, we discuss the nature of quantum oscillations and of the quantum Hall effect of thin Cd₃As₂ films grown in both orientations. The quantum Hall effect of (112) Cd₃As₂ films is characterized by a degeneracy factor of two that is lifted in fields above approximately 10 T. Gated magnetotransport and quantum capacitance revealed ambipolar quantum transport, a zero-energy Landau level, and linear dispersion in the 2D electronic states giving rise to the quantum Hall effect. The important feature is that (112) surfaces host double Fermi arcs, which can give rise to two Fermi pockets near the center of the surface Brillouin zone and thus an even integer Hall effect until their degeneracy is lifted by the magnetic field. A single (112) surface can give rise to an integer quantum Hall effect and explain the observed characteristics. By contrast, the states of (001) films are non-degenerate and integer filling factors are due to crossing Landau levels. We will discuss other remarkable phenomena in the quantum Hall effect of (001) films. We will also discuss pathway towards realizing novel topological systems.

Topological f-Electron Materials Filip Ronning; Los Alamos National Laboratory, United States

f-electrons possess both strong electronic correlations and strong spin orbit coupling. This combination suggests that f-electron materials are ideal for discovering new topologically non-trivial phases, which arise as a consequence of strong electronic correlations. Broadly speaking, we adopt four approaches to discover new topological states of matter. First, we explore correlation driven narrow gap materials such as SmB₆. Second, in systems such as Eu₃In₅Sb₁₀ we exploit the fact that rare-earth magnetism is strongly localized, resulting in only minor perturbations to the non-interacting electronic structure. Third, we attempt to exploit (non-symmorphic) crystal symmetries for generating protected nodal crossings. Finally, we examine metallic systems such as U₅Ru₄Al₁₂ where broken time reversal symmetry can yield a finite and tunable Berry phase contribution to transverse transport measurements. This talk will review our strategies, efforts, lessons learned, and unexpected discoveries in searching for such new states of matter.
5:00 AM S.NM12.01.01
Topologically Nontrivial Interband Plasmon in Type-II Weyl Semimetal MoTe₂: Xun Jia¹,², Xuetao Zhu² and Jiandong Guo²; ¹Argonne National Laboratory, United States; ²Institute of Physics, Chinese Academy of Sciences, China

In many realistic topological materials, more than one kind of fermions contribute to the electronic bands crossing the Fermi level, leading to various novel phenomena that cannot be well understood by single kind of particle picture. Here, using momentum-resolved inelastic electron scattering, we investigate the plasmons in type-II Weyl Semimetal MoTe₂, in which both Weyl fermions and trivial nonrelativistic fermions contribute to the Fermi surface in the Td phase at low temperature. We observe one plasmon mode in the 1T’ phase at high temperature and two plasmon modes in the topological Td phase at low temperature. Combining with first-principles calculations, we show that the plasmon modes in the Td phase, dominated by the interband transitions between the topologically nontrivial bands for Weyl fermions and the trivial bands for nonrelativistic electrons, are attributed to band splitting due to inversion symmetry breaking and the spin-orbit coupling.

5:10 AM S.NM12.01.02
Quantum Designer Materials and Devices by Single-Atom Manipulation Roland M. Wiesendanger; University of Hamburg, Germany

The ability to construct nano-scale systems with atomic-level precision by using STM-based single-atom manipulation techniques has led to numerous outstanding examples of Quantum Designer Physics. In particular the combination of single-atom manipulation with spin-sensitive imaging and spectroscopy [1] based on the spin-polarized STM technique [2] offers an exciting approach towards the design of specific properties of 1D spin chains [3,4] as well as 2D arrangements of tailored nanomagnets [5]. Investigating such artificially built spin arrays on superconductor surfaces has recently led to the observation of Majorana zero-energy modes in atomically well-defined magnet-superconductor hybrid systems [6] allowing for a detailed comparison with theoretical predictions. Moreover, prototypes for all-spin atomic-scale spin logic devices could be demonstrated by a bottom-up fabrication technique [7]. Another exciting research direction is the tailoring of the spin dynamics of artificially built atomic arrangements on surfaces, such as few-atom clusters [8,9] or 2D spin arrays [10]. Making use of time- and spin-resolved STM techniques [11] the spin dynamics can be tuned by the choice of the substrate, the chemical identity and number of the adatoms as well as their geometric arrangement. Interestingly, the symmetry of the adatom arrangements can have a decisive influence on the spin dynamics. This can be explained by the effect of anisotropic indirect exchange interactions which can lead to a destabilization of the spin system for atomic arrangements exhibiting a lower symmetry [10].

SESSION S.NM12.02: Theory of Quantum Matter

On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM12

5:00 AM *S.NM12.02.01
The Chiral Qubit—Quantum Computing with Chiral Anomaly Qiăng Li; Brookhaven National Laboratory, United States

The quantum chiral anomaly enables a nearly non-dissipative current in the presence of chirality imbalance. We propose to utilize the chiral anomaly for the designs of qubits potentially capable of operating at THz frequency and at room temperature with a coherence time to gate time ratio of about 10^4. The proposed “Chiral Qubit” is a micron-scale ring made of a Weyl or Dirac semimetal, with the |0\rangle and |1\rangle states corresponding to the symmetric and antisymmetric superpositions of chiral currents circulating along the ring clockwise and counter-clockwise. A fractional magnetic flux through the ring induces a quantum superposition of the |0\rangle and |1\rangle quantum states. The entanglement of qubits can be implemented through the near-field THz frequency electromagnetic fields (EMF). We show that the Hamiltonian of the chiral qubit is similar to that of the superconducting qubit. This means that quantum gates can be implemented in a traditional way, and the algorithms developed for superconducting quantum processors will apply. Light-driven (THz) ultrafast topology switching, demonstrated experimentally in Dirac/Weyl semimetal recently, will be discussed, together with its implications on THz topological quantum gate applications.

The author is grateful for collaborations with Dmitri Kharzeev and Jigang Wang. This work is supported by the US Department of Energy, Office of Basic Energy Science, Materials Sciences and Engineering Division, under contract #DE-SC0012704.

5:15 AM *S.NM12.02.02
Machine Learning Data from Quantum Materials Eun-Ah Kim; Cornell University, United States

Decades of efforts in improving computing power and experimental instrumentation were driven by our desire to better understand the complex problem of quantum emergence. However, increasing volume and variety of data made available to us today present new challenges. I will discuss how these challenges can be embraced and turned into opportunities by employing machine learning. It is important to note that the scientific questions in the field of electronic quantum matter require fundamentally new approaches to data science for two reasons: (1) quantum mechanical imaging of electronic behavior is probabilistic, (2) inference from data should be subject to fundamental laws governing microscopic interactions. Hence machine learning quantum emergence requires collective wisdom of data science and condensed matter physics. I will review rapidly developing efforts by the community in using machine learning to solve problems and gain new insight. I will then present my group’s results on the machine-learning-based analysis of complex experimental data on quantum matter.

5:30 AM *S.NM12.02.03
Two-Dimensional Topological Quantum Materials with Room Temperature Stabilities—Engineered by Low-Dimensional Heterogeneities Mina Yoon; Oak Ridge National Laboratory, United States

Our understanding of two-dimensional (2D) materials has developed rapidly with the recent development of theoretical and computational capabilities, as well as the development of experimental synthesis and characterization tools. Now it has become feasible to perform atomic-level manipulations of 2D materials, such as introducing atomic defects and dopants, and engineering boundaries by applying strains and interfaces by growing them on different substrates. The rich parameter space of 2D materials makes them appealing candidates for new types of flexible electronic devices, such as topological electronics, that are stable at room temperature and operate at ambient conditions. Theoretical/computational modeling is desirable to guide experimental efforts in exploring the vast parameter space of 2D material and to identify desirable parameter space. On the other hand, modeling 2D materials in realistic experimental conditions is challenging; not only do these materials contain many atoms (exceeding thousands of atoms) but also the materials’ parameter space is highly complex. Using a prototypical topological 2D system as an example—
e.g., graphene, stanene, and 2D metal-organic frameworks—schemes combining various levels of theoretical/computational approaches were developed, including a tight-binding approach, high-throughput density functional theory calculations, data analytics, and large-scale ab initio dynamics using supercomputer capabilities at the Department of Energy’s Oak Ridge National Laboratory. The developed schemes are targeted to enhance theoretical predictability for topological materials while significantly narrowing the gap with the experimental effort toward robust topological materials.

SESSION S.NM12.03: Synthesis and Structure of Quantum Matter
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM12

5:00 AM S.NM12.03.01
Is Cd₃As₂ a Dirac or a Weyl Semimetal?—Symmetry Determination by Convergent Beam Electron Diffraction
Honggyu Kim¹, Manik Goyal², Salva S. Rezaie², Timo Schumann², Tyler Pardue², Jian-Min Zuo³ and Susanne Stemmer²; ¹University of Florida, United States; ²University of California, Santa Barbara, United States; ³University of Illinois at Urbana-Champaign, United States

Cadmium arsenide (Cd₃As₂) has been identified to belong to the family of three-dimensional topological semimetal, featuring topologically stable band crossing (“nodes”) in the bulk and unconventional surface states. Crystal structures reported for Cd₃As₂ differ, however, in a crucial aspect, namely the presence or absence of an inversion center, which determines whether Cd₃As₂ is Dirac or Weyl semimetals. Both types of semimetals exhibit band crossings in the bulk with linear energy dispersion in momentum space that are protected by the presence of certain crystal symmetries. While Dirac semimetals possess both time reversal and inversion symmetry, one of these (or both) is absent in Weyl semimetals. This difference defines their unique electronic structures and has profound effects on their properties. Here, we report on the determination of point group of Cd₃As₂ thin films grown by molecular beam epitaxy (MBE) using convergent beam electron diffraction (CBED). Using CBED patterns recorded from multiple zone axes and Bloch wave simulation, we demonstrate that Cd₃As₂ is a tetragonal structure with 4/mmm point group, possessing an inversion center and four-fold symmetry, indicative of Dirac semimetals. Lastly, we present that high-angle annular dark-field (HAADF) imaging recorded in scanning transmission electron microscopy (STEM) can be used to directly visualize the Cd vacancy ordering which further confirms our conclusion. The findings in this study offer new opportunities to unveil the symmetry-property relationship in a wide range of topological materials.

5:10 AM *S.NM12.03.02
Probing Order and Disorder in Quantum Materials Using Scanning Transmission Electron Microscopy
Lena F. Kourkoutis¹,²; ¹Cornell University, United States; ²Kavli Institute at Cornell, United States

Coupling between charge, spin, or orbital degrees of freedom gives rise to remarkable phenomena such as colossal magnetoresistance, metal–insulator transitions and superconductivity. Many aspects of these competing interactions, however, remain elusive. Traditional bulk measurements of phases transitions, which average the material’s response over large length scales, can infer the presences of spatial inhomogeneity. Understanding their character, however, requires local probes. Direct, real-space measurements of the onset of emerging order are key to understanding the diverse properties of complex electronic materials.

Today, atomic-resolution imaging is routinely achieved by aberration-corrected scanning transmission electron microscopy (STEM). Coupled with spectroscopy STEM provides direct information about the local structure and chemistry of thin films and heterostructures. In this talk, I will first discuss our results on two classes of superconducting materials, the layered perovskite ruthenates and the recently reported infinite-layer nickelates [1], with particular focus on the microscopic structure, strain and the role of defects in these thin film superconductors. Going beyond room temperature STEM, cryogenic sample cooling promises direct access to low temperature phases. While limitations in hardware currently hamper STEM measurements of ruthenates and nickelates in their superconducting states, high-precision cryogenic STEM near liquid nitrogen temperature has been demonstrated [2, 3]. These new capabilities have paved a path to visualize subtle lattice and electronic orders in emergent low temperature phases as I will show in the second part of the talk. Focus will be on the lattice behavior of charge-ordered manganites, where direct imaging can discriminate between multiple structure models, and
mapping over larger length scales shows phase coexistence and nanoscale inhomogeneities.

[4] Research performed in collaboration with Ismail El Baggari, Berit H. Goodge, David J. Baek, Michael J. Zachman and the groups of Harold Y. Hwang (Stanford), Darrell G. Schlom (Cornell), Kyle M. Shen (Cornell) and Beth Nowadnick (New Jersey Institute of Technology). This work was supported by the DoD, AFOSR (FA 9550-16-1-0305), NSF (DMR-1539918, DMR-1429155, DMR-1719875), and the Packard Foundation.

5:25 AM *S.NM12.03.03
Quantum Transport Properties of Cadmium Arsenide Films Grown by Molecular Beam Epitaxy Susanne Stemmer, David Kealhofer, Luca Galletti, Timo Schumann, Manik Goyal and Honggyu Kim; University of California, Santa Barbara, United States

Interfaces and heterostructures with topological semimetals offer new opportunities to control and manipulate their unique electronic states and a wealth of associated phenomena, for example, via electric field effect, strain, or symmetry breaking. In this presentation, we will discuss recent progress in heterostructures of a prototype three-dimensional Dirac semimetal, cadmium arsenide (Cd$_3$As$_2$), which are grown by molecular beam epitaxy. We show that high-mobility, epitaxial Cd$_3$As$_2$ films can be grown in different crystallographic orientations. The easy cleavage plane of single crystals, the tetragonal (112) plane, is also the most common growth surface. In this orientation, the bulk Dirac nodes project on two points in the surface Brillouin zone. The (001) plane differs from the (112) plane and indeed all others in that the two bulk nodes project onto one point, rather than two, of the surface Brillouin zone. Here, we discuss the nature of quantum oscillations and of the quantum Hall effect of thin Cd$_3$As$_2$ films grown in both orientations. The quantum Hall effect of (112) films is characterized by a degeneracy factor of two that is lifted in fields above approximately 10 T. Gated magnetotransport and quantum capacitance revealed ambipolar quantum transport, a zero-energy Landau level, and linear dispersion in the 2D states giving rise to the quantum Hall effect. The important feature is that (112) surfaces host double Fermi arcs, which can give rise to two Fermi pockets near the center of the surface Brillouin zone and thus an even integer Hall effect until their degeneracy is lifted by the magnetic field. A single (112) surface can give rise to an integer quantum Hall effect and explain the observed characteristics. By contrast, the states of (001) films are non-degenerate and integer filling factors are due to crossing Landau levels. We will discuss other remarkable phenomena in the quantum Hall effect of (001) films. We will also discuss pathway towards realizing novel topological systems.

5:15 AM *S.NM12.04.02
Inelastic X-Ray Scattering on Tungsten Carbide Qingan Cai; University of California, Riverside, United States

In the presence of strong interactions, the fluid of mobile electrons in a metal can spontaneously break the point group symmetries of its underlying host lattice, forming an electronic analogue of a classical liquid crystal. The experimental discovery of 2D electronic liquid crystals (ELCs) was first made nearly 20 years ago in semiconductor heterostructures and has since been reported in several other systems including the copper- and iron-based high-temperature superconductors. However whether or not a 3D version of an ELC can exist has remained unclear. In this talk, I will present signatures of a 3D ELC in the strongly spin-orbit coupled metallic pyrochore Cd$_2$Re$_2$O$_7$ detected using ultrafast coherent phonon spectroscopy and a recently developed spatially-resolved nonlinear optical polarimetry technique. I will discuss implications for the possible topological superconducting phase that has been reported to emerge in Cd$_2$Re$_2$O$_7$ under pressure.
Tungsten carbide (WC) is widely used in industrial field due to its excellent performance in hardness, roughness and high melting temperature. Bulk modulus measuring the resistant to compression is related to phonon dynamics as well. In recent work, phonon transport properties of topological metals WC and WN are investigated, the thermal conductivity of WC is found to be two orders of magnitude higher than that of WN because the large acoustic-optical gap prohibits the acoustic+acoustic®optical scattering[1]. A first-principles study on phonon related properties of tungsten carbide has been published and the calculated phonon dispersion of WC can be referred, but experimental investigations still need to be conducted. In our work phonon dispersion relation of tungsten carbide in high symmetry directions has been measured by inelastic X-ray scattering. Super resolution is applied to extract phonon lifetime. Ab initio phonon calculation based on Density Function Theory is compared to the experimental results with excellent agreements. Furthermore, inelastic scattering intensity has been simulated at various q points. Our dispersion results are essential for understanding the thermal conductivity and chiral phonons in tungsten carbide.

Polarized photons can excite the chiral phonons at Brillouin-zone corners in honeycomb lattices with threefold rotational broken inversion symmetry in monolayer tungsten disulfide. Tungsten carbide with space group P-6m2 (No.187) is a good candidate for experiments for underlying chiral phonons. We generate circular polarized X-ray to detect the phonon intensity change at zone boundary (K) in tungsten carbide. Present scattering theory could not be applied in our experiment results.
SESSION S.NM12.06/S.NM11.06: Joint Session: Correlated and Topological Quantum Matter
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM12

5:00 AM *S.NM12.06/S.NM11.06.02
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This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.

SESSION S.NM12.07: Ultrafast and Nonequilibrium States in Quantum Matter
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM12

5:00 AM *S.NM12.07.01
Exploring Non-Equilibrium Phases with Ultrafast X-Rays John Freeland; Argonne National Laboratory, United States

With the explosion of recent work exploring the out of equilibrium energy landscape of quantum materials, a need has developed to expand the set of available tools to be able to follow these dynamic pathways in as much details as possible. A key aspect of this mode of exploration is the ability to follow these trajectories to map the energy landscape to understand how the phases evolve and ideally seek out new states. However, this requires the ability to extract as much detail about the how the crystalline, electronic and magnetic properties change on ultrafast timescales. Here I will talk about how time-resolved X-ray probes at synchrotrons and free electron lasers can allow one to separate explore these degrees of freedom.
Such direct information about the evolution of lattice, electronic, and magnetic order can then be merged with theoretical studies to build a clear model to describe the ultrafast evolution of the system. To illustrate the possibilities, I will present examples ranging from decoupling order parameters in Nickelates and optical creation of hidden structural phases in Titanate superlattices[1]. This work will highlight what is possible with today’s X-ray sources and potential experiments we can consider in the very near future.

The work at Argonne is supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357. The development of the materials and ultrafast experiments is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC-0012375.


5:15 AM *S.NM12.07.02
Controlling Quantum Materials by Nonlinear Phononics Michael Först; Max Planck Institute for the Structure and Dynamics of Matter, Germany

Irradiation with light is able to dynamically push quantum materials away from equilibrium, driving them into states with transiently perturbed magnetic and electronic properties. This field has become a rich playground for fundamental research but may also be relevant for technical applications that require ultrafast switching capabilities. In this talk, I will focus on our use of intense terahertz and mid-infrared light fields to control quantum solids by resonant excitation of crystal lattice vibrations. This approach has been demonstrated to switch between different phases and reveal hidden states not accessible at equilibrium. Examples are the control of insulator-metal transitions[1]-[3], magnetism[4]-[5] and ferroelectricity[6]-[7], as well as the enhancement of superconducting coherence[8]. Anharmonicities in the crystal lattice dynamics, like rectification[9]-[10], parametric amplification[11] and harmonic generation[12] of optical phonons, are an important ingredient of the microscopic physics underlying these phenomena. I will present the fundamentals of these nonlinear physics and discuss how they connect to the manipulation of the magnetic and electronic phases.

Momentum Microscopy is a new technique in surface science, in which the momentum distribution of photoelectrons is projected onto an image plane. This image plane can be energy-filtered by a double-hemispherical electrostatic analyzer (NanoESCA) to achieve a monochromatic momentum distribution. Scanning the energy along the valence band is then used for band structure mapping which is a key technique to understand the electronic structure of novel materials. A new innovative method is to use the monochromatic electron distribution behind the double-hemispherical analyzer to retard it to the needed scattering energy of an Au/Ir (100) single crystal. This allows for spin-polarization dependent reflection, which enables a highly efficient imaging spin-filter technique [1].

We will show recent band-structure measurements of several TMDCs acquired with the NanoESCA and discuss the latest technical improvements of momentum microscopy with respect to 2D material characterization. First results of the imaging spin-filter installed at the ELI-Alps NanoESCA are shown, demonstrating its efficiency in real-space microscopy (e.g. imaging of magnetic domains) and in spin-resolved band-structure mapping.


SESSION S.NM12.08: Transport in Weyl and Dirac Systems
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM12

5:00 AM S.NM12.08.01
Synthesis and Transport Studies of Quasi-1D Topological Materials Bi4I4-xBrx Bing Ly1, Sheng Li1, Xiaoyuan Liu1, Yanfeng Zhou1, Yulu Liu1, Kadado Rashad2, Chun Lau2, Ming Yi1 and Fan Zhang1; 1The University of Texas at Dallas, United States; 2The Ohio State University, United States

In recent years, topological insulator materials have been attractive to many scientists because of their gapless conductive surface states that are protected against perturbations. Bi4I4 and Bi4Br4 are a quasi-one-dimensional van der Waals material which may offer a new platform for exploring the physics of topological phases. The β-phase Bi4I4 is predicted and experimentally confirmed by photoemission spectroscopy to be a weak topological insulator (WTI), and undergoes a nontrivial WTI to the trivial insulator α-phase around room temperature. The α-phase of Bi4Br4, on the other hand, is predicted to be intrinsic higher-order topological insulator, with 1D helical hinge states and 3D insulating bulk state. Intrinsic superconductivity in Bi4I4 and Bi4Br4 under high pressure have also been reported. Here we report the synthesis and transport studies of the Bi4I4, Bi4Br4, and doped Bi4I4-xBrx materials on the crystals as long as 6 mm. The detailed transport, electronic structures, and the associated control of topological phase transition upon chemical doping will be presented.

5:10 AM S.NM12.08.02
Suppression of Weak Antilocalization in Bi2Se3 Thin Films by Delta Doping Paramagnetic Co:Se Jason Lapano, Elizabeth Skoropata, Alessandro Mazza, Sangmoon Yoon and Matthew Brahlek; Oak Ridge National Lab, United States

Magnetic doping or interfacing magnetic materials with topological insulators such as Bi2Se3 has been shown to controllably break time reversal symmetry and induce exotic phenomena such as the quantum anomalous hall effect. In this work we study the effect of a buried paramagnetic metal, Co:Se within Bi2Se3. Trilayer structures were synthesized by molecular beam epitaxy, in which the Co:Se layer was sandwiched between a top and bottom Bi2Se3 layer. Magnetoresistance data reveals a sharp decrease in the weak-antilocalization (WAL) effect with the addition of a single Co:Se monolayer and is completely suppressed in as few as 4 atomic layers. Conversely, Co-doped Bi2Se3 films show only a milder suppression of the WAL effect for equivalent Bi:Co concentrations. As the Co:Se layer is non-magnetic and obeys time reversal symmetry, it is expected that the topology of the system remains protected. However, the suppression of the WAL effect suggests the spin-momentum locking and topological behavior is destroyed.

5:20 AM *S.NM12.08.03
Possible Manifestations of the Chiral Anomaly in the Type-I Weyl Semimetal TaAs Luis Balicas1,2; 1Florida State Univ, United States; 2National High Magnetic Field Laboratory, United States
Topological semimetals such as Weyl and Dirac systems are three-dimensional phases of matter characterized by topology and symmetry protected gapless electronic excitations. These three-dimensional analogs of graphene have generated a lot of interest recently given that their quasiparticles display properties akin to those of relativistic and chiral fermions in particle physics. Their unconventional electronic structures are predicted to lead to protected surface states and to unconventional responses to applied electric and magnetic fields. In the past few years, we have studied a few of these compounds [1-11] under high magnetic fields, with the goal of i) extracting their electronic structure at the Fermi level in order to ii) compare it with theoretical predictions, and of iii) exposing their transport properties which are expected to be unconventional due to their “topological” character. Here, after a brief introduction, we will focus on the magnetoresistivity and the Hall-effect of the type-I Weyl semimetal TaAs in an attempt to address the strong controversy surrounding its anomalous transport properties in relation to its bulk topological character. For fields and currents along the basal plane, we observe a very pronounced planar Hall effect (PHE) upon field rotation with respect to the crystallographic axes at temperatures as high as $T = 100$ K [10]. Parametric plots of the PHE signal as a function of the longitudinal magnetoresistivity (LMR), collected at $T = 10$ K, lead to concentric traces as reported for Na$_3$Bi and GdBiPt suggesting that both the negative LMR and the PHE observed in TaAs are intrinsically associated to the axial anomaly among its Weyl nodes. For fields nearly along the a axis we also observe hysteresis as one surpasses the quantum limit, where the magnetic torque indicates a change in regime as the field increases, i.e., from paramagnetism and diamagnetism due to Weyl fermions above and below the Weyl node(s), respectively, to a paramagnetic one associated with the field-independent $n = 0$ Landau level. Hysteresis coupled to the overall behavior of the torque would be consistent with a topological phase transition associated with the suppression of the Weyl dispersion at the quantum limit. This transition leads to the suppression of the negative LMR confirming that it is associated to the Weyl dispersion [10]. Finally, for fields along the c axis the Hall effect reveals two successive changes in slope, or two successive decrements in carrier mobility, one at the quantum limit and a second one at the critical field where a phase transition toward an insulating state was recently reported. This suggests the possibility of two successive phase transitions as a function of the field with the higher-field one involving solely the $n = 0$ Landau level. For both field orientations we observe Shubnikov–de Haas like oscillations beyond the quantum limit therefore involving quasiparticles at fractional filling factors.

This work is supported by the US Department of Energy, Basic Energy Sciences program through Award No. DESC0002613.

References

SESSION S.NM12.09: Correlated Quantum Matter
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM12

5:00 AM *(S.NM12.09.02)
Topological f-Electron Materials Filip Ronning; Los Alamos National Laboratory, United States

f-electrons possess both strong electronic correlations and strong spin orbit coupling. This combination suggests that f-electron materials are ideal for discovering new topologically non-trivial phases, which arise as a consequence of strong electronic correlations. Broadly speaking, we adopt four approaches to discover new topological states of matter. First, we explore correlation driven narrow gap materials such as SmB$_6$. Second, in systems such as Eu$_2$In$_2$Sb$_6$ we exploit the fact that...
rare-earth magnetism is strongly localized, resulting in only minor perturbations to the non-interacting electronic structure. Third, we attempt to exploit (non-symmorphic) crystal symmetries for generating protected nodal crossings. Finally, we examine metallic systems such as U$_3$Ru$_4$Al$_2$ where broken time reversal symmetry can yield a finite and tunable Berry phase contribution to transverse transport measurements. This talk will review our strategies, efforts, lessons learned, and unexpected discoveries in searching for such new states of matter.

SESSION S.NM12.10: Emergent Topological Phenomena and Superconductors
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-NM12

5:00 AM *S.NM12.10.03
Exotic Topological and Other Complex Phases of Quantum Matter—Progress toward First-Principles Modeling of Strongly Correlated Materials Arun Bansil; Northeastern University, United States

Predictive capabilities of the widely used band theory paradigm, despite its spectacular successes, have been limited to weakly correlated materials.[1-3] I will discuss how advanced density functionals are enabling new insights into the electronic structure, phase diagrams and magnetism of a wide variety of materials that have been considered to be so strongly correlated as to lie outside the scope of first-principles treatment. A spectacular example is that of the cuprate high-Tc superconductors in which the density functional theory fails to correctly predict the half-filled parent compounds to be insulators. In sharp contrast, however, the recently constructed SCAN functional [4] not only reproduces the insulating character and magnetism of the half-filled cuprates, but also captures the transition to the metallic state with doping without invoking any free parameters such as the Hubbard U. [5,6] I will also discuss with examples drawn from our recent work on the opportunities for a new generation of predictive modeling of correlated topological and non-topological phases of quantum matter more generally. Work supported by the U.S. Department of Energy.


5:15 AM S.NM12.10.04
Chiral Anomaly in Dirac Semimetal PtSe$_2$ for Field-Modulated Electronics with Integrated Sensing and Logic Functions Jiewei Chen; HKPU, Hong Kong

Efficient electric transport is one of the key topics in modern electronics. Generally, electrons scattering is unavoidable for ordinary current flowing through the materials. Different from this, chiral anomaly current in Dirac semimetals is the charge pumping process with inhibited electrons scattering. Here, we investigate the application of chiral anomaly current for field-effect efficient electronics with integrated sensing and logic functions. The type-II Dirac is theoretically predicted through first-principle calculations in Dirac semimetal PtSe$_2$ and experimentally investigated by magnetotransport behaviors. Angle-dependent longitudinal negative magnetoresistance (MR) is observed in prepared devices and when electric field is parallel to the magnetic field, there is the maximum magnetic conductance value proportional to $B^2$. Besides sensitive to the angles and magnetic field strength, chiral anomaly current can be well field-modulated by ion liquid. Moreover, AND-OR logic operation and three-inputs coincidence detection are demonstrated by using chiral anomaly properties. Our results provide new sights on achieving field-modulated electronics with integrated sensing and logic functions based on the chiral anomaly current with inhibited electrons scattering.

SESSION S.NM12.11: Synthesis of Topological Quantum Matter
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday
Morning, November 21, 2020
S-NM12

5:00 AM S.NM12.11.01
Epitaxial Growth of Topological Insulators on Compliant BaF₂/Si Substrates Karen Long¹, Patrick Taylor² and Jiwei Lu³; ¹Naval Surface Warfare Center, United States; ²U.S. Army Research Laboratory, United States; ³University of Virginia, United States

The rapid evolution of topological matter has led to strong interest in electronic and spintronic devices that can leverage the unique and attractive physics of the topological surface states. One path to integrate both topological-based devices with classical electronics (CMOS) would be to grow the materials on silicon. Because topological properties can be affected by strain and because the mismatch in thermal expansion coefficients between silicon and bismuth telluride is approximately a factor of 10, techniques to mitigate strain are of interest. In this report, we investigated the use of a unique strain-compliant barium-fluoride-based buffer layer to mitigate the effects of thermal expansion strain between Bi₂Te₃ and Si. Under our previous research we have shown that BaF₂ can be latticed matched to Si by first growing a compliant BaSi₂ layer. These thin films have been grown in our MBE (molecular beam epitaxy) system of various thicknesses and partial coverage. With partial coverage, the result is (111) BaF₂ triangles. We observe that growing Bi₂Te₃ on BaF₂ reduces twinning because of the excellent lattice matching. Ionic substrates such as BaF₂ have been shown to n dope graphene and their strong bonds can influence several monolayers, thus the nature of the substrate can be used to control the properties of the topological insulator. Recently, we have grown Bi₂Te₃ on BaF₂/Ba-Si/Si with good results. Growing on a substrate with partial coverage showed good Bi₂Te₃ domain alignment with the BaF₂ domain. The BaF₂ triangles effectively create a nanostructure surface where the topological insulator is exposed to different surface energies. Hall probe results have shown that the Bi₂Te₃ grown on BaF₂/Si is n type with good mobility. Excellent crystal structure was confirmed by XRD (x-ray diffraction). Here we report our results of growing Bi₂Te₃ on BaF₂/Si and Bi₂Se₃ on SrF₂/Si of various thickness and partial coverage as well as discuss potential applications for DoD.

5:10 AM S.NM12.11.02
Epitaxial Growth and Tuning of the Chiral Anomaly in MBE-Grown GₓLa₁₋ₓPtSb Thin Films and Membranes Dongxue Du¹, Laxman R. Thoutam², Chenyu Zhang¹, Sebastian Manzo¹, Vivek Saraswat¹, Patrick J. Strohbeen¹, Konrad Genser², Paul Voyles¹, Michael S. Arnold¹, Bharat Jalan³, Karin M. Rabe² and Jason K. Kawasaki¹; ¹University of Wisconsin-Madison, United States; ²Rutgers, The State University of New Jersey, United States; ³University of Minnesota, United States

Weyl semimetals (WSM) are topologically non-trivial materials hosting massless chiral fermions. However, to date nearly all measurements of Weyl semimetals have been conducted on bulk crystals, which have limited ability to tune via external parameters such as electrostatic gating or strain. Here, we report the first epitaxial growth of the Weyl semimetal candidate GdₓLa₁₋ₓPtSb, using molecular beam epitaxy. We grow these materials in two forms: (1) epitaxial GdₓLa₁₋ₓPtSb films on Al₂O₃ (0001) substrates, and (2) semi-freestanding membranes grown on graphene-terminated Al₂O₃, using the so-called "remote epitaxy."

For x<0.95 the GdₓLa₁₋ₓPtSb films adopt a hexagonal stuffed wurtzite structure (LiGaGe-type, P₆₃ 3mc), while the x=1 end member GdPtSb has cubic half Heusler structure. Angular dependent magnetotransport measurements of GdPtSb reveal a negative magnetoresistance that is highly dependent on angle, consistent with the chiral anomaly. More detailed measurements as functions of Gd/La doping (magnetic moment and cubic/hexagonal structural transition) and electrostatic gating will also be discussed.

We also demonstrate the epitaxial growth of LaPtSb on graphene-terminated Al₂O₃ (0001). Despite the presence of monolayer graphene, the LaPtSb film adopts epitaxial registry with the underlying Al₂O₃ substrate, as confirmed by X-ray diffraction and transmission electron microscopy measurements. Due to the weak coupling between film and substrate across the graphene barrier, the LaPtSb film can be mechanically exfoliated using tape, to yield a free-standing membrane. Using in-situ photoemission, electron diffraction, and scanning probe microscopy, we will comment on the atomic scale mechanisms for growth. We will also discuss how the magnetic and transport properties GdₓLa₁₋ₓPtSb membranes can be actively tuned via strain.
SYMPOSIUM S.SM01

Organ-on-a-Chip—Toward Personalized Precision Medicine
November 21 - December 3, 2020

Symposium Organizers
Nasim Annabi, University of California, Los Angeles
D. Sakthi Kumar, Toyo University
Dorian Liepmann, University of California, Berkeley
Venkatesan Renugopalakrishnan, Boston Children's Hospital/Harvard University/Northeastern University

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SESSION Tutorial S.SM01: Microfluids and Mricofluidic Devices
Session Chairs: D. Sakthi Kumar and Dorian Liepmann
Saturday Afternoon, November 28, 2020
S.SM01

2:45 PM *
History of BioMEMS and Fabrication Processes Dorian Liepmann; University of California, Berkeley, United States

The tutorial sessions will introduce an overview of the history of BioMEMS materials and fabrication processes. Then the fundamentals of microfluidics will be presented focused on the designing microfluidic systems. This will include application of scaling analyses. The effects of two-phases, e.g. molecules and particles, on the dynamics of the system will be discussed along with the appropriate non-dimensional numbers needed to predict the overall behavior of the flow. A similar discussion of the effects and uses of increasing the size of the flow channels in 3-D printed devices will be given. After the microfluidic section, the tutorial will switch focus to measurement techniques that can be used in bioMEMS devices including optimization of the signal to noise for accurate measurements. Lastly, current systems and applications will be presented and discussed.

4:15 PM BREAK

4:30 PM *
Nanotechnology for Microfluidics and Advanced Sensors D. Sakthi Kumar; Toyo University, Japan

Microfluidic devices are getting lot of attractions to use as an intermediate step between in vitro and in vivo conditions since it can mimic and simulate the in vivo conditions. Currently, work is progressing to construct microfluidic devices, having many organs, implanted using multiple cell lines, in other way to develop “Human on a Chip”, which may be able to obtain the physiology of an individual human being as such, will enable to work towards personalized precision medicine and can be used for many advanced rug related experiments. Based on this concept, the area of microfluidics is rapidly evolving into a sophisticated technology that may cater the futuristic need for the point-of-care (POC) devices and human-on-chip (HOC) systems with integrated sensors for autonomous and specific applications in biomedical, chemical, food or environmental research. Futuristic application of HOC system, can be visualized to integrate it to Artificial Intelligence (AI) so that it can provide the information about the potential threat for the health conditions in very early stage itself that can transform the medical field and can be the next development in the medical field sought for.
**SESSION S.SM01.08: Live Keynote I: Oligonucleotide**  
Session Chairs: Venkata Krishnamurthy and Venkatesan Renugopalakrishnan  
Monday Afternoon, November 30, 2020  
S.SM01

5:15 PM *S.SM01.04.01  
Re-engineering RNA Molecules into Therapeutic Agents—The Expanding Universe of Nucleic Acid Modifications  
Martin Egli; Vanderbilt University, United States

First-generation nucleic acid analogs such as 2′-deoxy-2′-fluoro-RNA (2′-F RNA), 2′-O-methyl RNA (2′-OME RNA), and the phosphorothioates (PS-DNA/RNA) have remained staples of oligonucleotide modification strategies in the discovery and optimization of potential RNAi therapeutics.\(^1,2\) The first FDA-approved siRNA drug, patisiran (Onpattro) contains eleven 2′-OME ribonucleotides in the sense and antisense strands formulated in a lipid nanoparticle (LNP) delivery system.\(^3\) Despite their overall appeal in terms of enhanced nuclease resistance, increased pairing stability (2′-F/OME RNAs) and safety, newer analogs are needed to further improve the therapeutic potential of unformulated siRNAs like GalNAc conjugates. The search for oligonucleotides with therapeutic efficacy has given rise to an expanding universe of analogs, including the second-generation 2′-O-(2-methoxyethyl)-RNA (MOE-RNA)\(^4\) and the third-generation bicyclic nucleic acids (BNAs or LNAs).\(^5\) The key enzyme in RNA interference (RNAi) is Argonaute 2 (Ago2), a dynamic multi-domain enzyme that binds multiple regions of the guide (antisense) and passenger (sense) siRNAs. Considering the complexity of protein-RNA interactions in RNA interference, it is imperative to expand the process of discovery and optimization of modified siRNAs to new analogs.\(^6\) We have explored the potential benefits for efficacy of incorporating into siRNAs sugar modifications like N-methylacetamide (NMA), 5′-E-vinylphosphonate (5′-E-VP) and, more recently, xeno-nucleic acid (XNA)\(^7\) residues such as glycol nucleic acid (GNA),\(^8\) altritol nucleic acid (ANA),\(^9\) and threofuranosyl nucleic acid (TNA).\(^10\) The talk will summarize siRNA modification strategies with an emphasis on regiospecific interactions between oligonucleotide and Ago2 and how structural insights based on crystallographic data for modified RNAs alone and in complex with Ago2 from molecular modeling studies can guide the choice of chemical modification at a given position of siRNA for optimizing its therapeutic efficacy.


5:45 PM *S.SM01.04.02  
Delivery of RNAi Therapeutics—Tackling a Billion Years of Evolutionary Defenses with New Chemistry  
Steven F. Dowdy and Ian Huggins; University of California, San Diego, United States

Cancer is a complex genetic moving target that requires a therapeutic modality capable of selectively targeting all driver oncogenes combined with the inherent ability to undergo pharmaco-evolution to target new mutations at pace with the cancer cell mutation rate. siRNA RNA-interference (RNAi) therapeutics fulfill these criteria and have great potential to treat cancer and other human diseases. However, due to their 14 kDa size and 40 negative anionic charges, siRNAs have no bioavailability to overcome a billion years of evolutionary defenses to prevent RNAs from crossing the endosomal lipid bilayer to enter the cytoplasm. Consequently, developing anti-cancer RNAi therapies requires targeted delivery to malignant cells and paradigm-shifting technology to enhance endosomal escape into the cytoplasm, the critical rate-limiting delivery step. Our research is focused on solving these problems by synthesis of bioreversible charge neutral RNAi prodrugs,
called short interfering RiboNucleic Neutrals (siRNNs), and synthesis of novel hydrophilic-masked, hydrophobic endosomal escape domains (EEDs). For targeting domains, we have focused on conjugating antibodies to siRNN RNAi triggers to generate Antibody-RNAi Conjugates (ARCs).

6:15 PM *S.SM01.04.04
A Traceless Linker for Aliphatic Amines that Rapidly and Quantitatively Fragments after Reduction
Niren Murthy1,2; 1University of California, Berkeley, United States; 2Innovative Genomics Institute, United States

Reduction sensitive linkers have the potential to transform the field of drug delivery due to their ease of use and selective cleavage in intracellular environments. However, despite their compelling attributes, using reduction sensitive linkers for biomolecule conjugation reactions is still challenging because linkers have not been developed that can efficiently modify aliphatic amines and release them rapidly and completely after reduction. Developing reduction sensitive self-immmolative linkers for aliphatic amines has been challenging due to their poor leaving group ability and high pKa values. Here we present a traceless linker (TRAILER), which can for the first time modify aliphatic amines and release them rapidly and quantitatively after disulfide reduction. We show here that TRAILER can reversibly modify the lysine residues on the Cas9 protein, with the cell penetrating peptide Arg10, and was able to generate a self delivering Cas9 RNP that could edit cells without transfection reagents. TRAILER has numerous applications in biotechnology given the ubiquitous presence of aliphatic amines on small molecule and protein therapeutics.

6:45 PM S.SM01.04.06
Escaping from microRNA Biogenesis—A Crucial Factor for Designing Functional Antisense microRNAs for Therapy
Ramasamy Paulmurugan1 and Venkatesan Renugopalakrishnan2,3; 1Stanford University School of Medicine, United States; 2Harvard Medical School, United States; 3Northeastern University, United States

Non-coding ribonucleic acids (ncRNAs) are a diverse group of RNA molecules that are not translated into proteins following transcription. Mainly, microRNAs and long non-coding RNAs (IncRNAs) are predominant in this group. Aberrant expression of these ncRNAs has been observed in various pathological conditions including cancer. Especially, aberrant expression of microRNAs and the associated pathology has been extensively studied in cancer. Hence, targeting microRNAs has been considered a new generation of molecularly targeted therapy for various diseases. While downregulation of cellular microRNAs can be supplemented by delivering microRNA mimics, functional knock down of microRNAs that are overexpressed in diseases is a challenging task. The secondary structure of microRNAs determines how to functionally inhibit the translation of target mRNAs. MicroRNAs with even a few base homologies to the target can functionally regulate mRNA degradation/translation. The secondary structure of microRNA is crucial for recognizing target mRNA for functional effect. Since the double stranded RNA is an important intermediate in the biogenesis process of matured microRNA, delivering antisense microRNA for functional knock down of endogenous microRNAs needs a careful design. Especially challenging is their site-targeted delivery. We study antisense microRNAs with various structural determinants (mere homology, end loops, base pair modifications, artificial linkage, etc.,) by molecular dynamics of the duplex formation at 1 micro second and beyond, for the evaluation of the therapeutic effect of microRNAs in various cancer models (GBM: antisense miR-21 and antisense miR-100; Breast cancer antisense miR-21 and antisense miR-10b; Hepatocellular carcinoma: antisense miR-21, antisense miR-10b and antisense miR-100). In this presentation, we summarize how structural modification in antisense microRNAs can be used for potential applications in cancer therapy, either microRNA targeting as a monotherapy, or for improving clinical chemotherapy.

SESSION S.SM01.09: Live Keynote II: Oligonucleotide
Session Chairs: Venkata Krishnamurthy and Venkatesan Renugopalakrishnan
Wednesday Morning, December 2, 2020
S.SM01

8:00 AM *S.SM01.04.10
Chemical Engineering of Therapeutic Oligonucleotides
Anastasia Khvorova; University of Massachusetts Medical School, United States

8:25 AM *S.SM01.04.11
mRNA Therapy for Inhererited Metabolic Diseases Lisa Rice; Moderna, United States

8:50 AM *S.SM01.04.12  
**Boosting Intracellular Delivery of Messenger RNA** Gaurav Sahay; Oregon Health & Science University, United States

9:15 AM *S.SM01.04.14  
**Role of Protein Corona on Oligonucleotide Delivery and Transfection with Lipid Nanoparticles** Mansoor Amiji; Northeastern University, United States

Upon systemic administration of nanoparticles used in drug and gene delivery, they acquire a “biological identity” upon adsorption of plasma proteins. The protein corona layer has significant implication in the biodistribution, target specific localization, and toxicity of nanoparticle-based delivery systems. Additionally, specific enrichment of proteins may allow for an endogenous and more efficient approach for targeted delivery.

Using a wide ranging of lipid nanoparticle (LNP) formulation where individual lipid composition was varied, we have shown specific protein enrichment pattern and differential biodistribution and tumor-specific delivery of small interfering RNA (siRNA). For instance, DOTAP functionalized LNPs showed vitronectin enrichment and enhanced *in vivo* tumor delivery of the nanoparticles to αvβ3 expressed tumors and endothelial cells as compared to αvβ3 negative tumors.

9:40 AM *S.SM01.09.01  
**Intracellular Delivery of mRNA: Exploration of Delivery Materials for Next Generation Therapeutics** David Ulkoski; AstraZeneca PLC, United Kingdom

Current advances in RNA-based technologies such as therapeutic gene editing, mRNA therapeutics, and vaccines have produced strong interest and attention in safe and effective nonviral vectors for nucleic acid delivery. Nevertheless, the comprehensive application of nucleic acid therapeutics is still limited by the need for better delivery systems. Thus, the analysis of these delivery materials can be advanced to offer sharper insights into SAR learnings and provide a clearer picture of their therapeutic potential. Lipid- and polymer-based materials can be regarded as the most prominent partners for nucleic acid delivery, providing *in vivo* transfection. Over the past few decades, a variety of cationic lipids and polymers have been synthesized, evaluated and applied as successful delivery vehicles for nucleic acids. Here, I will discuss some of the challenges for clinical translation of mRNA-based therapeutics and give examples of the biomaterials and delivery strategies we are investigating for the application of mRNA delivery.

SESSION S.SM01.10: Live Keynote III: CRISPR Based Technologies  
Session Chairs: Kiana Aran and Dorian Liepmann  
Thursday Morning, December 3, 2020  
S.SM01

8:00 AM *  
**CRISPR-Powered Transistors—Harnessing Biology as Technology** Kiana Aran; Keck Graduate Institute, United States

We have recently developed a CRISPR powered, electronic biosensor termed, CRISPR Chip, capable of detecting the binding interactions between nuclease deactivated CRISPR with its target DNA sequence. CRISPR-Chip is a graphene field effect transistor (gFET) where the surface of the graphene is functionalized with nuclease deactivated CRISPR RNA-guided ribonucleoproteins (dRNPs). dRNPs within the CRISPR-Chip construct interact with their target sequence by scanning the genomic sample until they find and bind to their target. The selective hybridization of the target DNA to the dRNP complex modulates the graphene’s conductivity and results in a detectable change in electrical signal output which can be measured with a simple handheld reader. CRISPR-Chip was able to detect dRNP binding to two commonly deleted exon target sequences within the human dystrophin gene, without amplification. CRISPR-chip is the first example of CRISPR-powered electronic transistors that harnesses the search function of CRISPR/Cas9 and the ultra-sensitivity of graphene-based nanoelectronics to enable a complete label-free and amplification-free DNA biosensor.
8:35 AM HARNESSING CRISPR DIVERSITY FOR AT-HOME COVID TESTING, JONATHAN GOOTENBERG AND OMAR ABUDAYAEH

9:00 AM CRISPROFF: SPATIO-TEMPORAL CONTROL OF CRISPR EDITING, JARED CAROLSON-STEVERMER

9:20 AM PIPR - PROTEOME ANALYSIS OF CRISPR CELLS, JENS-OLE BOCK

9:40 AM AM THE CRISPR PLATFORM FOR DIAGNOSTICS, SARAH SHAPIRO

SESSION S.SM01.01: Point of Care Systems
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-SM01

5:00 AM *S.SM01.01.02
Nonenzymatic Biosensor Based Lab-on-a-Chip Device for Multi Organ Functional Analysis Satheesh Babu; Amrita Vishwa Vidyapeetham, India

A lab-on-a-chip diagnostic device for the point of care testing of non-communicable diseases has been developed considering the requirements of low cost, ease of use and diagnosis at every door-step. The device is capable of monitoring diabetes, chronic kidney and liver disorders, gout and oxidative stress-related diseases through simultaneous measurement of glucose, creatinine, bilirubin, uric acid and ascorbic acid from a single drop of body fluid. This device eliminates geographic, economic and rural barriers in healthcare and will revamp healthcare by providing access to affordable technology for better management of major non-communicable diseases.

The device consists of three parts, nanomaterial-based electrochemical sensors, a microfluidic chip and an electronic meter with read-out.

A disposable non-enzymatic, electrochemical creatinine sensor was developed using copper nanoparticles modified screen-printed carbon electrodes. The detection was based on the formation of soluble copper–creatinine complex at the applied potential. The sensor exhibited excellent response towards creatinine in the range of 6.25–378.5 μM at the physiological pH making it highly suitable for real sample analysis.

Non-enzymatic, electrochemical detection of bilirubin was carried out on disposable screen-printed carbon electrodes. The sensor exhibited excellent catalytic response towards bilirubin in the range of 5–600 μM at pH 8.5 making it highly suitable for real sample analysis. The sensor was successfully used to analyze albumin-bilirubin complex formation. The effect of ibuprofen on the unbinding of bilirubin-albumin complex was also demonstrated with the sensor.

Non-enzymatic, electrochemical detection of glucose was carried out on Pt-CuO-rGO modified SPE. The sensor exhibited excellent catalytic response towards glucose in the range of up to 27 mM in alkaline pH. A disposable non-enzymatic electrochemical sensor for AA was fabricated using copper hydroxide nanorods. The sensor works at very low potential with excellent linearity (0.0125–10 mM), sensitivity (268 μA/mM/cm²) and selectivity. The electrochemical detection of UA was carried out on activated SPCE in 0.1 M PBS. The sensor showed good linear response for UA in the range 100–1000 µM. A comparison of blood serum analysis results with those obtained from conventional clinical methods was highly correlative which further reiterates the potential of the developed sensors for POCT application.

Non-enzymatic electrochemical sensors were integrated into the microfluidic chip and tested with the indigenously developed programmable electronic meter. The device provides the preprogrammed potentials to the sensor electrodes which resulted in the oxidation of respective analyte on the working electrode. The voltage proportional to the reaction current was fed to the microcontroller from each analog front end. With the help of the calibration equation programmed into the microcontroller, the obtained voltage is converted into the corresponding analyte concentration and the results were displayed on the graphical LCD screen.

The developed LOC device is completely portable, handheld and can provide test results typically within a few minutes. The device is very simple to use and can be operated even by an individual with minimal technical training. Thus, the device will play a positive role in the prevention and management of non-communicable diseases namely diabetes, chronic kidney and liver disorders, gout and oxidative stress-related diseases, ensure better quality of life and also reduce the economic and social burden.
5:15 AM *S.SM01.01.04
Resonance Frequency Modulation for Rapid Point-of-Care Ebola Glycoprotein Diagnosis with a Graphene-Based Field-Effect Bio-Transistor Junhong Chen1,2; 1The University of Chicago, United States; 2Argonne National Laboratory, United States

Recent outbreaks of the Ebola virus infection in several countries demand a rapid point-of-care (POC) detection strategy. This talk reports on an innovative pathway founded on electronic resonance frequency modulation to detect Ebola glycoprotein (GP), based on carrier injection-trapping-release-transfer mechanism and standard antibody-antigen interaction principle within a dielectric-gated reduced graphene oxide (rGO) field-effect transistor (GFET). The sensitivity of the current Ebola detection can be significantly enhanced by monitoring the device’s electronic resonance frequency, such as inflection frequency (f_i), where phase angle reaches maximum (θ_max). In addition to excellent selectivity, a sensitivity of ~36-160 % and ~17-40 % for 0.001-3.401 mg/L Ebola GP can be achieved at high and low inflection resonance frequencies, respectively, which are several orders of magnitude higher than the sensitivity from other electronic parameters (e.g., resistance-based sensitivity). Using equivalent circuit modelling on contributions of channel and contact, analytical equations for resonance shift have been generalized. When matching with the incoming ac measurement signal, electronic resonance from the phase angle spectrum is evolved from various relaxation processes (e.g., trap and release of injected charge at surface trap sites of channel-gate oxide and channel-source/drain interface) that are associated with a characteristic emission frequency. Using charge relaxation dynamics, a high-performance bio-FET sensing platform for healthcare and bio-electronic applications is realized through resonance shifting.

5:30 AM *S.SM01.01.05
Nanostructured Metal Oxides-Based Biosensors for Oral Cancer Detection Bansi D. Malhotra; Delhi Technological University, India

Oral cancer (OC) is currently one of the most wide-spread cancers and it is known to occur more often in men than women.[1] If not detected early, this cancer can be life threatening. Smoking, alcohol consumption, diet (red and processed meat, fried foods, chewing tobacco, human papillomavirus, and exposure to certain chemicals (e.g. sulfuric acid, asbestos, and formaldehyde) are some of the common reasons behind the onset of OC. Many techniques such as laser capture microdissection, visualization adjuncts, cytopathology, and biopsy can be for detection and monitoring of OC. These methods are time-consuming, expensive, labour intensive and invasive. Biosensors are, however, user-friendly, reliable and offer increased assay speed, high sensitivity and require low sample volumes.

Nanostructured metal oxides have recently aroused much interest as immobilizing matrices for development of biosensors since these materials provide desired orientation, better conformation and high biological activity resulting in enhanced sensing characteristics for oral cancer detection.[2–5] In this context, nanostructured oxides of metals such as zirconium, yttrium and hafnium have been found to show interesting functional, biocompatible, non-toxic and catalytic properties for oral cancer detection. These materials have been predicted to yield enhanced electron-transfer kinetics and strong adsorption capability and provide suitable microenvironments for the immobilization of oral cancer biomarkers e.g interleukin-8 (IL-8), interleukin-6 (IL-6), vascular endothelial growth factor (VEGF) and cytokeratin fragment-21-1(Cyfra-21-1) resulting in enhanced electron transfer and improved characteristics for OC detection. Among the various biomarkers, CYFRA-21-1 is a water-soluble proteinaceous biomarker and is a fragment of 40 kD of cytokeratin 19. [1] The cut-off concentration of CYFRA-21-1 in saliva for normal persons is 3.8 ng mL−1 and patients have been found to have CYFRA-21-1 concentration as high as 17.46 ng mL−1 in saliva. I will focus on the results of some the recent experiments obtained in our laboratories on nanostructured metal oxides based biosensors for non-invasive oral cancer detection.[3-5]

References

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5:45 AM *S.SM01.01.06
Selectively Placed Graphene-Based Microfluidic Device for Point-of-Care Device Application Vivekanand Palaninathan1, Tomofumi Ukai1, Yoshikata Nakajima2, Narayanath Tharangattu1, Subhabrata Das3, Stephen Grage4, Anne S Ulrich5, Pingzuo Li6, Subrahmanyam A7, Ramasamy Paulmurugan4, Dorian Liepmann5, Ponisseril Somasundaran5, Pulickel Ajayan1, Venkatesan Renugopalakrishnan1,2,6 and Sakthi Kumar1, 1Toyo University, Japan; 2Institute for NanoScience Design, Osaka University, Japan; 3Tata Institute of Fundamental Research, India; 4Langmuir Center of Colloids and Interfaces, Columbia University, United States; 5Karlsruhe Institute of Technology, Institute of Biological Interfaces (IBG-2), Germany; 6Boston Children’s Hospital, Harvard Medical School, United States; 5Indian Institute of Technology, India; 6Cellular Pathway Imaging Laboratory (CPIL), Department of Radiology, Stanford University, United States; 6University of California Berkeley, United States; 8Columbia University, United States; 11Rice University, United States; 12Department of Chemistry, Northeastern University, Boston, MA 02115. USA., United States

Graphene has numerous applications in biomedicine as its unique physicochemical properties could be tuned to functionalize proteins, enzymes and other macromolecules for biosensor applications, or can be used as a therapeutic delivery vehicle for drug and nucleic acids delivery that can improve human life. Miniaturization of devices comes with a prerequisite need for precision control and selective placement of nanomaterials, which is still a challenge in most biosensing applications. In this study, we explore the potential of a graphene-based Field Effect Transistor (G-FET) device for glucose sensing. Specifically, we aim to selectively and precisely place monolayer of graphene on Si/SiO2 substrates through the Langmuir-Blodgett technique (self-assembly process) and electrodes are fabricated on top of the graphene. Subsequently, the microchannels were integrated with the device and were functionalized with linker molecules and further immobilized with enzymes, which can catalyze glucose metabolism by direct electronic transport. Our study will highlight the potential use of graphene-based nanomaterials as a platform for developing devices that can be used for electrochemical biosensing, optical biosensing as well as the creation of graphene-metal nanoparticle hybrids for enhanced performance.

6:00 AM *S.SM01.01.07
Biphasic Nanodot Zirconia Based Efficient Biosensor for Non-Invasive Oral Cancer Detection Suveen Kumar1,2, Venkatesan Renugopalakrishnan3 and Bansi D. Malhotra1,4; 1Delhi Technological University, India; 2University of Delhi, India; 3Harvard Medical School, United States; 4Northeastern University, United States

We report results of the studies relating to the synthesis of biphasic (monoclinic and tetragonal) nanodot zirconia (zero dimension with size < 4 nm) that has been utilized for the fabrication of electrochemical biosensing platform for the detection of CYFRA-21-1 biomarker; secreted in saliva samples of oral cancer patients. In the synthesis of nanodot zirconia, hydrothermal process was used at 180 °C for 24 h. The 3-aminopropyl triethoxy silane (APTES) functionalized nanodot zirconia (APTES/ndZrO2) was electrophoretically deposited onto prehydrolyzed indium tin oxide (ITO) coated glass electrode at the potential of 14V for 120s. The monoclonal anti-CYFRA-21-1 (50 µg mL-1) was drop-cast onto the obtained uniform thin film of APTES/ndZrO2/ITO via EDC-NHS coupling. The non-specific binding sites were blocked using bovine serum albumin (BSA, 1 mg dL-1). The X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM) and Fourier transforms infrared spectroscopy (FT-IR), were used for characterization of nanomaterials. The electrochemical characterization and sensing response studies; cyclic voltammometry (CV) and differential pulse voltammetry (DPV) techniques were used. The fabricated biosensing platform (BSA/anti-CYFRA-21-1/APTES/ndZrO2/ITO) exhibited electrochemical response in the range of 2-20 ng mL-1, sensitivity of 3.2 µA mL ng-1cm-2 and lower detection limit of 1.96 ng mL-1. The observed electrochemical response of the BSA/anti-CYFRA-21-1/APTES/ndZrO2/ITO was in good agreement with the results obtained through the enzyme linked immunosorbsorbent assay technique (ELISA) in saliva samples of oral cancer patients.

References:
Drop-on-Demand Inkjet Bioprinting for Tissue Engineering  
**Sungjune Jung**; Pohang University of Science and Technology, Korea (the Republic of)

Inkjet printing technology encompasses the generation, control and deposition of 1-100 picolitre liquid drops. Besides graphic printing applications, new opportunities for inkjet printing are starting to be exploited commercially in the manufacture of high value, high precision products. The applications include the fabrication of 3D biological tissues and organs for regenerative medicine as well as flexible electronics such as biosensors, solar cells, and light emitting diodes. This talk present inkjet-based cell printing technology and its applications to regenerative medicine and tissue engineering. I will show how living cells are ejected from micron-sized nozzle with single-cell level accuracy and how multiple types of cells can be patterned into 2D and 3D biological structures with high-resolution. Then, our recent studies on the applications of 3D inkjet bioprinting, including high-throughput screening for personalized medicine, 3D alveolar barrier models, engineered skin substitutes will be presented. We believe that drop-on-demand, cell-accuracy inkjet printing is a versatile tool to fabricate complex tissues for drug discovery, disease model, and toxicity.

**SESSION S.SM01.02: Organ on a Chip**

On Demand Abstracts Available for Viewing Starting Saturday, November 21, 2020

5:00 AM S.SM01.02.02

**In Vitro Modeling of Non-Alcoholic Fatty Liver Disease by Integrated Gut-Liver on a Chip**  
**Jiandong Yang**¹, Yoshikazu Hira¹, Ken-ichiro Kamei¹, Marika Trumm²⁺¹, Toshiyuki Tsuchiya¹ and Osamu Tabata¹¹; ¹Kyoto University, Japan; ²Heidelberg University, Germany

Non-alcoholic fatty liver disease (NAFLD) is one of the most common chronic liver diseases, leading to cirrhosis, liver cancer and cardiovascular diseases, and is the important stage to cure the diseases without liver transplantation [1]. Until now, any effective drugs/treatments have been established due to the improper in vitro cell-based assays and animal models, misleading the results to study the disease mechanisms. A gut-liver axis (GLA) might play a critical role in NAFLD by disrupting intestinal barriers towards liver damages and fibrosis, and could be a good candidate model to study NAFLD in vitro. However, the conventional cell-culture settings did not allow recapitulating inter-tissues interactions like GLA. On the other hand, the recent Organs-on-a-Chip technology may offer recapitulating such interactions by utilizing microengineering/fluidic technology [2]. Here we report a gut-liver on a chip (iGL Chip) enabling the precise closed-loop medium circulation to represent GLA as an in vitro NAFLD model. We demonstrated to culture gut and liver cell lines (CaCO2 and HepG2 cells, respectively) under the medium recirculation, perturb with free fatty acids (FFAs) for cells to initiate NAFLD process, and monitor cellular responses in a chip.

The microfluidic device in iGL Chip composed with three polydimethylsiloxane (PDMS) layers, i.e., from top to bottom, perfusion, thin membrane, and control layers. To incorporate precise pressure-driven micro valves and pneumatic pumps utilizing thin elastic membrane, the part of a perfusion channel of the pneumatic pump has semicircular shape for the complete seal by deformed membrane. The designed device was fabricated by the combination of the simulation based-grayscale lithography and the softlithography process [3].

It is well-known that PDMS has the critical issue of an absorption of small hydrophobic molecules, and might cause FFA absorption. To reduce the absorption and improve cell growth on PDMS, PDMS surface was treated with n-dodecyl-D-maltoside (DDM) amphiphilic molecule, followed by Matrigel extracellular matrices mixture. The DDM coating reduced the background of adipoRed lipid fluorescent staining about 20% compared to bare PDMS. Next HepG2 cells and CaCO2 cells were separately introduced into their corresponding cell-culture chambers with 1.0×10⁶ cells/ml. The circulation flow (15 nL/min) was actuated by the micropump after 12 hours of cell attachment. For 5-7 days of cell culture, both cells reached to the full confluence in the cell culture chamber area. The effect of coating method on cell attachment and viability were tested by the Calcein-AM living-cell staining. The cell viability of DDM/Matrigel coating was similar with those of only Matrigel
coating. The DDM/Matrigel coating could improve cell culture condition with the reduction of molecules absorption.

Next, co-culture of HepG2 and CaCO2 cells in a iGL Chip was demonstrated to investigate the effects of medium recirculation flow. Although HepG2 cells showed comparable cell viability among tested conditions, CaCO2 cells under flow conditions had higher cell viability than that of static conditions. Finally, to observe the cellular response after FFAs treatments, HepG2 and CaCO2 cells were treated with FFAs-contained medium (oleic acid : palmitic acid = 2:1) and kept under recirculation flow for 24 hours to investigate whether NAFLD-like cellular phenotypes. The intercellular lipid in HepG2 cells was increased with the increase of FFA concentrations, resulting the reduction of cell viability, on the other hands, CaCO2 cells did not change their viability after FFAs treatments. These results suggest the iGL Chip represented the initial state of NAFLD and has potential for disease modelling towards drug developments for NAFLD.


5:10 AM *SM01.02.03
Defective Organ-on-a-Chip Strategy Xiuli Zhang1, Jiu Deng2, Yong Luo2 and Bingcheng Lin2; 1Soochow University, China; 2School of Chemical Engineering, Dalian University of Technology, China; 3Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China

Defective models, such as gene-knockout cell model, gene-knockout mouse model, or immune-system-inhibited nude mouse model, have played critical roles in biological studies. We extrapolated this kind of idea into the field of organ-on-a-chip research, and proposed a defective organ-on-a-chip strategy, which we believe would find wide applications in the field of pharmaceutical and biomedical researches. To demonstrate this strategy, we developed an immuno-liver-chip featuring T cells, and realized preclinical drug-hepatotoxicity-typing by exploiting defective liver chips. In detail, we removed T cells, Kupffer cells, Stellate cells, and the artificial bile duct from the immuno-liver-chip, respectively, thus deriving four distinct defective liver chips. We then measured the hepatotoxicity of a same drug with these immuno-liver-chip series. By analysis of the difference between the measured hepatotoxicity, we can identify the role of different types of hepatic cells in the drug hepatotoxic process and therefore deduced the mechanism of the drug hepatotoxicity. As a demonstration, we used defective liver chip strategy to successfully discriminate the hepatotoxicity mechanism of four classical drugs, Abacavir, Ethynyl estradiol, Paracetamol, and Sulfamethoxazole.

5:25 AM SM01.02.04
A Human Kidney on a Chip Microphysiological System Jonathan Himmelfarb and Edward Kelly; University of Washington, United States

Chronic kidney disease is a public health problem affecting 850 million people worldwide, 37 million people in the US adult population, and is the 9th leading cause of death according to the Centers for Disease Control and Prevention. Until recently there has been a lack of human in vitro models that recapitulate critical aspects of kidney physiology, mimic the unique complexities of specific nephron segments, model disease heterogeneity or assess reparative mechanisms in response to injury. The lack of in vitro models, coupled with numerous challenges in available animal models for modeling most human kidney diseases, has hindered the development of safe and effective therapies. This is in part because microfluidic flow is so essential to kidney structure and cellular function. In response to this critical unmet need, we and others have developed three-dimensional flow directed “kidney-on-a-chip” microphysiologics systems (MPS) populated with a variety of human kidney cells, with functional characterization of key component structures of the proximal tubule, the peritubular microvascular network, and more recently the glomerular filtration barrier. Use of our kidney-on-a-chip MPS platform has been accompanied by the development of multiple reproducible data readouts, including immunocytochemistry, advanced microscopy, deployment of protein and microRNA biomarkers and mRNA gene expression data. The kidney MPS is characterized by precise control of cellular composition, extracellular matrix, vascular and tubular geometry and flow. Our integrated approach for in vitro disease modeling includes differentiating human kidney cells and organoids from diseased patient-derived inducible pluripotent stem cells (iPSC), CRISPR gene editing, single cell transcriptional profiling and engineering living human kidney vascular networks. We have demonstrated success in delineating novel molecular drivers of several disease processes and drug induced nephrotoxicity. Our in vitro on chip models recapitulate critical aspects of kidney physiology, assess the mechanisms and response to injury, have established translatable biomarkers and target engagement readouts, and test reparative mechanisms, all of which can substantially enhance therapeutic discovery and evaluation for a varity of kidney diseases.
Human Organs Chips For Drug Discovery and Personalized Medicine Rachelle Prantil-Baun and Donald Ingber1,2,1; 1Harvard University, United States; 2Vascular Biology Program, Boston Children’s Hospital and Harvard Medical School, United States

The human ‘Organ-on-a-Chip’ (Organ Chip) microfluidic culture technology was originally developed as a tool to provide better predictive models for drug efficacy and toxicity. We have developed 2-channel Organ Chip devices that recapitulate tissue-tissue interfaces, vascular perfusion and organ-level functionality seen in vivo by incorporating multiple cell types, mechanical cues (e.g., breathing or peristalsis-like motions), and fluid flow, as well as immune cells. Using this approach, we have created Organ Chip models of over 10 different human organs, as well as rat and dog Liver Chips. We have also developed a robotic Interrogator instrument that can link up to 10 different Organ Chips to form a ‘Human Body-On-Chips’ platform, which we have used in combination with computational modeling to carry out predicted in vitro-to-in vivo extrapolation (IVIVE) of human drug pharmacokinetic and pharmacodynamics (PK/PD) parameters in vitro. Using these approaches to carry out human experimentation in vivo, we have not only addressed key challenges relating to drug PK/PD, toxicity, and efficacy, we also have gained new insights into human physiology and disease mechanisms, and have been able to model various diseases and rare gene disorders using patient-derived cells. Thus, Organ Chips offer a powerful new approach to confront challenges relating to mechanistic pathophysiology as well as drug development and personalized medicine.

Engineering of Microfluidic Tumor On-Chip Models to Study Cancer Metastasis Mehdi Nikkhah; Arizona State University, United States

Cancer is currently the second leading cause of death in the United States, claiming the lives of over half of a million Americans annually. Poor patient prognosis and treatment outcomes are in large part due to the biological complexities of this devastating disease. Improved treatment and early diagnosis have yielded a steady decrease of cancer-related mortalities, but metastatic cancers are still deadly due to a lack of effective targeted treatment options. Upon tumor formation at the primary sites, metastasis progresses through a stepwise cascade of events, in which the key initial steps include stromal desmoplasia/fibrosis, immune response, tumor invasion and cancer cell escape into the vasculature (i.e. intravasation). Tumor cells adopt an aggressive phenotype through continuous interactions with their surrounding microenvironment (TME) and the multitude of physiochemical signaling cues that emerge from their surrounding extracellular matrix (ECM) and resident stromal cells. To that end, the complexities of the native TME and the limitations of conventional in vitro platforms and in vivo tumor models pose a non-trivial challenge in identifying the key molecular and cellular signaling cues involved in the dynamic tumor-stroma crosstalk as potential therapeutic targets. In the past few years, microengineering technologies have been widely utilized in various scientific disciplines, from physics and chemistry to biology. These technologies have proved immensely beneficial for the fields of experimental biology and medicine through development of miniaturized biomimetic living tissue systems for cellular- and molecular-based studies. In addition, these technologies have gained significant attention in their ability to precisely control cell-microenvironment interactions to better understand the mechanisms of human disease progression, particularly cancer. In this seminar, I will present the multidisciplinary research focus of our laboratory at ASU on the integration of microscale technologies, advanced biomaterials and biology to develop the next generation ex vivo on-chip tumor microenvironment models to study cancer progression at the earliest stages of the metastatic cascade. I will specifically discuss our recent efforts and findings on engineering of organotypic breast and brain tumor microenvironment models to dissect the role of stromal cells (e.g. cancer associated fibroblasts) on tumor cell invasion, intravasation and vascular homing.

Micro/Nano-Engineering Approach for Developing Advanced Microphysiological Systems Ken-ichiro Kamei; Kyoto University, Japan

Impediments to drug discovery include increasing costs (over 10 billion USD per drug), long period of development (more than 10 years), insufficient drug efficacy, and serious side effects. These issues can largely be attributed to the current improper approach to pre-clinical testing that involves the use of experimental animals, often yielding misleading results because of variation in responses due to species difference. In addition, the use of experimental animals has become restricted in many countries due to ethical issues. Therefore, drug development by pharmaceutical companies is a high-risk endeavor and new approaches for drug discovery are urgently required.
The microphysiological system (MPS, which is also termed organs/body-on-a-chip) has considerable potential for use in drug development and toxicological testing. MPs aim to recapitulate in vivo physiological and pathological conditions in a chip without the use of actual organs, similar to an in vitro human model. Compared with conventional animal models, MPSs are advantageous for predicting drug efficacy and toxicity in humans, obtaining more quantitative results, shortening experimentation time, improving the reproducibility and cost-effectiveness, and reducing the use of animals. The MPS platform could become an alternative to animal testing.

However, the current MPS platforms have several issues that need to be resolved. Most MPS platforms still possess a one-way flow stream or a few branches on a chip, so they cannot completely represent the inter-tissue interaction that occurs through the blood circulation system. Some studies have utilized external rotary peristaltic pumps for cell-culture medium circulation, but they require a large amount of medium, and drugs, metabolites, and products secreted from cells could be diluted and lost as a result of this process. Notably, most of the previously developed MPS platforms can only examine a set of samples on the chip, and do not have the capability to compare samples next to each other within a device. Furthermore, it is still challenging to directly integrate micropumps into a device, because the existing fabrication methods are not simple and reliable. Therefore, it is important to develop new microfabrication technologies capable of integrating pumps into a device to minimize medium volume and sample loss.

Moreover, it is also important to integrate an in situ sensor to monitor cell or tissue behavior after administering the treatments on a chip. Majority of the current cell monitoring methods used in the MPS platform are based on microscopic imaging with cell staining. However, this approach often requires cell-labeling materials that could perturb cells, influencing the drug treatment or killing the cells. Additionally, this approach only permits end-point experiments and there is loss of information over time. Accordingly, it is necessary to integrate in situ and non-invasive cell monitoring systems to obtain “living cell” information.

In the present study, we introduce an interdisciplinary approach comprising aspects of stem cell biology, material science, and micro/nano-engineering that is designed to solve the aforementioned issues. We present some applications, such as in vitro recapitulation of anti-cancer drugs on the heart as well as in vitro modeling of non-alcoholic fatty liver diseases. We envision that this technological development will allow a precise recapitulation of human physiology and pathology, which will enhance our understanding of the mechanisms underlying various diseases for which effective treatments remain elusive, and will help identify new therapeutic drugs.

6:20 AM S.SM01.02.08
Construction And Application of a Multi-Organ Microfluidic Chip Mimicking the In Vivo Pathological Process of Lung Cancer Brain Metastasis Qi Wang; Dalian Medical University, China

Brain metastasis (BM) is a leading cause of mortality in patients with non-small cell lung cancer (NSCLC). However, the molecular mechanisms underlying BM of NSCLC remain largely unknown because of the lack of models to accurately investigate such a dynamic and complex process. Here we developed a multi-organ microfluidic chip as a new methodological platform to study BM. The chip consisted of two bionic organ units – an upstream “lung” and a downstream “brain” characterized by a functional “blood-brain barrier (BBB)” structure, allowing real-time visual monitoring of the entire BM process, from the growth of primary tumor to its breaking through the BBB, and finally reaching the brain parenchyma. The chip was then applied for the BM research where we first demonstrated that the protein expression of Aldo-keto reductase family 1 B10 (AKR1B10), which was identified by proteomics profiling, was significantly elevated in lung cancer BM. Silencing AKR1B10 in brain metastatic tumor cells suppressed their extravasation through the BBB in the in vitro Transwell model, in our ex vivo microfluidic chip, as well as the in vivo model of brain metastasis in nude mice. With the combined application of our new model and traditional research platform, it was suggested that our multi-organ microfluidic chip is a practical alternative to study BM pathogenesis, and AKR1B10 is a diagnostic biomarker and a prospective therapeutic target for NSCLC BM.

6:30 AM *S.SM01.02.12
3D Printed Device Mimicking Hepatic Lobule-Like Flow Conditions for Toxicity Testing Anil Kumar P R, Shiny Velayudhan, Roopesh R. Pai and Vinod Kumar V; Sree Chitra Tirunal Institute for Medical Sciences and Technology, India

Hepatic tissue is a complex organ with very specific fluid flow characteristics. The adverse effects of chemicals and drugs are studied in vitro by conventional two dimensional monolayer cultures. 2D cultures results in loss of cell viability and decreased liver-specific functionality. In vitro models such as spheroid culture, sandwich culture and 3D printed tissues have been proposed to overcome these limitations. When culture systems are upgraded from 2D to three dimension (3D), the microenvironment also needs to be upgraded. We propose a 3D Printed hepatic lobule-Like bioreactor for in vitro Hepatotoxicity testing. The multi chamber in the perfusion device can hold functional hepatocytes and is nourished by flow conditions. Various flow conditions were simulated in silico to understand the fluid flow inside the device. Bifabricated
tissues, either cell encapsulated or 3D bioprinted, placed inside the device receives fluid flow similar to liver lobule and are functional. The device can perform like a miniaturized disposable bioreactor for hepatotoxicity testing.

6:45 AM S.SM01.02.14
Fabrication of a Physiologically Relevant and Novel Lung-on-a-Chip Device for the Study of Human Pulmonary Disease and Drug Toxicity  
David J. Blake, Marcus A. Williams and Jeff Jessing; Fort Lewis College, United States

In the scope of biomedical research, many advances have been made in the field of pulmonology with the use of multiple animal models and traditional cell culture experimentation. While these methods are useful when studying single cellular pathways or overarching biological processes, they often falter when studying the meticulous nature of human disease. In this work, we propose the development of a novel Lung-on-a-Chip device that would more accurately mimic the physiological boundaries of human alveoli than animal models or traditional in vitro studies. Utilizing multiple microfabrication techniques, we are developing a microfluidic device with an ultra-thin (25 µm) biodegradable porous silicon membrane. Current data suggests that human pulmonary epithelial and endothelial cells are viable and prolific on the proposed microfabricated silicon membrane in extended studies (14 days). Due to the biodegradability of the fabricated novel silicon membranes, it has been observed in long term studies that cells can remodel and degrade the porous silicon membrane. This degradation allows for physiological cellular contact between membranes mimicking a true blood gas exchange interface as observed in vivo. To further validate this model’s ability to recapitulate human physiology, we have begun to co-culture with immunological cell types and are monitoring for response to bacterial and tumor antigens. Preliminary data suggests that immunological cells are able to remodel the porous silicon membrane substrate and migrate across cellular boundaries in response to environmental cues as seen in vivo. Broadly, we believe that this model may be used to further characterize and study human pulmonary disease and drug toxicity.

6:55 AM *S.SM01.02.16
Innovative Organ-on-a-Chip (OOC) Platform Combined 3D Bioprinting Technology for Highly Reliable Human Tissue Mimicry  
Yimin Guan; Shanghai Industrial Technology Research Institute, China

Organ-on-a-chip (OOC) technology progresses rapidly and has attracted tremendous interest in research due to its capabilities of emulating in-vivo microenvironment and tissue structure. It has great potentials for pharmaceutical research development and precision medicine. Microfluidic technology and precision 3D cell printing are the two key enablers to make OOC. However, current OOC has some drawbacks including low throughput, inconsistency, high-cost, unmanufacturable. These issues have prevent wide use of OOC technology in industry scale.

In this work, we demonstrate an approach to standardize Organ-on-a-chip (OOC) fabrication and testing process. In this process, A inkjet printing system with special designed MEMS printhead has been built and employed to printing multiple types of cells and structural bio materials in a precise and repeatable way. In addition, a special designed trans well structure and removable wells are used to hold OCC with multiple replicas. This standardized OOC process is able to provide a standardized and reliable method for 3D multi-type cell co-culture with a integrated perfusion system which can adjust flow rate to provide stable shear-force microenvironment for better simulating human-like in vivo system including hepatic sinusoids, blood-brain-barriers (BBB), intestinal villi.

7:10 AM S.SM01.02.17
A Novel Micro-injection Droplet Microfluidic System for Studying Locomotive Behavior Responses to Cu²⁺ induced Neurotoxin in Individual C.elegans  
Zongzheng Chen¹, Xiuli Zhang², Yong Luo³ and Bingcheng Lin⁴; ¹First Affiliated Hospital of Shenzhen University, China; ²Soochow University, China; ³Dalian University of Technology, China; ⁴Chinese Academy of Sciences, China

Analysis of C.elegans by droplet microfluidics has been widely used in study of locomotive behavior responses to neurotoxicity due to the capacity of high-throughput manipulating single cells. However, it has been difficult to manipulate droplets flexibly and actively on account of the limitation the dimension of individual C. elegans droplets. In this study, a novel MiDMS (Micro-injection Droplet Microfluidic System) was proposed, which consist of three parts: single C. elegans droplet generator, droplets drug micro-injection channels and drug-incubation observation array. Individual C.elegans droplets were produced initiatively by regulating the flow rates between oil and water phase as well as the concentration of C.elegans in suspension. Then, the drug solution was precisely injecting into each C.elegans droplet, which by electricity induced surface tension of droplet changing. In addition, the effect of neurotoxic Cu²⁺ on locomotive behavior of C. elegans was evaluated at single cell resolution. The results showed that the neurotoxicity induced behavioral disorder of the C. elegans was more obvious with the increase of Cu²⁺ concentration treatment time, and these dose-effect and time-effect relationship in MiDMS were similar as in petri dish. It will be providing a powerful platform for the study of
the response of C. elegans to quantitative drug at single cell resolution.

SESSION S.SM01.03: 2D Nanomaterials Platform
On Demand Abstracts Available for Viewing
Starting Saturday Morning, November 21, 2020
S.SM01

5:00 AM S.SM01.03.01
Low-Dimensional Nano-Carbons—Form Doped Graphene to 3D Hybrids and Biological Applications
Mauricio Terrones; The Pennsylvania State University, United States

We will discuss the synthesis of carbon nanotubes and nanotube networks using different dopants during chemical vapor deposition. In particular, the effects of sulfur, boron and nitrogen will be discussed. It will be demonstrated that it is indeed possible to assemble/grow carbon nanotube networks if a careful control of dopants is achieved during chemical vapor deposition (CVD) growth. High-resolution electron energy loss spectroscopy (HR-EELS) studies on these nanotube materials will be presented, and the locations of boron, sulfur and nitrogen within nanotubes will also be shown. First principles theoretical calculations on nanotubes containing pentagon, hexagons and heptagons in the presence of these dopants will be discussed. We will also discuss the cytotoxicity and applications as molecular sensors and virus traps of these doped nanocarbons. This talk will also discuss the synthesis of large-area, high-quality monolayers of nitrogen-, silicon- and boron-doped graphene sheets on Cu foils using ambient-pressure chemical vapor deposition (AP-CVD). Scanning tunneling microscopy (STM) and spectroscopy (STS) reveal that the defects in the doped graphene samples arrange in different geometrical configurations exhibiting different electronic and magnetic properties. Interestingly, these doped layers could be used as efficient molecular sensors in conjunction with Raman spectroscopy. In addition, the synthesis of hybrid carbon materials consisting of interconnected graphene layers (graphene foams) by solvothermal routes will be discussed. These foams are highly conducting, very robust and can operate at temperatures ranging from 77K to 1173K.

References:

5:10 AM S.SM01.03.03
Engineering Conductive and Adhesive Cardiopatches for Cardiac Tissue Regeneration
Brian Walker¹, Roberto Portillo Lara² and Nasim Annabi¹,³,⁴; ¹University of California, Los Angeles, United States; ²Tecnologico de Monterrey, Mexico; ³Brigham and Women's Hospital, United States; ⁴California NanoSystems Institute, United States

Heart failure following myocardial infarction (MI) is the number one cause of death in the United States, and western world due to the myocardium’s inability to regenerate to a significant degree once fully matured, leaving behind a fibrous scar tissue that is unable to contract or propagate electrical impulses. Cardiac tissue engineering (TE) is a field of biomedical engineering that aims to develop materials for the treatment of patients suffering from heart failure after MI. Development of these materials may involve electrospinning, a technique utilized for engineering fibrous scaffolds for tissue engineering applications. Here, we introduce electrospun cardiopatches based on gelatin methacryloyl (GelMA), due to its tunable mechanical properties, favorable biodegradation, and the presence of cell binding sites, which promote adequate cell adhesion and proliferation. Further, we introduce electrical conductivity properties to the engineered fibrous GelMA scaffold through the incorporation of a choline-based bio-ionic liquid (Bio-IL) within the fabricated GelMA electrospun sheet, and photocrosslink the constructs in the presence of UV light.

Here, we performed mechanical characterization on these cardiopatches, which showed that the electrospun GelMA/Bio-IL scaffolds had a tunable elastic modulus based on GelMA and Bio-IL concentrations. The elastic modulus was shown to increase concomitantly with an increase in the concentration of Bio-IL incorporated onto fibrous GelMA mats. The Bio-IL incorporated GelMA fibers exhibited tunable electrical conductivity that increased consistently by increasing the concentration of Bio-IL. In addition, \textit{ex vivo} experiments using excised rat abdominal tissues placed on electroconductive
cardiopatches showed that the excitation threshold of these tissues decreased with and increasing concentration of Bio-IL. This test demonstrated the ability for fibrous scaffolds to propagate an electrical impulse and excite peripheral tissues. These electroconductive cardiopatches could be readily attached to the epicardial surface of the heart via photocrosslinking, which eliminates the need for sutures that could lead to further tissue trauma. *In vitro* cell studies performed by seeding cardiomyocytes and cardiac fibroblasts on the surface of our GelMA/Bio-IL cardiopatches demonstrated the scaffolds ability to support cell adhesion, and proliferation. Further, cells seeded on conductive cardiopatches exhibited a markedly improved contractile profile when compared with non-conductive patches due to the overexpression of the gap junction protein connexin 43 (Cxn43). Lastly, we were able to demonstrate the cardioprotective efficacy of these cardiopatches using a rat MI model where these electroconductive scaffolds were placed on the surface of the heart following permanent ligation of the left anterior descending coronary artery. Our histological assessment was indicative of comparatively lower thinning of the ventricular wall 3 weeks after induction of the experimental MI.

The results presented here demonstrate a new method to fabricate a highly conductive fibrous GelMA/Bio-IL cardiopatch with tunable mechanical and conductivity properties through incorporation of Bio-IL into a fibrous scaffold. Cardiopatches were also highly adhesive to wet tissue and was shown to be biocompatible in vitro using cardiomyocytes and cardiac fibroblast cells. Conductive cardiopatches were able to support the overexpression of Cxn43, necessary for cell-cell interaction. This conductive GelMA/Bio-IL cardiopatch has the potential to be implanted onto damaged site in the heart to provide mechanical stabilization to the injured myocardium and to restore electromechanical coupling at the site of MI.

5:20 AM S.SM01.03.05
Ion-Selective Graphene-Hexagonal Boron Nitride Heterostructures for Biosensing Adarsh D. Radadia and Nowzesh Hasan; Louisiana Tech University, United States

An intrinsic ion sensitivity exceeding the Nernst-Boltzmann limit and an sp²-hybridized carbon structure make graphene a promising channel material for realizing ion-sensitive field-effect transistors with a stable solid-liquid interface under biased conditions in buffered salt solutions. We will present on the performance of graphene field-effect transistors coated with ion-selective membranes as a tool to selectively detect changes in concentrations of Ca²⁺, K⁺, and Na⁺ in individual salt solutions as well as in buffered Locke’s solution. Both, the shift in the Dirac point and transconductance could be measured as a function of ion concentration with repeatability exceeding 99.5%, and reproducibility exceeding 98% over 60 days. However, an enhancement in selectivity, by about an order magnitude or more, was observed using transconductance as the indicator when compared to Dirac voltage, which is the only factor reported to date. Fabricating a hexagonal boron nitride multilayer between graphene and oxide substrate further increased the ion sensitivity and selectivity of transconductance. These findings incite investigating ion sensitivity of transconductance in alternative architectures as well as urge the exploration of graphene transistor arrays for biomedical applications.

5:30 AM *S.SM01.03.06
Self-Renewing Neural Circuits in a Millimeter-Sized Invertebrate Jacob T. Robinson; Rice University, United States

Nervous systems are remarkable for supporting stable animal behavior despite dramatic changes to neurons’ number and connectivity, yet many questions remain. For example, how do new neurons differentiate from stem cells and integrate into existing circuits? Small invertebrate model organisms offer several advantages for studying this type of neural plasticity. Unlike organoids or cultured cells, the properties of the neural circuit in an animal can be directly related to behavior; however, most invertebrates show modest regeneration or lack well-developed transgenic techniques. Here we show that *Hydra vulgaris*, a millimeter-sized transparent cnidarian, with 12 neural subtypes shows simple sensory-motor transformations that are maintained despite dramatic changes to the numbers of neurons. The small size and deformable body make allow us to study neural activity in microfluidic platforms that permit chemical, electrical, and optical interrogation. By studying this type of self-renewal in a simple and tractable model organism we can discover fundamental principles that enable neural circuits to self-assemble and reorganize to maintain stable sensory-motor responses.

5:45 AM *S.SM01.03.07
2D Nanomaterials Pulickel Ajayan and Anand Puthirath; Rice University, United States

There has been significant advances in the synthesis and characterization of graphene and related two-dimensional atomic layers. For many applications, including biological, these materials need to be modified to introduce specificity, functionality and flexibility. The talk will focus on the generation of two-materials and approaches for their chemical and electronic modification. Various low dimensional structures that can result from 2D layers, such as quantum dots, ribbons and heterostructures, will be described showing how chemical and dimensional modifications can change their intrinsic
properties. Interface engineering of these structures within matrices or as multilayers will be considered as opportunities to
design and create new material interface systems. The talk will also address the usefulness of 2D materials in applications
such as sensors, coatings and biological interfaces.

SESSION S.SM01.04: Advancing Oligonucleotides Based Therapeutics; Challenges and Recent Advancements
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-SM01

5:00 AM *S.SM01.04.10
Chemical Engineering of Therapeutic Oligonucleotides Anastasia Khvorova; University of Massachusetts Medical
School, United States

5:15 AM *S.SM01.04.11
mRNA Therapy for Inhererited Metabolic Diseases Lisa Rice; Moderna, United States

5:30 AM *S.SM01.04.01
Re-engineering RNA Molecules into Therapeutic Agents—The Expanding Universe of Nucleic Acid
Modifications Martin Egli; Vanderbilt University, United States

First-generation nucleic acid analogs such as 2¢-deoxy-2¢-fluoro-RNA (2¢-F RNA), 2¢-O-methyl RNA (2¢-OMe RNA), and
the phosphorothioates (PS-DNA/RNA) have remained staples of oligonucleotide modification strategies in the discovery and
optimization of potential RNAi therapeutics. The first FDA-approved siRNA drug, patisiran (Onpattro) contains eleven 2¢-
OMe ribonucleotides in the sense and antisense strands formulated in a lipid nanoparticle (LNP) delivery system. Despite
their overall appeal in terms of enhanced nuclease resistance, increased pairing stability (2¢-F/OMe RNAs) and safety, newer
analogs are needed to further improve the therapeutic potential of unformulated siRNAs like GalNAc conjugates. The search
for oligonucleotides with therapeutic efficacy has given rise to an expanding universe of analogs, including the second-
generation 2¢-(2-methoxyethyl)-RNA (MOE-RNA) and the third-generation bicyclic nucleic acids (BNAs or LNAs). The
key enzyme in RNA interference (RNAi) is Argonaute 2 (Ago2), a dynamic multi-domain enzyme that binds multiple
regions of the guide (antisense) and passenger (sense) siRNAs. Considering the complexity of protein-RNA interactions in
RNA interference, it is imperative to expand the process of discovery and optimization of modified siRNAs to new
analogs. We have explored the potential benefits for efficacy of incorporating into siRNAs sugar modifications like N-
methylacetamide (NMA), 5¢-E-vinylphosphonate (5¢-E-VP) and, more recently, xeno-nucleic acid (XNA) residues such as
glycol nucleic acid (GNA), altritol nucleic acid (ANA), and threofuranosyl nucleic acid (TNA). The talk will summarize
siRNA modification strategies with an emphasis on regiospecific interactions between oligonucleotide and Ago2 and how
structural insights based on crystallographic data for modified RNAs alone and in complex with Ago2 from molecular
modeling studies can guide the choice of chemical modification at a given position of siRNA for optimizing its therapeutic
efficacy.

535-539.
8195-8197.
8. Schlegel, M. K.; Foster, D. J.; Kel’ in, A. V.; Zlatev, I.; Bisbe, A.; Jayaraman, M.; Lackey, J. G.; Rajeev, K. G.; Charisse,
Cancer is a complex genetic moving target that requires a therapeutic modality capable of selectively targeting all driver oncogenes combined with the inherent ability to undergo pharmaco-evolution to target new mutations at pace with the cancer cell mutation rate. siRNA RNA-interference (RNAi) therapeutics fulfill these criteria and have great potential to treat cancer and other human diseases. However, due to their 14 kDa size and 40 negative anionic charges, siRNAs have no bioavailability to overcome a billion years of evolutionary defenses to prevent RNAs from crossing the endosomal lipid bilayer to enter the cytoplasm. Consequently, developing anti-cancer RNAi therapeutics requires targeted delivery to malignant cells and paradigm-shifting technology to enhance endosomal escape into the cytoplasm, the critical rate-limiting delivery step. Our research is focused on solving these problems by synthesis of bioreversible charge neutral RNAi prodrugs, called short interfering RiboNucleic Neutrals (siRNNs), and synthesis of novel hydrophilic-masked, hydrophobic endosomal escape domains (EEDs). For targeting domains, we have focused on conjugating antibodies to siRNN RNAi triggers to generate Antibody-RNAi Conjugates (ARCs).

A Traceless Linker for Aliphatic Amines that Rapidly and Quantitatively Fragments after Reduction

Niren Murthy1,2; 1University of California, Berkeley, United States; 2Innovative Genomics Institute, United States

Reduction sensitive linkers have the potential to transform the field of drug delivery due to their ease of use and selective cleavage in intracellular environments. However, despite their compelling attributes, using reduction sensitive linkers for biomolecule conjugation reactions is still challenging because linkers have not been developed that can efficiently modify aliphatic amines and release them rapidly and completely after reduction. Developing reduction sensitive self-immolative linkers for aliphatic amines has been challenging due to their poor leaving group ability and high pKa values. Here we present a traceless linker (TRAILER), which can for the first time modify aliphatic amines and release them rapidly and quantitatively after disulfide reduction. We show here that TRAILER can reversibly modify the lysine residues on the Cas9 protein, with the cell penetrating peptide Arg10, and was able to generate a self delivering Cas9 RNP that could edit cells without transfection reagents. TRAILER has numerous applications in biotechnology given the ubiquitous presence of aliphatic amines on small molecule and protein therapeutics.

Boosting Intracellular Delivery of Messenger RNA

Gaurav Sahay; Oregon Health & Science University, United States

Non-coding ribonucleic acids (ncRNAs) are a diverse group of RNA molecules that are not translated into proteins following transcription. Mainly, microRNAs and long non-coding RNAs (lncRNAs) are predominant in this group. Aberrant expression of these ncRNAs has been observed in various pathological conditions including cancer. Especially, aberrant expression of microRNAs and the associated pathology has been extensively studied in cancer. Hence, targeting microRNAs has been considered a new generation of molecularly targeted therapy for various diseases. While downregulation of cellular microRNAs can be supplemented by delivering microRNA mimics, functional knock down of microRNAs that are overexpressed in diseases is a challenging task. The secondary structure of microRNAs determines how to functionally inhibit the translation of target mRNAs. MicroRNAs with even a few base homologies to the target can functionally regulate mRNA degradation/translation. The secondary structure of microRNA is crucial for recognizing target mRNA for functional effect. Since the double stranded RNA is an important intermediate in the biogenesis process of matured microRNA, delivering antisense microRNA for functional knock down of endogenous microRNAs needs a careful design. Especially challenging is their site-targeted delivery. We study antisense microRNAs with various structural determinants (mere homology, end loops, base pair modifications, artificial linkage, etc.) by molecular dynamics of the duplex formation at 1 micro second and beyond, for the evaluation of the therapeutic effect of microRNAs in various cancer models (GBM: antisense miR-21 and antisense miR-100; Breast cancer antisense miR-21 and antisense miR-10b; Hepatocellular carcinoma: antisense miR-21, antisense miR-10b and antisense miR-100). In this presentation, we summarize how structural modification in antisense microRNAs can be used for potential applications in cancer therapy, either microRNA targeting as
a monotherapy, or for improving clinical chemotherapy.

6:40 AM *S.SM01.04.08
CRISPR-Powered Transistors—Harnessing Biology as Technology Kiana Aran; Keck Graduate Institute, United States

We have recently developed a CRISPR powered, electronic biosensor termed, CRISPR Chip, capable of detecting the binding interactions between nuclease deactivated CRISPR with its target DNA sequence. CRISPR-Chip is a graphene field effect transistor (gFET) where the surface of the graphene is functionalized with nuclease deactivated CRISPR RNA-guided ribonucleoproteins (dRNPs). dRNPs within the CRISPR-Chip construct interact with their target sequence by scanning the genomic sample until they find and bind to their target. The selective hybridization of the target DNA to the dRNP complex modulates the graphene’s conductivity and results in a detectable change in electrical signal output which can be measured with a simple handheld reader. CRISPR-Chip was able to detect dRNP binding to two commonly deleted exon target sequences within the human dystrophin gene, without amplification. CRISPR-chip is the first example of CRISPR-powered electronic transistors that harnesses the search function of CRISPR/Cas9 and the ultra-sensitivity of graphene-based nanoelectronics to enable a complete label-free and amplification-free DNA biosensor.

6:55 AM S.SM01.04.09
Sense Anti-Sense MicroRNA Duplex—A Label Free Raman Study as an Approach for Functional Evaluation of Anti-Sense miRNA for Cancer Therapy Preetham Ravi1, Surya P. Singh2, Jeon Woong Kang3, Ramachandra R. Dasari3, Peter So3, Dinesh R. Katti1, Kalpana Katti1, Dorian Liepmann4, Jairam Eswara5, Venkatesan Renugopalakrishnan6 and Ramasamy Paulmurugan7; 1NDSU, United States; 2Stanford University, United States; 3Massachusetts Institute of Technology, United States; 4University of California, Berkeley, United States; 5St. Elizabeth Medical Center, United States; 6Harvard Medical School, United States

MicroRNAs are emerging as a novel diagnostic and therapeutic targets of human pathologies. Since the expression levels of various microRNAs are dysregulated in different cellular diseases, including cancer, understanding structural dependency of microRNAs for their biological functions is essential for designing synthetic oligos with various base and linkage modifications to develop high-sensitive diagnostic devices, and to use them in therapeutic applications. Here we use a label-free Raman spectroscopy to understand the structural difference of a selective microRNA, the microRNA-21, by hybridizing it with complementary RNA, DNA, and DNA with multiple base mutations for analysis. To verify the spectral changes induced by hybridization, the spectral profiles obtained from single-stranded microRNA-21 mimic, and RNA and DNA oligos complementary to microRNA-21 were compared with microRNA-21 in the form of hybrid and mixed with complementary oligos in solutions. The spectral changes were also analyzed for the concentration of complementary DNA with single, double and triple base mutations to understand Raman specific detection signal that can specifically distinguish different structural variants within a mixture. The analysis of the results identified prominent spectral features around 930 cm\(^{-1}\), 1017 cm\(^{-1}\) and 1068 cm\(^{-1}\) for C-C and C=O stretching of the ribose ring. Similarly, the broad spectral features including a sharp band and a shoulder in the area of 1350-1380 cm\(^{-1}\) were attributed to be adenine (C8–H and C2–H out of plane bending) and guanine (C8–H bending and C8–N stretching) bases. A band at 1418 cm\(^{-1}\) was assigned to be N=C–H bending modes from adenine, guanine and cytosine bases of RNA sequence. While analyzing the intramolecular structure in RNA, we also analyzed the DNA spectrum of Raman bands at 841 cm\(^{-1}\), 874 cm\(^{-1}\) and 930 cm\(^{-1}\) which were identified to be C2’-endo (B-DNA) conformation of DNA. In addition, we identified that the Raman band around 785 cm\(^{-1}\) to be the phosphodiester bond of the backbone linking 5’ phosphate of nucleic acid with 3’ OH of the other nucleotide. This study successfully utilized label-free Raman spectroscopy to differentiate structural features such as intermolecular (ssRNA and ssDNA) and intramolecular (RNA-RNA and RNA-DNA hybrid) interaction which can be utilized for developing biosensors to quantify microRNAs in clinical samples and to design therapeutic microRNAs with strong functionality for the treatment of cellular diseases.

7:10 AM *S.SM01.04.14
Role of Protein Corona on Oligonucleotide Delivery and Transfection with Lipid Nanoparticles Mansoor Amiji; Northeastern University, United States

Upon systemic administration of nanoparticles used in drug and gene delivery, they acquire a “biological identity” upon adsorption of plasma proteins. The protein corona layer has significant implication in the biodistribution, target specific localization, and toxicity of nanoparticle-based delivery systems. Additionally, specific enrichment of proteins may allow for an endogenous and more efficient approach for targeted delivery. Using a wide ranging of lipid nanoparticle (LNP) formulation where individual lipid composition was varied, we have shown
specific protein enrichment pattern and differential biodistribution and tumor-specific delivery of small interfering RNA (siRNA). For instance, DOTAP functionalized LNPs showed vitronectin enrichment and enhanced \textit{in vivo} tumor delivery of the nanoparticles to \(\alpha\beta3\) expressed tumors and endothelial cells as compared to \(\alpha\beta3\) negative tumors.

**7:25 AM *S.SM01.04.13**

\textbf{Intracellular Delivery of mRNA; Exploration of Delivery Materials for Next Generation Therapeutics} David Ulkoski; AstraZeneca PLC, United Kingdom

Current advances in RNA-based technologies such as therapeutic gene editing, mRNA therapeutics, and vaccines have produced strong interest and attention in safe and effective nonviral vectors for nucleic acid delivery. Nevertheless, the comprehensive application of nucleic acid therapeutics is still limited by the need for better delivery systems. Thus, the analysis of these delivery materials can be advanced to offer sharper insights into SAR learnings and provide a clearer picture of their therapeutic potential. Lipid- and polymer-based materials can be regarded as the most prominent partners for nucleic acid delivery, providing \textit{in vivo} transfection. Over the past few decades, a variety of cationic lipids and polymers have been synthesized, evaluated and applied as successful delivery vehicles for nucleic acids. Here, I will discuss some of the challenges for clinical translation of mRNA-based therapeutics and give examples of the biomaterials and delivery strategies we are investigating for the application of mRNA delivery.

**SESSION S.SM01.05: Molecular Imaging**

On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

**S.SM01**

**5:00 AM *S.SM01.05.01**

\textbf{Mechanobiological Markers for Cancer Metastasis} Dinesh R. Katti\textsuperscript{1,2}, MD S. Molla\textsuperscript{1}, Sumanta Kar\textsuperscript{1,2} and Kalpana Katti\textsuperscript{1,2}; \textsuperscript{1}North Dakota State University, United States; \textsuperscript{2}NDSU, United States

According to the World Health Organization, 9.6 million people worldwide died from cancer in 2018 (an estimated 1 in 6 global deaths) with a total economic impact of $1.16 trillion per year. Deaths due to prostate and breast cancer are often the result of metastasis to bone. Currently, there are no viable markers for metastasis. We report the development of novel \textit{in vitro} models of breast cancer and prostate cancer metastasis through bone tissue engineering approaches. The tissue engineered scaffold uses amino acid modified nanoclay to develop polymeric nanocomposites. This scaffold uses biomimetic mineralization of hydroxyapatite inside nanoclays galleries, mimicking remodeling human, characterized by low Ca/P stoichiometry, a niche to which cancer cells migrate. Seeding the tissue engineered bone scaffolds with prostate and breast cancer cell lines, after bone formation, led to the creation of tumoroids of cancer. Bone metastasis is characterized by unique and complex biochemical, morphological, and genetic changes. The overall nanomechanical response of cancer tumors is representative of the complex changes at progression of metastasis. Here we report static and dynamic evaluation of nanomechanical properties of cancer cells during disease progression at the metastatic site. We report a significant softening of cancer cells as disease progression occurs at metastasis. We also examine the cytoskeletal changes that result in the observed mechanical behavior and its evolution at metastasis. The significant reduction in elastic modulus of cancer cells was attributed to reorganization of cytoskeletal elements. We report here the use of mechanics as a potential new marker for cancer metastasis progression.

**5:15 AM S.SM01.05.02**

\textbf{Development of Molecular Imaging Smart Probes Based Technologies for High-Resolution Images of Prostate Cancer in MRI} Jebasingh Bhagavathsingh\textsuperscript{1}, Divya Rajendran\textsuperscript{1}, Sundar Manoharan\textsuperscript{2}, Jannet Vennila\textsuperscript{1} and Nagabhushan Vellala\textsuperscript{3}; \textsuperscript{1}Karunya Institute of Technology and Sciences, India; \textsuperscript{2}Satyabama Institute of Science and Technology, India; \textsuperscript{3}Microbiological Laboratory Research and Service P Ltd, India

Development of Molecular Imaging Smart Probes Based Technologies for High Resolved Images of Prostate Cancer in MRI

Jebasingh Bhagavathsingh,\textsuperscript{1*} Divya Rajendran,\textsuperscript{1} Sundar Manoharan,\textsuperscript{2} Jannet Vennila,\textsuperscript{1} Nagabhushan Vellala,\textsuperscript{3}

\textsuperscript{1}Department of Chemistry, Karunya Institute of Technology and Sciences, Coimbatore-641114, INDIA

\textsuperscript{2}Department of Nanoscience and Technology, Satyabama Institute of Science and Technology, Chennai, INDIA
Abstract:
Currently much attention has been devoted to the image quality emerging from any of the imaging modalities such as MRI, PET, SPECT, Optical Imaging, etc.. There are two major approaches to achieve the high-resolution images from the existing imaging modalities as such i) by tuning the hardware parameters like magnetic field strength, signal-to-noise ratio, matrix size, field of view, etc., and/or ii) by using smart or responsive probe as an imaging agent for the in-vivo imaging of biochemical or physiological abnormalities as the origin of the diseases. It is well-known that much of in-vivo experiments were unsuccessful after the successful standardization of in-vitro experiments due to the competitive in-vivo targets and/or administration of non-specific imaging agents. Therefore, molecular imaging probe allows earlier with more personalized diagnosis and also facilitates to understand their molecular factors underlying pathological process using the smart behavior of imaging agents. Smart or responsive probe often provides well-resolution images from MRI detectable responses depending on the specific parameter such as pH, the concentration of ions or metabolites, temperature, enzyme sensitive, etc., at the molecular or cellular level. The multimeric paramagnetic chelates have proven with promising results in diagnosis, risk stratification, localization and staging of clinically significant prostate cancer. Herein we report the development of sugar capped biphenolic systems as enzyme sensitive smart probes and its Gd(III) chelates for high-resolution MRI applications. The sugar capped dopamine intermediate is synthesized by the glycosylation of protected dopamine using acetobromogalactose. The as-prepared intermediate is reacted with DOTA-Monoamide moiety for the paramagnetic metal ions chelation. Upon the removal of protecting groups, the high polar compound was purified by flash chromatography followed by the complexation with lanthanides. Upon the cleavage of the sugar moieties by the enzyme β-galactosidase, the relaxivity is significantly enhanced due to the formation of macromolecular adducts with the metal centers during the self-assembly process. The aggregation of Gd(III) based imaging agents provides the high-resolution MR Images at the conventional MRI (1.5 Tesla).

Reference

5:25 AM *S.SM01.05.03
Raman Spectroscopy Investigation of Metastatic Prostate Cancer Jeon Woong Kang1, Ramachandra R. Dasari1, Peter So1, Sumanta Kar2, Kalpana Katti2, Dinesh R. Katti2, Ramasamy Paulmurugan3, Dorian Liepmann4 and Venkatesan Renukopalakrishnan5; 1Massachusetts Institute of Technology, United States; 2North Dakota State University, United States; 3Stanford University, United States; 4University of California, Berkeley, United States; 5Northeastern University, United States

Prostate cancer in its late stage is likely to metastasize to bone. However, a reliable marker for bone metastasis does not exist to date. The purpose of this study is to test the feasibility of using Raman spectroscopy for diagnosis of bone metastasis. MDA PCa 2b cells (metastatic prostate cancer cell from bone) were grown in the previously developed bone mimetic scaffolds. Our results indicate distinct time-dependent differences of metastatic prostate cancer cells grown in the scaffolds. Raman spectroscopic features in lipid, protein and DNA regions of these cells represent valuable diagnostic information which can be potentially translated into a clinic through fiber optic Raman probes. We also used a variety of novel spectral and statistical methods such as PCA to classify the event of bone metastasis. Overall, we demonstrate the feasibility for using Raman spectroscopy along with the powerful data analysis tools for next generation metastasis diagnosis and prediction.

5:40 AM *S.SM01.05.04
Image Guided Delivery of microRNAs by Polyfunctional Gold-Iron Oxide Nanoparticles as a Diagnostic Platform for Monitoring Therapeutic Response of GBM In Vivo Ramasamy Paulmurugan; Stanford University, United States

Image guided delivery of therapeutics offer a novel approach to correlate therapeutic outcome with the level of delivered agents. Especially in neurological disorders, including GBM, the biological barriers of the brain present a major challenge in achieving adequate delivery of therapeutic drugs for treatment. Hence it is important to develop novel delivery agents with theranostic potentials to address these issues. We explore here the potential of the nose-to-brain direct transport pathway to bypass the blood-brain barrier (BBB) to enable targeted delivery of theranostics while implementing imaging as a complementary strategy to monitor the delivery. We adopted polyfunctional gold-iron oxide nanoparticles (polyGIONs)
Emerging Clinical Applications of Cutting Edge MRI

MRI is currently used as a modality to detect, characterize, and monitor disease entities. Despite its inherent high soft tissue resolution and lack of ionizing radiation, the modality can be further enhanced to function as a biomarker for specific disease processes. This invited talk will highlight key advances that can further the use of MRI in the era of precision medicine and allow it to function as a useful biomarker, eventually to a single molecule resolution.

Osteogenesis Pathways and Dysregulation at Bone Site in Breast Cancer Bone Metastasis

Breast cancer, in the late stages, disseminates to the bones, resulting in bone metastasis. Currently, there is no cure available for bone metastasis as the underlying mechanism of the processes that occur at the cellular level is poorly understood due to the failure of animal models and the scarcity of human metastasized samples as most patients with advanced stages of cancer are already in palliative care. Therefore, it is imperative to develop translational disease models to find a cure for cancer by elucidating disease mechanisms at the cellular and molecular level. In recent years, three-dimensional (3D) culture models have attracted substantial attention due to their ability to recapitulate in vivo characteristics, leading to altered gene expression, cytokine secretion, and improved drug response. In the present study, we have developed a 3D in vitro model of breast cancer bone metastasis mimicking later stages of breast cancer pathogenesis to the bones, using osteogenically differentiated human mesenchymal stem cells (MSCs) and human breast cancer cells (MDA-MB-231 & MCF-7) on nanoclay-based scaffolds. These two cell lines represent to highly and less metastatic breast cancer. Here we specifically describe the nature of bone regulation at metastatic site due to these two cell lines. Specifically, we have evaluated the effects of breast cancer cells secreted factors on bone formation in terms of the Wnt/β-catenin signaling pathway. We noticed that stimulation of Wnt/β-catenin signaling in sequential cultures of MSCs with MCF-7 by endothelin-1 (ET-1) led to the increased bone formation while inhibition of Wnt/β-catenin signaling by dickkopf homolog 1 (DKK-1) exhibited reduced bone formation, thus mimicking mixed bone lesions observed in human breast cancer patients. We also evaluated drug-resistance of our 3D culture model using anti-cancer drug paclitaxel and found tumor-microenvironment released cytokine Interleukin-6 (IL-6) may be involved in conferring drug resistance via STAT3 pathway. Taken together, these critical findings not only further our understanding of breast cancer-induced bone metastasis but also have broader implications in patient-specific therapies in particular those that address skeletal complication due to metastasis.

Spectral Changes in Primary and Secondary Bone Metastasis Site Prostate Cancer Tissues Evaluated by Raman Mapping

Prostate cancer in its late stage is likely to metastasize to bone. A reliable marker for bone metastasis does not exist. This study evaluates the use of Raman mapping to evaluate subcellular changes and responses as a marker for bone metastasis. We
have obtained patient tissues from prostate cancer at primary and secondary (bone sites). Raman spectra and Raman maps were obtained for these tissues. A complete and comprehensive study that involved comparison of the spectral maps from the human tissues was compared with data obtained from tumors grown using MDA PCa 2b prostate cell line grown on tissue engineered bone mimetic scaffolds. Our results indicate distinct differences and changes between the prostate cancer samples obtained at primary and secondary sites. Raman spectroscopic features in the lipid, protein, DNA regions of bone metastatic prostate cancer tissues represent very valuable diagnostic information since these experiments can be conducted in a clinical regime with minimal patient discomfort through use of fiber optics. We also used a variety of novel spectral and statistical methods such as PCA to classify the event of bone metastasis. Overall, we demonstrate the potential for use of Raman Mapping combined with powerful data analysis technologies for next generation metastasis diagnosis and prediction.

SESSION S.SM01.06: Poster Session: Organ-on-a-Chip—Toward Personalized Precision Medicine
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
5:00 AM - 8:00 AM
S-SM01

S.SM01.06.01
Boron-Doped Graphene, Wide Band Gap 2D Nano Material as an Emerging Biosensor Platform
David Bryce1, Cesar Leroy2, Abhirup Patra3, Chetan J. Panchal4, Mitesh B. Panchal5, Sivaram Arepalli6, Pulickel Ajayan6, Ramasamy Paulmurugan7, Muhammad A. Naradipa8, Angga D. Fauzi8, Andriivo Rusydi9, Dorian Liepmann9, Piran R. Kidambi10, Narayanan Tharangattu11, Subbiah Alwarappan12 and Venkatesan Renugopalakrishnan13,14; 1University of Ottawa, Canada; 2CNRS, France; 3University of Pennsylvania, United States; 4University of Baroda, India; 5Nirma University, India; 6Rice University, United States; 7Stanford University School of Medicine, United States; 8National University of Singapore, Singapore; 9University of California Berkeley, United States; 10Vanderbilt University, United States; 11Tata Institute of Fundamental Research, India; 12CSIR-Central Electrochemical Research Institute, India; 13Boston Children’s Hospital, Harvard Medical School, Boston, United States; 14Northeastern University, United States

Two-dimensional materials, such as graphene and monolayer hexagonal Boron doped Graphene, are attractive for demonstrating fundamental physics in materials and potential applications in next-generation electronics. Atomic sheets containing hybridized bonds involving elements B and C over wide compositional ranges could result in new materials with properties complementary to those of graphene and Boron doped Graphene, enabling a rich variety of electronic structures with tunable properties and applications. Here we report the synthesis and characterization using spectroscopic techniques of large-area atomic layers of Boron doped Graphene material, consisting of hybridized, randomly distributed domains of B and C phases with compositions ranging from pure BNNTs to pure graphene. Our experimental and theoretical studies (based on Density Functional Theory and Continuum calculations) reveal that their structural features and bandgap are distinct from those of graphene and doped graphene. Boron -11 magic-angle spinning NMR experiments confirm the presence of boron in the sample, and the small quadrupolar broadening coupled with the center-of-gravity shift of -4.4 ppm is suggestive of a four-coordinate boron site. Similarly, the two-dimensional 11B MQMAS NMR spectrum presents a broad signal centered at -4.4 ppm (Figure 1b). Slight spectral broadenings are consistent with a small distribution of local chemical environments, such as differences in the identity of geometry about the boron nearest neighbors in boron-doped graphene. This new form of hybrid Boron doped graphene material enables the development of bandgap-engineered applications in bioelectronics and biosensors and properties that are distinct from those of graphene and h-BN.

S.SM01.06.02
Fabrication and Characterization of Semiconducting Fluorographene on Borosilicate Substrates
Rahul Sharma1, Krishna R. Sahoo1, Teguh C. Asmara2, Stephen Grage3, Ruiqi Zhang4, Jianwei Sun4, Anne S Ulrich4, Andriivo Rusydi2, Subrahmanyam A3, Ramasamy Paulmurugan5, Dorian Liepmann6, Vivekanandan Palaninathan7, Sakthi Kumar6, Venkatesan Renugopalakrishnan9,10 and Narayanan Tharangattu11; 1Tata Institute of Fundamental Research, India; 2Department of Physics, National University of Singapore, Singapore, Singapore; 3Karlsruhe Institute of Technology, Institute of Biological Interfaces (IBG-2), Germany; 4Tulane University, United States; 5Indian Institute of Technology, India; 6Stanford University School of Medicine, United States; 7University of California Berkeley, United States; 8Toyo University, Japan; 9Boston Children’s Hospital, Harvard Medical School, United States; 10Northeastern University, United States

The structural and electronic properties of Fluorographene (FG) ultra-thin films directly grown on flexible and non-flexible
insulating silicate substrates have been characterized. FG has been identified as an in-plane heterostructure consisting of sp² and sp³ hybridized carbon domains. ¹⁹F NMR shows a uniform distribution of fluorine throughout the plane in thin-film FG, unlike in other chemically derived FG variants, indicating the presence of sp³ carbon along with the sp² hybridized domains. It is found that dangling bonds (sp³ carbons without fluorine) cause paramagnetic behavior leading to sidebands in the NMR spectra. The fluorine doping and band-structure of FG are further confirmed by spectroscopic ellipsometry studies, showing a band-gap of 1.2 eV, consistent with ab-initio SCAN-META GGA Functional based Density Functional Theory (DFT) calculations for 7% Fluorination of the Graphene honeycomb structure. This semiconducting FG layer has been identified as an ambipolar material from gate-controlled transport measurements. The transport properties of FG resemble those of reduced graphene oxide, another functionalized graphene derivative, with an Arrhenius type temperature dependence of resistance at high temperatures. This study unravels new avenues in atomic layer-based electronic circuitries and biosensors, where FG can be used as an active layer or dielectric support by tuning its fluorine content to the requisite level.

S.SM01.06.04
Well-Free Cell Agglomeration and Spheroid Forming Using Guided Surface Acoustic Waves through a Couplant Layer
Jiyang Mei¹, Aditya Vasan¹, Uri Magaram², Kenjiro Takemura⁴, Sreekanth Chalasani² and James Friend¹; ¹University of California, San Diego, United States; ²Salk Institute for Biological Studies, United States; ³University of California San Diego, United States; ⁴Keio University, Japan

Cell agglomeration has been useful and crucial for tissue engineering, cell culturing and drug testing, such as for cancer drug development. And a 3D structured spheroid is superior to 2D cell cultures for many aspects: greater stability, longer lifespan, more detailed cell-cell interactions, more accurate cell polarization depiction and so on. However, most of the methods require specific and complex experimental setups and the resulting agglomerates are generally slow or of poor quality. We propose a microfluidic device using surface acoustic waves (SAWs), a contact-free means, in the application of cell engineering. It is composed of a piezoelectric substrate, 127.86° Y-rotated X-propagating lithium niobate, and a focused interdigital transducer to generate focused surface waves with resonant frequency at 100 MHz. A conducting metal guiding layer is deposited on top of the substrate to overcome the beam steering and lateral diffraction problems due to the anisotropy nature of the piezoelectric material, further trapping the wave to a small region of a few wavelengths (~10¹ μm). The SAWs generated travel into a thin layer of liquid and diffract at the Rayleigh angle so that the acoustic radiation is coupled and propagates into the superstrate, which can be a bio-friendly container culturing cells. The localized acoustic streaming induced from the radiation carries and accumulates the cells to the center of the recirculation. By slightly tuning up the power, the stronger recirculation is able to levitate the periphery of the cell cluster and fold the structure to a three-dimensional configuration, and thus a spheroid can be formed. Our data shows the agglomerations can be created in less than 5 min, and the separation between the living human embryonic kidney cell agglomeration islands is as small as Δx =720 μm. With the help of waveguides, the efficiency can be further improved by establishing multiple spheroid formations simultaneously in one well-free container. Therefore, this device is proven to be an effective, reliable and easy-to-handle approach for 3D cell manipulation and spheroid construction, rendering potentials in cell engineering.
Two-dimensional materials, such as graphene and monolayer hexagonal Boron doped Graphene, are attractive for demonstrating fundamental physics in materials and potential applications in next-generation electronics. Atomic sheets containing hybridized bonds involving elements B and C over wide compositional ranges could result in new materials with properties complementary to those of graphene and Boron doped Graphene, enabling a rich variety of electronic structures with tunable properties and applications. Here we report the synthesis and characterization using spectroscopic techniques of large-area atomic layers of Boron doped Graphene material, consisting of hybridized, randomly distributed domains of B and C phases with compositions ranging from pure BNNTs to pure graphene. Our experimental and theoretical studies (based on Density Functional Theory and Continuum calculations) reveal that their structural features and bandgap are distinct from those of graphene and doped graphene. Boron -11 magic-angle spinning NMR experiments confirm the presence of boron in the sample, and the small quadrupolar broadening coupled with the center-of-gravity shift of -4.4 ppm is suggestive of a four-coordinate boron site. Similarly, the two-dimensional 11B MQMAS NMR spectrum presents a broad signal centered at -4.4 ppm (Figure 1b). Slight spectral broadenings are consistent with a small distribution of local chemical environments, such as differences in the identity of geometry about the boron nearest neighbors in boron-doped graphene. This new form of hybrid Boron doped graphene material enables the development of bandgap-engineered applications in bioelectronics and biosensors and properties that are distinct from those of graphene and h-BN.

S.SM01.06.02
Fabrication and Characterization of Semiconducting Fluorographene on Borosilicate Substrates
Rahul Sharma1, Krishna R. Sahoo1, Teguh C. Asmara1, Stephen Grage1, Ruqi Zhang4, Jianwei Sun4, Anne S Ulrich1, Andivo Rusydi2, Subrahmanyam A2, Ramasamy Paulmurugan6, Dorian Liepmann3, Vivekanandan Palaninathan6, Sakthi Kumar3, Venkatesan Renugopalakrishnan9,10 and Narayanan Tharangattu1; 1Tata Institute of Fundamental Research, India; 2Department of Physics, National University of Singapore, Singapore, Singapore; 3Karlsruhe Institute of Technology, Institute of Biological Interfaces (IBG-2), Germany; 4Tulane University, United States; 5Indian Institute of Technology, India; 6Stanford University School of Medicine, United States; 7University of California Berkeley, United States; 8Toyo University, Japan; 9Boston Children’s Hospital, Harvard Medical School, United States; 10Northeastern University, United States

The structural and electronic properties of Fluorographene (FG) ultra-thin films directly grown on flexible and non-flexible insulating silicate substrates have been characterized. FG has been identified as an in-plane heterostructure consisting of sp2 and sp3 hybridized carbon domains. 19F NMR shows a uniform distribution of fluorine throughout the plane in thin-film FG, unlike in other chemically derived FG variants, indicating the presence of sp3 carbon along with the sp2 hybridized domains. It is found that dangling bonds (sp3 carbons without fluorine) cause paramagnetic behavior leading to sidebands in the NMR Spectra. The fluorine doping and band-structure of FG are further confirmed by spectroscopic ellipsometry studies, showing a band-gap of 1.2 eV, consistent with ab-initio SCAN-META GGA Functional based Density Functional Theory (DFT) calculations for 7% Fluorination of the Graphene honeycomb structure. This semiconducting FG layer has been identified as an ambipolar material from gate-controlled transport measurements. The transport properties of FG resemble those of reduced graphene oxide, another functionalized graphene derivative, with an Arrhenius type temperature dependence of resistance at high temperatures. This study unravels new avenues in atomic layer-based electronic circuitries and biosensors, where FG can be used as an active layer or dielectric support by tuning its fluorine content to the requisite level.

S.SM01.06.04
Well-Free Cell Agglomeration and Spheroid Forming Using Guided Surface Acoustic Waves through a Couplant Layer
Jiyang Mei1, Aditya Vasan1, Uri Magaram2,3, Kenjiro Takemura4, Sreekanth Chalasani2 and James Friend1; 1University of California, San Diego, United States; 2Salk Institute for Biological Studies, United States; 3University of California San Diego, United States; 4Keio University, Japan

Cell agglomeration has been useful and crucial for tissue engineering, cell culturing and drug testing, such as for cancer drug development. And a 3D structured spheroid is superior to 2D cell cultures for many aspects: greater stability, longer life-span, more detailed cell-cell interactions, more accurate cell polarization depiction and so on. However, most of the methods require specific and complex experimental setups and the resulting agglomerates are generally slow or of poor quality. We propose a microfluidic device using surface acoustic waves (SAWs), a contact-free means, in the application of cell engineering. It is composed of a piezoelectric substrate, 127.86° Y-rotated X-propagating lithium niobate, and a focused interdigital transducer to generate focused surface waves with resonant frequency at 100 MHz. A conducting metal guiding layer is deposited on top of the substrate to overcome the beam steering and lateral diffraction problems due to the anisotropy nature of the piezoelectric material, further trapping the wave to a small region of a few wavelengths (~104 μm). The SAWs generated travel into a thin layer of liquid and diffract at the Rayleigh angle so that the acoustic radiation is coupled and propagates into the superstrate, which can be a bio-friendly container culturing cells. The localized acoustic streaming induced from the radiation carries and accumulates the cells to the center of the recirculation. By slightly tuning up the
power, the stronger recirculation is able to levitate the periphery of the cell cluster and fold the structure to a three-dimensional configuration, and thus a spheroid can be formed. Our data shows the agglomerations can be created in less than 5 min, and the separation between the living human embryonic kidney cell agglomeration islands is as small as $\Delta x = 720 \mu m$. With the help of waveguides, the efficiency can be further improved by establishing multiple spheroid formations simultaneously in one well-free container. Therefore, this device is proven to be an effective, reliable and easy-to-handle approach for 3D cell manipulation and spheroid construction, rendering potentials in cell engineering.

**SYMPOSIUM S.SM03**

Flexible, Stretchable Biointegrated Materials, Devices and Related Mechanics
November 21 - November 28, 2020

**Symposium Organizers**
Coskun Kocabas, The University of Manchester
Keon Jae Lee, Korea Advanced Institute of Science and Technology
Tae-Woo Lee, Seoul National University
John Rogers, Northwestern University

**Symposium Support**
*Bronze*
MilliporeSigma

* Invited Paper

Session Tutorial S.SM03: Introduction to Flexible, Stretchable Biointegrated Electric Devices and Related Mechanics
Session Chair: John Rogers
Saturday Morning, November 28, 2020
S.SM03

**8:00 AM * An Overview of Materials and Design Principles for Skin-Integrated, Stretchable Electronic and Microfluidic Devices in Medicine and Sports** John A. Rogers; Northwestern University, United States

Biological systems are mechanically soft, with complex, time-dependent 3D curvilinear shapes; modern electronic and microfluidic technologies are rigid, with simple, static 2D layouts. Eliminating this profound mismatch in physical properties will create vast opportunities in man-made systems that can intimately integrate with the human body, for diagnostic, therapeutic or surgical function with important, unique capabilities in fitness/wellness, sports performance and clinical healthcare. Over the last decade, a convergence of new concepts in materials science, mechanical engineering, electrical engineering and advanced manufacturing has led to the emergence of diverse, novel classes of 'biocompatible' electronic and microfluidic systems with skin-like physical properties. This talk describes the key ideas and presents some of the most recent device examples, including wireless, battery-free electronic 'tattoos' with applications in continuous monitoring of vital signs in neonatal and pediatric intensive care; and microfluidic/electronic platforms that can capture, manipulate and perform biomarker analysis on microliter volumes of sweat, with applications in sports and fitness.

**9:30 AM BREAK**

**9:45 AM * Flexible, Stretchable Bio-Inspired Artificial Nervous Systems** Tae-Woo Lee; Seoul National University, Korea (the Republic of)
Living organisms have evolved to efficiently developing their functions and structures. For adopting their superior characteristics in many latest technologies, bio-inspired electronics have been extensively developed. Particularly, artificial nervous systems are one of bio-inspired electronics to replicate the functions and operating principles of biological nervous systems. Here, bio-inspired artificial nervous systems were demonstrated by using flexible and stretchable organic electronics. For the artificial mechanoreceptor nervous systems, pressure sensors (artificial mechanoreceptors), organic ring oscillators (artificial nerve fibers), and synaptic transistors (artificial synapses) were integrated like biological counterparts. The applicability for neural prostheses of this artificial sensory nerve was verified by connecting the artificial sensory nerve to the biological motor nerves in a detached inset leg and successfully actuating the biological motor nerves depending on external pressure information. Besides, an organic nanowire-based artificial sensorimotor nervous system was developed by employing a self-powered photodetector (an artificial light-sensory organ), a stretchable artificial synapse, and a polymer actuator (an artificial muscle). The voltage pulses of a self-powered photodetector triggered by optical signals drove the stretchable synaptic transistor, and synaptic outputs were used for actuation of an artificial muscle fiber in the same way that a biological muscle fiber contracts. Lastly, an organic artificial synapse was integrated with a triboelectric sensor for demonstrating an artificial auditory system. The morphology of organic semiconductors of the artificial synapses was modulated to emulate the facilitation recover time of biological synapses. Our bio-inspired artificial nervous systems based on flexible and stretchable organic electronics would be a platform for developing bio-inspired soft electronics, neuro-inspired robots, and electronic prostheses.

11:15 AM BREAK

11:30 AM *
Self-Powered Flexible Electronics Beyond Thermal Limits Keon Jae Lee; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

This seminar introduces three recent progresses of self-powered flexible electronic systems beyond thermal limits. The first part will introduce self-powered systems for IoT sensors and flexible energy source. Flexible nanogenerator converts external bio-mechanical movement into electrical energy for self-powered IoT and biomedical devices such as pacemaker and transportation. In addition, flexible piezoelectric materials detect the minute vibration of membrane or human skin that expands the application of self-powered acoustic sensor and healthcare monitor. The second part will introduce laser material interaction for flexible applications. Laser technology of ultra-short pulse duration becomes important for future flexible electronics since high temperature process can be adopted on plastic substrates, which is essential for high performance electronics. Exciting results of flexible laser material interaction will be explored from both material and device perspectives including nanomaterial synthesis, inorganic laser liftoff and plasmonic material reaction. The third part will discuss flexible large scale integration (f-LSI) for flexible CPU and high density memory. Flexible LSI is an essential part of future electronics for data processing, storage, and radio frequency (RF) communication. To fabricate f-LSI, we integrated 0.18 CMOS process of single crystal silicon nano-transistors with flexible electronics. Simultaneous roll transfer and interconnection of flexible NAND Flash memory was achieved using anisotropic conductive film (ACF). Finally, we introduce the highly efficient and long-term stable flexible vertical micro LED (f-VLED) for full color displays, wearable and biomedical applications. Using optogenetic mouse models, f-VLED stimulated motor neurons deep below layer III from the brain surface and induced mouse behavior changes. These f-VLED can be also used as tools of skin research and phototherapy.
Chronic In Vivo Recording and Modulation of Intact Mouse Spinal Cords with Implanted Tissue-Like Electronics

Tao Zhou1, Robert Viveros1, Xiao Yang1, Jung Min Lee1,2, Guosong Hong1,3, Tian-Ming Fu1,4, Hong-Gyu Park1,2 and Charles M. Lieber1,1,1; 1Harvard University, United States; 2Korea University, Korea (the Republic of); 3Stanford University, United States; 4Janelia Research Campus, United States

Devices interfaced with the spinal cord are critically important for investigations and treatment of spinal cord injury (SCI) as well as diseases such as spinal muscular atrophy and amyotrophic lateral sclerosis. Traditional intraspinal probes, which are capable of recording and stimulating spinal cord neurons have been used to study and develop protheses for the spinal cord. However, these rigid intraspinal devices generally cause immune responses that lead to glial scar formation and neuronal cell depletion at the tissue/probe interface, thus making chronic applications difficult. Here we report a minimally-invasive and chronically-stable intraspinal cord interface based on tissue-like mesh electronics. Mesh probes containing recording and stimulation electrodes are injected into the mouse spinal cord spanning both the dorsal and ventral regions without removal of vertebrae. Implanted probes do not adversely affect motor behavior and show a similar recovery times as mice undergoing sham surgery but without implants. Significantly, histology analyses show that mesh probes form a seamless interface with surrounding spinal cord tissue and do not elicit glial scar formation or neuronal cell depletion near the probe surface. The seamless mesh implants yield stable in vivo chronic electrophysiology recordings of spinal cord neurons for at least 6 weeks, and have been used to measure neural spike correlations between the motor cortex and spinal cord using optogenetic methods for well-defined stimulation in the motor cortex. Notably, implanted mesh probes have been used to evoke stable movement of mouse limbs via electrical stimulation of spinal cord motor neurons. This ultra-flexible, tissue-like spinal cord interface provides advantages complementary to other spinal cord implants that can enable opportunities for in vivo studies and therapies relevant to SCI and spinal cord diseases.

Enhanced Acoustic Sensitivity of Piezoelectric Sensors with Ultrathin Porous Substrates

Md Osman Goni Nayeem1, Sunghoon Lee1, Tomoyuki Yokota1 and Takao Someya1,2; 1The University of Tokyo, Japan; 2Center for Emergent Matter Science (CEMS), RIKEN, Japan

Wearable acoustic sensors have become an important and efficient platform for human-machine interactions (HMI) and body acoustics monitoring. To enable next generation applications, such sensors should be flexible, ultrathin, self-powered and highly sensitive. In contrast to conventional microphone technologies, piezoelectric acoustic sensors have greater flexibility and sensitivity1,2. In the past, the effect of Young’s modulus and thickness of substrates on piezoelectric performance has been investigated3. However, the sensitivity of such flexible piezoelectric sensors is still limited to meet the next generation voice-activated human machine interactions or wearable body acoustics monitoring.

Here, we have developed an ultrathin piezoelectric acoustic sensor with 1.5 µm thick parylene substrates having multiple millimeter sized square holes. The holes on the substrates were created by using green laser. The sensor fabrication was done by sandwiching polyvinylidene fluoride (PVDF) nanofiber between two Au-coated substrates. The overall device is ~8 µm thick and can generate a peak voltage of ~11.2 V when a sound wave of 110 dB at 250 Hz is applied. The sensitivity of our sensor is ~1770 mV/Pa which is ~9 times higher compared to the sensors having similar thickness of substrates without holes. To show the practical applicability as voice sensors, human voice uttering the words were measured and compared with the sensor having planar 1.5 µm thick parylene substrates.


Bioderived and Degradable Gels with Extreme Mechanics for Soft Devices

Martin Kaltenbrunner; Johannes Kepler University, Austria

Nature inspires a wide range of bio-mimetic systems ranging from soft robotic actuators to perceptive electronic skins that enhance and support our life. The growing demand on assistive, medical and bioelectronic technologies however raises concerns on the ecological footprint of this emerging platforms, as they are often designed for a defined, limited operational lifetime. Introducing a key feature essential to nature - biodegradability - will enable soft electronic and robotic devices that reduce (electronic) waste and are paramount for a sustainable future.
We here introduce materials and methods such as tough yet biodegradable biogels for soft systems that facilitate a broad range of applications, from transient wearable electronics to metabolizable soft robots. These embodiments are highly stretchable, are able to heal and are resistant to dehydration. Our forms of soft electronics and robots are built from resilient biogels with tunable, extreme mechanical properties that uniquely combine performance and durability with degradability. They are engineered for long-term operation in ambient conditions without fatigue, but fully degrade after use through biological triggers. Electronic skins that measure pressure, strain, temperature and humidity serve as human-friendly on-skin interfaces or equip robotic systems with sensory feedback. Such advances in the synthesis of biodegradable, mechanically tough and stable gels that do not compromise in performance when compared to their non-degradable counterparts may bring biological triggers. Electronic skins that measure pressure, strain, temperature and humidity serve as human-friendly on-skin biogels with tunable, extreme mechanical properties that uniquely combine performance and durability with degradability.

5:50 AM S.SM03.01.06
Investigating the Role of Extracellular Vesicles in Cancer Metastasis Using Bioelectronic Technologies Walther Traberg-Christensen¹, Anna-Maria Pappa¹, Malak R. Kawan², Sahika Inal², Susan Daniel³ and Roisin Owens¹; ¹University of Cambridge, United Kingdom; ²King Abdullah University of Science and Technology (KAUST), Saudi Arabia; ³Cornell University, United States

Extracellular vesicles (EVs) (30-1000nm) have garnered much attention lately due to their role in cancer metastasis. EVs act as mediators in cell-cell communication and have the ability to transfer genetic information between donor and recipient cells. Tumor cell-derived EVs (TDEs) have recently been reported to play an active role in tumorigenesis and metastasis owing to their ability to transmit oncogenes. One hypothesis is that TDEs contribute to metastasis by inducing the epithelial-to-mesenchymal transition (EMT), characterized by the loss of barrier function in barrier tissue-forming cells.

This study aims to elucidate the mechanisms of TDE egress and uptake by investigating the process by which TDEs “infect” normal cells inducing EMT prior to metastasis. Current strategies for investigating the spatial and temporal aspects of EV uptake, often optical, lack the ability to obtain quantitative data in real time. We have shown that organic electronic devices (OEDs) based on the conducting polymer poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) can be interfaced with biological systems of varying complexity allowing for quantitative real-time monitoring of biological interactions. The optical transparency of our PEDOT:PSS-based OEDs provides the unique advantage of dual transduction increasing the credibility of our platform and enriching the biological information obtained. Moreover, their compatibility with microfabrication methods allows for high throughput studies.

We have shown that transistor-based OEDs are highly sensitive to the integrity and interactions with barrier tissue-forming cells. As proof-of-principle, we show the chemically-induced disruption of these tissue barriers, and their subsequent recovery, in Madin-Darby Canine Kidney (MDCK) epithelial cells grown on our OEDs. In ongoing studies, monolayers of MCF-10A human mammary epithelial cells will be exposed to TDEs extracted from the human breast cancer cell line MDA-MB-231 to electrically monitor the phenotypic changes elicited by TDEs. This data will be further substantiated by monitoring the expression of immunofluorescently labelled barrier-forming tight junction proteins at set intervals. These combinatorial optical and electrical measurements of TDE interactions with cell monolayers provide invaluable information for developing strategies for inhibiting TDE interactions by e.g. blocking specific surface markers, thereby preventing TDE-induced EMT.

6:00 AM S.SM03.01.07
Facilitating Hair Growth via Flexible Vertical RED μLEDs Jae Hee Lee; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

A lot of people around the world have suffered from alopecia, which can lead to aesthetic issues, low self-esteem, and social anxiety. Therapeutic technology including thermal, electrical, pharmacological, and photo stimulation have been suggested to treat hair loss. Among them, laser stimulation to hair is a strong treatment, activating the proliferation of hair follicles without side effects. Particularly, periodically irradiating red light with a wavelength of 650nm in the hairless area can help efficient stimulation of hair follicles under the skin, because this light can penetrate deeper into the skin tissue than blue and green light with short wavelengths. However, this laser stimulation treatment has difficulty in high power consumption, large size, and spatiotemporal restriction. Recently, flexible micro-light-emitting diodes (μLEDs) have been a great attention for future biomedical devices, such as biosensors, pulse oximetry (SpO2) sensors, and optogenetic stimulators due to its high performance and outstanding stability. However, flexible μLEDs still have significant drawbacks in application to wearable phototherapeutic devices, such as high heat, low optical efficiency, and high energy consumption. Herein, we report high-performance 30 × 30 AlGaInP fVLEDs fabricated with transfer-free monolithic method for a wearable phototherapeutic...
device. Ultrathin flexible μLEDs were fabricated by vertically interconnecting top and bottom electrodes. The red f-VLED arrays were conformally attached on a human wrist with high irradiance of ∼30 mW mm−2 and low forward voltage of ∼2.8 V. The red light with 650 nm wavelength deeply penetrate the skin and stimulate the hair follicles, which is located 2 mm under the skin. The thermal stability of the monolithic f-VLED was theoretically investigated by using finite element method (FEM) simulation and experimentally optimized by operating f-VLEDs on the skin. Mechanical stability of monolithic f-VLEDs was confirmed by harsh periodic bending/unbending motions, which is necessary for skin-attachable phototherapeutic devices. Finally, photostimulation in hairless region was performed to promote hair growth in a living depilated mouse via f-VLED array with thermal stability. Hair regrowth in the mice via f-VLED was verified by analyzing immuno-fluorescent and histological effects.

6:10 AM S.SM03.01.09
Near-Infrared Light Emitting Contact Lens for the Treatment of Diabetic Retinopathy Geon-Hui Lee and Sei Kwang Hahn; Pohang University of Science and Technology, Korea (the Republic of)

Recently, photobiomodulation using near-infrared (NIR) light has been widely investigated for non-invasive healthcare applications including skin and hair therapy, and ocular therapy for diabetic retinopathy, methanol toxicity, and light damaged retina [1-3]. NIR light activates the photoreceptor of mitochondria and increases the therapeutic effect by accelerating the production of growth factors and the cell proliferation. Here, we successfully developed a NIR light emitting contact lens for the treatment of diabetic retinopathy possibly with greatly improved patient compliance. A NIR light emitting diode (LED) connected with an application specific integrated-circuit (ASIC) chip and a wireless power and communication system was fabricated on a PET film, which was embedded by photo-crosslinking in a silicone hydrogel contact lens. The LED contact lens could be on-off controlled wirelessly even in the presence of water without any significant deformation. The retinal vascular hyper-permeability induced by diabetic retinopathy in rabbits was reduced to the statistically significant level by simply wearing the NIR light emitting contact lens. Histological analysis also confirmed the safety and feasibility of LED contact lenses for treating diabetic retinopathy. This platform technology for LED contact lens might be harnessed for various applications to photomedicines, and augmented and virtual reality display applications.


6:20 AM *S.SM03.01.10
Point-of-Use Flexible Sensors for Assessment of Motor Disorders and Wound Healing Pathways Moran Amit, Udit Parekh, Kaiping Wang, Brian Eliceiri, Harinath Garudadri and Tse Nga Ng; University of California, San Diego, United States

Rapid, on-site assessment is highly desirable in the medical diagnosis and treatment. To achieve this goal, our research aims to develop low-cost, flexible, large-area sensor devices for different health applications. In this presentation, we discuss case studies using flexible sensors for two different applications:

1) Motor skills characterization. There is no objective metric for evaluating motor skill training progress, and current assessments rely on qualitative surveys. We have fabricated an instrumented glove with pressure and motion sensors for motor characterization. This glove is useful for characterizing motor skills of people suffering from spasticity, a neuromuscular disorder that causes muscle stiffness/resistance and jerky movement. Analyses of force versus velocity show movement-dependent muscle resistance in a patient with spasticity. Through the flexible sensor systems, the shift from subjective scores to objective measurement will promote better diagnosis and dramatically improve the accuracy in tracking patient response to therapy.

2) Wound healing characterization. Wound healing is a complex process involving diverse changes in multiple cell types where the application of electric fields has been shown to accelerate wound closure. We show on an in vivo electrical stimulation model in which flexible electrodes were applied to an animal model for monitoring inflammation in a wound. The wound site was subjected to electric fields using flexible electrode arrays, and immune cells were then harvested for flow cytometry analysis to study molecular mechanisms, to identify a signaling pathway that is activated during the healing process.

6:35 AM S.SM03.01.12
Flexible, Bi-modal Sensor Array for Pressure and Temperature Sensing by Combinational Design of Thermochromic
**Composite Elastomer and Transparent Ionic Hydrogel** Thanh-Giang La1,2, Hemant Charaya3, Hyun-Joong Chung1 and Lawrence H. Le1,1; 1University of Alberta, Canada; 2VinUniversity, Viet Nam; 3Log 9 Materials, India

Flexible sensor arrays have been developed for a broad spectrum of electronic skin (e-skin) applications such as human-machine interfaces, functional prostheses, and health monitoring devices. In many applications, high sensitivity of pressure and temperature are necessary for e-skins. Such multi-functionality, especially bio-modal sensing, of e-skins often requires complex fabrication and integration processes. We present a simple and effective design strategy of a bimodal e-skin sensor array that is capable of visual indication of temperature sensing by changing color in a range of 26 – 40 °C, as well as an ability to sense finger tap as a pressure sensor. We fabricated a 4 × 4 flexible array of soft, small-diameter capacitive bimodal sensors. The sensors consisted of a dielectric layer of elastomer composite containing thermochromic liquid crystal (TLC), which were sandwiched by transparent electrodes made of ion conductive, compliant, and adhesive polyampholyte (PAm) hydrogels. They were able to sense gentle touching of ~20 kPa and to perform reliably over a thousand repeated cycles of pressing up to 300 kPa. As functioning bimodally, these sensors also changed color in response to temperature, where the quantification of the temperature was achieved from calibration of hue-temperature curves of the elastomer composite at the precision of 0.1 °C. The e-skin array has demonstrated a promising potential for applications in medical devices and biorobots due to its biocompatibility and stretchability.

6:45 AM *S.SM03.01.13
**A Bioelectronic In Vitro Model of the Microbiome-Gut-Brain Axis** Roisin Owens; University of Cambridge, United Kingdom

In vitro models of biological systems are essential for our understanding of biological systems. In many cases where animal models have failed to translate to useful data for human diseases, physiologically relevant in vitro models can bridge the gap. This is particularly true for modelling the effect of microbiome interactions on the gut-brain axis. An in vitro model of the gut-brain axis provides the opportunity to deepen our understanding at a molecular level, of the intriguing findings emerging from studies on germ-free mice and clinical studies on humans, about the interplay between the microbiome, the gut and the brain. However, many difficulties exist in interfacing complex, 3D models with sensing technology adapted for monitoring function of cells within these models. The introduction of polymeric electroactive materials into the heart of the tissues being modeled, simultaneously provides the opportunity to host the tissues in question, and monitor their growth and differentiation. In this presentation I will discuss our recent progress in developing 3D sponge-like electrodes that host a multi-cellular models with continuous monitoring and show how we are getting towards our goal of a complete platform to model microbiome-gut-brain interactions.

7:00 AM S.SM03.01.15
**Soft Wireless Device Sensing Mechanoacoustic Signals of Multiple Physiological Processes and Body Motions at the Suprasternal Notch** KunHyuck Lee, Xiaoyue Ni, Jongyoon Lee and John A. Rogers; Northwestern University, United States

The human body consists of complex and dynamic systems that network throughout the body. The neck is an essential crossroads of several critical systems under soft tissue in a spatially confined area. These unique characteristics of the neck allow access to a rich set of mechanical and acoustic signals of key dynamic systems – all observable at a single location. In our recent work, we demonstrate the application of a novel wireless flexible sensor that can capture these mechano-acoustic signals effectively. The sensor design combines low modulus, elastic mechanics with mechanically isolated islands of conventional rigid electronic components along with added reinforcements. Together, the sensor can conform to intricate and irregular mounting surfaces and maintain contact during the natural motion of the neck without causing skin irritation and mechanical failure of the internal electronics.

SESSION S.SM03.02: Transferring Processes of Inorganic/Hybrid Semiconductor Materials
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-SM03

5:00 AM S.SM03.02.01
**Three-Dimensional Curvy Electronics Created Using Conformal Additive Stamp (CAS) Printing** Cunjiang Yu;
Electronic devices are typically manufactured in planar layouts but many emerging applications, from optoelectronics to wearables, require three-dimensional curvy structures. The fabrication of such structures has though proved challenging due, in particular, to the lack of an effective manufacturing technology. This presentation will show our development of conformal additive stamp (CAS) printing technology and its employment to reliably manufacture 3D curvy electronics. CAS printing employs a pneumatically inflated elastomeric balloon as a conformal stamping medium to pick up pre-fabricated electronic devices and print them onto curvy surfaces. To illustrate the capabilities of the approach, we will demonstrate various devices with curvy shapes: silicon pellets, photodetector arrays, electrically small antennas, hemispherical solar cells, and smart contact lenses. We also show that CAS printing can be used to print onto arbitrary 3D surfaces.

5:10 AM S.SM03.02.02
Ultra-Fast R2R Manufacturing Process for Highly-Sensitive Flexible Devices Ying Zhong1, Long Wang2, Rui Kou2 and Zijian Weng1; 1University of South Florida, United States; 2University of California, San Diego, United States

Flexible skin-like sensors are the essential component for future human health monitoring and therapeutic treatment. However, the price of flexible devices is still too high for wide applications. The development of ultra-fast and low-cost roll-to-roll (R2R) printing technology of flexible devices is critical for the actual application of flexible devices. In current printing technologies, organic additives are often mixed into the functional components to offer the flexibility of the printed flexible sensors. However, the time-consuming drying process of those additives is the major hinder for the low cost and fast R2R printing of flexible sensors. We present a new ultra-fast R2R printing technology by taking advantage of the "induction induced absorption" behavior of dry powders in strong electric field. Dry graphene, CNT, silver nanowire, and many kinds of functional powders can be printed. The printing speed can reach as high as 50 cm2/s. The specially printed and naturally formed 3D structure offered high flexibility and sensitivity, allowing our skin-like sensors able to obtain extremely high sensitivity. Different kinds of materials can be integrated into one device. Different kinds of substrates with various surface condition can also be printed, including flat surface and complex 3D structures (e.g. textiles). The printing parameters were studied and optimized, the printing mechanism was simulated, and the printed devices were tested. Those devices are capable of detecting stain, stress, temperature, and even the frequency of sound. This technology opens a new door for fast and low-cost high-performance flexible sensor processing.

5:20 AM S.SM03.02.03
Monolithic Flexible Vertical-Structured GaN Based MicroLEDs for Biomedical Stimulator Sang Hyun Park1, Han Eol Lee2, Jung Ho Shin1, Jung Hwan Park1, Jae Hee Lee1 and Keon Jae Lee1; 1Korea Advanced Institute of Science and Technology, Korea (the Republic of); 2Massachusetts Institute of Technology, United States

With the upcoming of internet of things (IoT) era, visual IOT platforms for hyperconnected visual communication attract a lot of attention and flexible inorganic based micro light emitting diode (micro LED) is one of the most promising candidates for visual communication applications. Inorganic micro LEDs have been considered as a strong candidates to replace the conventional light sources such as organic light emitting diodes (OLEDs), liquid crystal displays (LCDs) for display applications, because of their great electrical/optical properties, long lifetime, fast response time and high stability in severe environments. Despite of several previous researches about the micro LEDs, flexible vertical structured GaN micro LEDs (f-VLEDs) on plastic substrates have not yet been demonstrated due to the difficulty of vertical electrical interconnection with high power efficiency and thermal stability.

Herein, we demonstrated a high-performance flexible 30 x 30 GaN f-VLEDs array through a simple monolithic process. Inorganic-based laser lift-off (ILLO) process separated GaN LED chips from the sapphire substrates which is the mother substrate of GaN epilayer. The separated micro LED chips were electrically isolated by biocompatible polymer layers and electrically interconnected vertically via silver nanowires (AgNWs). These Flexible and transparent GaN VLEDs devices were conformally attached to a human fingernail emitting bright blue light with high optical power of 30 mW/mm2. The lifetime of f-VLEDs was investigated experimentally via high accelerated stress test (HAST) and measured theoretically via finite element method (FEM) simulation. In addition, periodic bending test was employed to verify excellent mechanical stability of f-VLEDs. The wireless power supply system successfully transmitted electrical power to the f-VLEDs on human skin. Finally, the monolithic GaN f-VLEDs successfully inserted into a living mouse brain and emitted bright blue light without severe histological damage in mouse brain.
Materials Approaches Towards Biointegrated Polymer Electronics

Jonathan Rivnay\textsuperscript{1,2}, Northwestern University, United States; Simpson Querrey Institute, United States

Direct measurement and stimulation of ionic, biomolecular, cellular, and tissue-scale activity is a staple of bioelectronic diagnosis and/or therapy. Such bi-directional interfacing can be enhanced by a unique set of properties imparted by organic electronic materials. These materials, based on conjugated polymers, can be adapted for use in biological settings and show significant molecular-level interaction with their local environment, readily swell, and provide soft, seamless mechanical matching with tissue. At the same time, their swelling and mixed conduction allow for enhanced ionic-electronic coupling for transduction of biosignals. Such properties stress the importance of bulk transport processes and serve to enable new capabilities in bioelectronics, including new device concepts and form factors. I will demonstrate how such materials properties relax design constraints, allowing for flexible amplification systems for electrophysiological recordings. I will also discuss the unique form factors as applied to electroactive scaffolds and bioactive composites to module tissue state and/or cell fate. New materials design will continue to fill critical need gaps for challenging problems in bio-electronic interfacing.

An Ambient-Stable and Stretchable Ionic Skin with Multimodal Sensation

Binbin Ying\textsuperscript{1,2}, Jianyu Li\textsuperscript{2} and Xinyu Liu\textsuperscript{1}; University of Toronto, Canada; McGill University, Canada

Skin is the largest organ of the human body, serving as physical and hygroscopic barriers to protect the inner body and control transdermal water exchange and also containing signal sensors to perceive various environmental stimuli such as pressure, deformation, and temperature. These functions are linked with salient features of the skin: highly deformable polymer networks to resist physical damages; hygroscopic compositions to retain water; a variety of sensory neurons powered by biological sources to transduce stimuli into controlled ion movements and propagation of action potentials. To recapitulate these features for wearable electronics and healthcare applications, significant efforts have been made on engineering electronic counterparts of the human skin (i.e., electronic skin), leading to various design strategies involving electronic components, elastomeric substances or a combination of thereof. Despite their remarkable functionalities and applications that have been demonstrated, existing electronic skins differ from the native skin in terms of charge carriers (electrons versus ions in native skin), the content and permeability of water, resulting in limited biocompatibility and suboptimal human-machine interfaces especially for the long-term usage.

While the gap between real and electronic skins persists, recent progress of iontronics highlights the use of hydrated and ionic materials like hydrogels for making ionic devices (i.e., pressure sensors and touchpad) capable of transducing mechanical stimuli into electrical signals such as of capacitance or resistance. The existing ionic devices usually convert the applied touch, pressure, deformation or temperature into a change in their resistance or capacitance, the electrical readout of which requires continuous power supply. Although stretchable batteries can be integrated with those ionic devices, the requirement of external or on-chip power supplies still, to some extent, compromises long-term usage. Further development is needed toward a multifunctional self-powered ionic device. First, the devices should equip with self-generated power to mitigate the need of external power supply for long-term usage. Second, they need to enable the sensing of more than one stimulus like the human skin. In addition, the devices must be physically stable (i.e., mitigating water loss) during usage and biocompatible when interfacing with the human body.

Herein, a novel artificial ionic skin (Alskin) has been demonstrated to recapitulate the salient features of the human skin. Alskin exhibits excellent skin-like mechanical deformability and ambient stability. It can sustain more than 400% strains without rupture and maintain its function after storage and 800 cycles of deformation. Different from the previous ionic devices consisting of homogenous hydrogels and/or elastomer, our design utilizes a heterogenous hydrogel of bilayer structure, which can realize controlled ion movements responsive to the mechanical deformation and humidity. This design resembles the conventional electronic diodes structurally and the sensory neurons in human skin in terms of stimuli sensing function. The Alskin converts both mechanical stimuli and humidity into four types of electrical signals: resistance, capacitance, open circuit voltage (OCV) and short circuit current (SCC), among which the latter two signals are self-generated without external power supply. Its multimodal sensation maintains in a wide range of relative humidity (13%–85%). It has been demonstrated for wearable strain-humidity sensing, human-machine interaction and walking energy.
These features of our AIskin can potentially blur the boundary between humans and devices, and promise broad applications ranging from wearable and implantable devices, soft robotics to wound dressing capable of monitoring the local body motion and moisture of the wound bed.

5:25 AM *S.SM03.03.04
A Tailored, Conformable Suit for Large-Scale Spatiotemporal Physiological Sensing In Vivo Canan Dagdeviren;
Massachusetts Institute of Technology, United States

The rapid advancement of electronic devices and fabrication technologies has further promoted the field of wearables and smart textiles. However, most of the current efforts in textile electronics focus on a single modality and cover a small area. In this work, we introduce a new platform of modular, conformable (i.e., flexible and stretchable) distributed sensor networks that can be embedded into digitally-knit textiles. This platform can be customized for various forms, sizes and functions using standard, accessible and low-cost manufacturing techniques. Here, we have developed a tailored, electronic textile conformable suit (E-TeCS) to perform large-scale, multi-modal physiological (temperature, heart rate, and respiration) sensing in vivo. The modular approach results in a conformable suit integrated with a large assortment of conformable electronic components for large-scale physiological sensing. The E-TeCS can detect skin temperature with an accuracy of 0.1 °C and a precision of 0.01 °C, as well as heart-rate and respiration with a precision of 0.0012 m/s² through mechano-acoustic inertial sensing. The knit textile electronics can be stretched up to 30 % under 1000 cycles of stretching without significant degradation in mechanical and electrical performance.

5:40 AM *S.SM03.03.05
Transfer Printing of Flexible, Stretchable Materials for Sticker-Like Electronics in Bio-Integrated Applications Chi Hwan Lee; Purdue Univ, United States

Advanced materials engineering and processing technologies provide means to realize a range of thin, flexible and stretchable biosensors for human body-integrated healthcare systems, opening up a new prospect in wearable technology. The mechanical flexibility and stretchability allow the devices to intimately integrate with biological systems such as the skins and organs at their length scale. The embedded semiconducting nanomaterials provide the functionalities that can monitor the clinically useful bio-signals with sufficient spatial and temporal controls. This presentation will introduce a novel technology so called as sticker-like electronics (or sticktronics) in which integrated functional circuits are defined on a temporary sticker that can be attached to anywhere of interests including the skin and organs for their wearable and implantable biomedical applications. Mechanically soft, compliant skin sensor patches and tissue-injectable silicon nano-needles will be discussed to show the representative applications in wearable healthcare monitoring and intratissue drug delivery. The novel design concepts by combining highly networked nanomaterials or nature-inspired layouts offer a route to enhance important mechanical properties, allowing for reliable contact to the skin and tissues even under dynamic motions. These strategies also provide long-term longevity of such devices against potential fracture and delamination by improving the overall crack resistance, contact adhesion, and normal/shear strength. Discussions about the results of detailed experimental and theoretical studies will be followed to reveal the essential attributes of the materials, mechanics, fabrication processes, and system configurations. Pilot demonstrations on patients with swallowing disorders for their efficient rehabilitation will demonstrate an example utility of the devices in current clinical settings.

5:55 AM S.SM03.03.06
Stretchable Epidermal Electronics on Skin Sweat Monitoring Zhibo Chen and Jie Hu; Hong Kong University of Science and Technology, Hong Kong

Clinical prevalence of electrolyte imbalances is frequently seen in kids, beginner athletes, elderly and critically ill patients, and occur in the progression of diseases such as severe cardiovascular events like myocardial infarction, acute or chronic renal failures, etc. Sweat, due to the ease of non-invasive collection and the on-demand of convenient generation, shows great promise for wearable sensing, which is ideal for real-time continuous indicating body’s deeper biomolecular state and personal health condition. Recent advances in soft bioelectronics, especially epidermal sweat sensors, serve as the foundations for novel epidermal-based healthcare systems that overcome critical limitations of conventional personalized healthcare monitoring. However, a bottleneck of advanced sweat sensing is achieving accurate and stable measurement performance, comfortability, and high-throughput fabrication of sweat sensor components, including soft integration, epidermal packaging, and data analysis. Some reports have shown the possible methods of disposable sweat sensor components for fitness application, which still stands in an early research exploration with poor epidermal compatibility and low-efficiency sensing performance.
In this work, we introduce a hybrid stretchable epidermal sweat sensor, comprised of a miniaturized thermistor, signal processor and analog front-end, etc. for integrating into a soft system in package patch module. The sensor allows sweat sensing by using a group of gold-based fine bus electrode with a micro-chamber for real-time measurement of sweat electrolyte parameters. Analytical and experimental study optimized the system to establish a trade-off between the comfort of the user, the capacity for long-term use, and the reliable epidermis sensing data. The hybrid stretchable circuit technology, which is interconnected by a meander shaped conductive line, allows a good compromise between rigid chip components and bio-compatible elastomer packaging. The electrode pattern demonstrates the minimum bio-electricity interference by body organs and fluid. The soft mechanics of the sweat sensor patch allow multi-day wear in the presence of outdoor activity.

This work overcomes current engineering challenges in fabricating a bio-stretchable soft electronics system comprising multiple functional electronic components. As such, by using the existing micro-electrical fabrication process, the design of the sensor is enabling a low-cost technology in soft electronics manufacture. Overall, by enabling a comprehensive sweat analysis, the presented sensor is a promising monitor for advancing sweat testing in the point-of-care medical and fitness applications.

6:05 AM S.SM03.03.07
Self-Healing Dielectric Supramolecular Elastomer through Multiple Hydrogen Bonds  Matthew Tan, Gurunathan Thangavel and Pooi See Lee; Nanyang Technological University, Singapore

The application of self-healing materials to flexible and stretchable devices that can conform to biological components and deform with soft bodies in a mechanical invisible manner have been emerging. This is driven by the need to prolong their lifetime through spontaneous recovery upon physical damages. Despite these astounding abilities, these materials are often soft and lack intrinsic toughness, attributed to the high mobility of polymer chains to form entanglements and reassociations across the damaged region for self-healing purposes. Consequently, these materials usually fail at high tensile stresses (>1 MPa) making it susceptible to damages upon high loads. In this work, we address this dichotomy of achieving high self-healing efficiency and toughness simultaneously by introducing multiple hydrogen bonds into thermoplastic polyurethane to increase its intrinsic toughness, absorbing energy without fractures. With the introduction of multiple strong, reversible and complementary non-covalent hydrogen bonds, self-healing is achieved as these dynamic bonds are able to reassociate after breaking effectively. We further found that introducing particular solvents during the healing process, leads to a drastic improvement to the healing efficiency. This can be attributed to the solvent’s role as a plasticizer and a de-crosslinking agent that allows greater chain mobility. The healed polymer displayed exceptional mechanical properties of elongation at break of 1800%, a tensile strength of 5.30 MPa and toughness of 37.8 MJ m⁻³ within 12 hours. Proving to be one of the first healed polymers that realized both high tensile strengths and elongations concurrently. Furthermore, these hydrogen bond moieties are polar in nature, contributing to the high dielectric permittivity of the film. As such, when applied as a dielectric elastomer actuation (DEA) layer, the DEAs delivers higher actuator performance and achieves significant recovery of its actuator performance in terms of area strains after self-healing.

SESSION S.SM03.04: Inorganic & Hybrid Materials-Based Bio-Integrated Devices
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
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5:00 AM S.SM03.04.01
Metal Oxide-Polymer Semiconductor Blends for Flexible TFTs—Influence of the Polymer Structure and Amine Nitrogen Content  Antonio Facchetti¹,²; ¹Northwestern University, United States; ²Flexterra Inc., United States

In this presentation we report the correlation between polymer structure and charge transport in solution-processed indium oxide (In₂O₃):polymer blend films by using several polymers having different amine nitrogen atom content (N%). These amine containing polymers control the electron mobilities of the semiconducting oxide films by tuning the carrier/trap concentrations via a combination of electron transfer/doping and charge trap/scattering center formation, effects which depend on the polymer species and loading contents in the metal oxide matrix. All polymer addition enables the formation of more ductile semiconductor metal oxide films, as measured in a flexible thin-film transistor architecture. However, while
PVP addition reduces the field-effect mobility vs. the pristine (no polymer added) In$_2$O$_3$ matrix, for all other N-containing polymers there is always a certain polymer weight addition to the In2O3 precursor formulation which increases the mobility of the In2O3 matrix. Equally interesting, increasing N% in the polymer from 0% in polyvinyl phenol (PVP) to 34% in polyethyleneimine (PEI), the electron doping capacity gradually increases, enabling to increase the polymer content in the formulation at which the mobility is maximized from 0 wt.% to 1.0 wt.%, thus further enhancing blend ductability. Note, the positive effect of the N-containing polymer remains effective even with a polymer (PVP-NH2) having a N% as low as 3.9%.

Finally, we discovered correlations between the electron donating capacity of the polymer, charge transport, polymer chemical structure and thermal stability, as well as elemental composition in the final In$_2$O$_3$-polymer blend film.

5:10 AM *S.SM03.04.02
Freestanding Functional Structures by Aerosol-Jet Printing for Stretchable Electronics and Sensing Applications Sohini Kar-Narayan; University of Cambridge, United Kingdom

Modern electronics is rapidly evolving away from rigid devices to soft, flexible and stretchable devices. This evolution is being driven largely by the growing demand for wearable and human health monitoring applications, which require the development of conformal electronics with added functionality. Much of the effort in this area has relied on printing or transferring structures onto elastomeric substrates. However, the processing involved can often be cumbersome, and the structures themselves tend to suffer from poor fatigue characteristics. Here, I will describe a customised aerosol-jet printing (AJP) process to fabricate fully freestanding stretchable multi-layered devices. The AJP technique has distinct advantages in terms of fast-prototyping, wide ink compatibility with minimum printed feature size down to 10 µm. This versatile method facilitates the incorporation of multiple materials for added functionality that can serve a variety of applications. The ability to print multiple layers of different materials means that multiple conductive wires could be stacked up into one freestanding wire, separated by a dielectric polymer to prevent shorting. This feature makes single-wire circuitry possible by reducing the level of design complexity for practical stretching applications. For example, such freestanding structures can be used as stretchable interconnects, strain and humidity sensors, or even for printed thermoelectric energy harvesters. Desired structures consisting comprising both conductive and functional layers can be printed layer by layer on a substrate with a sacrificial film, that is subsequently dissolved to release the printed structures, thus yielding freestanding self-supported stretchable interconnects and/or functional devices. Devices made from this approach showed good electrical stability and stretchability, and are thus well-suited for applications in flexible/stretchable electronics, such as in conformal tactile, strain and humidity sensing applications, as well as in energy harvesting.

5:25 AM *S.SM03.04.05
Recent Progress on Compliant Electronic and Electromechanically Responsive Materials and Device Explorations Qibing Pei; University of California, Los Angeles, United States

The emergence of devices that combine rubbery elasticity with electronic, optoelectronic, and mechanically transductive properties offers exciting new opportunities for applications, but brings significant materials challenges. This presentation will describe our latest results in the materials efforts in developing highly compliant conductors, semiconductors, and dielectric polymers, as well as in the demonstration of integrated functional devices. Specific examples include a touch responsive sensors, a bistable electroactive polymer for tactile display, dielectric elastomer actuators, and compliant electrode for neural detection and stimulation.

5:40 AM *S.SM03.04.06
Wearable Electronics Using 1D-2D Hybrid Nanomaterials Jang-ung Park$^{1,2}$; $^1$Yonsei University, Korea (the Republic of); $^2$Institute for Basic Science (IBS), Korea (the Republic of)

Research on wearable electronics with flexible and stretchable forms has been grown remarkably by adopting the advent of various nanomaterials and their hybrid. This talk presents multifunctional wearable electronic devices for humans based on RLC circuits, where R (resistance) responds to molecular binding of biomarkers in the body fluid while L (inductive) and C (capacitance) change in accordance with structural changes of capacitance materials induced by varying pressure. These devices are based on diverse nanomaterials and their hybrid structures in order to exhibit high transparency and superb mechanical stretchability, with wireless sensing capability. Furthermore, in-vivo tests demonstrate their reliable operations.

5:55 AM S.SM03.04.07
Point-of-Care Soft Contact Lens System for Monitoring and Treatment of Dry Eye Syndrome Jiuk Jang$^{1,2}$, Joohee Kim$^1$ and Jang-Ung Park$^{1,2}$; $^1$Yonsei University, Korea (the Republic of); $^2$Institute for Basic Science (IBS), Korea (the Republic of)
Contact lenses, which make continuous contact with the ocular surface and tear fluids, have been utilized recently as a wearable platform for the healthcare device. However, most of the sensors used in contact lenses have been fabricated on lens-shaped plastic substrates with low oxygen permeability using opaque electronic materials, which means that the safety of the devices is not guaranteed. To solve difficulties associated with wearable healthcare devices, the substrate materials of a wearable platform in the entire system must be convenient and harmless for people to wear, and the individual components that make up the system, such as sensors and interconnects, should be stretchable and transparent.

Here, we fabricated a graphene field-effect transistor (FET)-based biosensor on a soft contact lens and skin-attachable thermal therapeutic device using stretchable and transparent electrodes for monitoring and therapy of dry eye syndrome (DES). The smart contact lens that makes up this system is the first point-of-care device to quantitatively diagnosis MMP-9, which is a biomarker for DES. By incorporating both diagnostic and therapeutic devices and the wireless communications into an integrated system, real-time biomarker monitoring signals from the biosensors are transmitted to the smartphone, and the hyperthermia command is issued to the therapeutic device simultaneously. Furthermore, in-vivo and in-vitro test using a live rabbit exhibited the reliable operation of the system. This integrated system can provide ultimate solutions for personal health management when it is combined with advanced technologies such as artificial intelligence and virtual reality.

SESSION S.SM03.05: Mechanics, Modeling & Design for Flexible and Stretchable Inorganic/Hybrid Materials and Devices
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
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5:00 AM S.SM03.05.02
Skin-Mountable Submental Sensor Patch for Remote Management of Patients with Oropharyngeal Swallowing Disorders Min Ku Kim, Cagla Kantarcigil, Georgia Malandraki and Chi Hwan Lee; Purdue University, United States

Every year approximately 9.44 million of adults, and more than 500,000 children, are diagnosed with swallowing disorders (a.k.a. oropharyngeal dysphagia) in the US. Swallowing is a fundamental human need and an act of pleasure; yet, oropharyngeal dysphagia is a common symptom in many diseases (e.g., head and neck cancer, stroke, dementia, Parkinson’s disease, cerebral palsy). Without proper treatment, dysphagia can lead to devastating consequences such as malnutrition, dehydration, respiratory compromise (due to aspiration of food/liquid into the lungs), or even death. Successful rehabilitation of oropharyngeal dysphagia requires frequent performances of head/neck exercises that primarily rely on expensive biofeedback equipment (e.g., oral manometers, electromyographic devices, and endoscopy), often only available in large medical centers. Such conditions require patients to make frequent visits to the clinic for a treatment session, which is often not feasible or economically viable for many patients. This directly affects treatment compliance and outcomes which highlights the need to develop a portable and inexpensive remote monitoring system for the rehabilitation and the tele-rehabilitation of dysphagia. Alternative strategies involve the use of portable monitoring devices to obtain biofeedback signals during swallow exercises in a form that allows real-time data collection or cloud storage for post-data processing. However, much of currently available systems suffer from rigid or semi-flexible platforms that are not well suited to dynamically interface with the curvilinear surface of the submental area (under the chin), particularly within the context of head/neck movement, thereby often resulting in poor data acquisition and discomfort to patients. This talk will outline materials and optimal mechanical design for a non-invasive, skin-mountable sensor patch that can fit conformably on the surface of the submental area and can be attached and detached multiple times without causing skin irritation. The sensor patch can remotely provide high-fidelity recording of surface electromyography signals from the submental muscles, as well as, mechanical strain waveforms from thyroid notch movement during a swallow. The sensor patch has been successfully demonstrated on a patient with Parkinson’s disease suffering from dysphagia and on a healthy control subject to show the feasibility and effectiveness of this system for the remote monitoring of patients with swallowing disorders.

5:10 AM S.SM03.05.04
Organic Mixed Ion-Electron Conductors for Bioelectronics Magnus Berggren; Linkoping University, Sweden

Organic mixed ion-electron conductors (MIEC), included in electrodes and devices, are now being heavily explored as the signal translation interface at the biology-technology interface, targeting biology, medicine and a vast array of internet-of-things applications. Commonly, the MIECs are based on polymers including conjugated conducting pathways for electronic charges and ion transport-promoting side-groups or polyelectrolytes. These MIECs operate as polarizable electrodes and the
coupled charge depletion-ion exchange defines the mode of operation for many bioelectronic devices. The fundamentals of MIECs are reported along with a few targeted device concepts targeting both electrode, sensor and actuator concepts for various applications.

5:25 AM S.SM03.05.05
Distortion-Free Direct-Patterning of Graphene on a Soft Contact Lens Using Self-Aligning Nanojet (SA-N) Dongwoon Shin, Abiral Regmi, Jonghyun Kim, Noori Na and Jiyoung Chang; University of Utah, United States

Recently, smart contact lens technology has been rapidly growing as a multi-purpose wearable device such as shielding electromagnetic waves, sensing glucose, display, and protecting eye dehydration in addition to its original vision-aid ability. Among many candidate materials for electrodes, graphene, a two-dimensional honeycomb lattice structure of the carbon atoms, has garnered much attention due to the excellent mechanical flexibility and electrical conductivity. Above all, it has superior optical transmittance, proving itself as an excellent alternative for the metal electrodes for a vision device such as a contact lens.

In order to adapt graphene as electrodes for soft smart contact lenses, one of the issues to address is developing a method for the scale-up, cost-effective, and precise graphene patterning on a surface of contact lens. Up to date, the graphene is mostly pre-patterned on a 2D substrate and then transferred onto a target 3D substrate, and such sequence inevitably causes not only distortion of the pattern but also low-yield production. In order to eliminate the distortion of the pattern and increase the yield of the production, transferring the bulk sheet of graphene on the surface of the contact lenses, followed by patterning the graphene directly on the 3D surface would be one of the ideal methods. However, to the best of our knowledge, there has been no report on a direct, nanoscale, and cost-effective patterning method of graphene on 3D surfaces.

Herein in this work, we present Self-Aligning Nanojet (SA-N) as a distortion-free and cost-effective direct-patterning-method of graphene on a soft smart contact lens. The SA-N is enabled at the lowest regime of flow rate in near-field electrospinning, which based upon surface current-induced electrostatic force without relying on hydrodynamic force. Therefore, kinematics of the SA-N is dominated by the electric force, by which the direction of the jet always self-aligns normal to the surface of the substrate rather than being pulled down by the gravity. As a result, by controlling the stage to follow the profile of the 3D surface, the precise patterning of nanofiber on multi-dimensional surfaces, such as the surface of the contact lens, is realized by the SA-N. Using the SA-N, nanofiber can be precisely patterned on top of pre-transferred-graphene as a bulk sheet on the surface of the contact lens. The patterned nanofiber serves as a masking layer during the plasma etching process, providing distortion-free patterned graphene that is ready to be used as electrodes. The proposed process is also much cost-effective compared to the typical graphene patterning method, such as photolithography or e-beam lithography.

In the presentation, we will present a study of the governing mechanism of the SA-N and show a demonstration of the direct writing of functional nanofiber on a 3D surface of the soft contact lens. Moreover, mechanical and electrical characterization of the precisely patterned nanoscale graphene will be analyzed. We believe that the SA-N can provide a promising fabrication-strategy for a wide range of functional materials, including nanoparticles and polymers, for the smart contact lens as well as other 3D structures.

5:35 AM S.SM03.05.07
Poisson Effect in Structured Dielectrics and Impacts on Sensitivity of Capacitive Sensors Mirza S. Sarwar, Kieran Morton, Tan N. Nguyen, Bertille Dupont and John Madden; University of British Columbia, Canada

Flexible and stretchable sensors with abilities to detect a light touch, pressure and even shear have been investigated. Most of these sensors are either resistive or capacitive in nature. In case of capacitive sensors, the sensitivity primarily depends on the ease of deformation of the dielectric. To enhance sensitivity to the applied force, a lot of implementations have air cavities in the dielectric material in order to obtain a lower effective Young’s modulus. This, in turn brings about a greater change in capacitance for a given applied pressure. The greater the fraction of air in the total volume of the dielectric, the softer it is. However, the architecture of the dielectric can cause this to differ due to the Poisson effect. Upon applying a force along the perpendicular direction of a unit elemental structure in the dielectric, the structure expands in the longitudinal axis. Depending on the architecture, this effect can lead to a change in the effective Young’s modulus. In addition to the Young’s modulus, the deformation of the dielectric can also couple the electric fields differently and can even be designed to enhance the coupling. Under these circumstances, the capacitance increase due to an applied pressure will not only be due to the decrease in dielectric thickness but also due to the change in the effective dielectric constant.

Typically, the Young’s modulus of a patterned dielectric with air cavities is expected to decrease with a reduction in the volumetric ratio of solid dielectric material to air cavities. In this work, we investigated capacitive pressure sensors with various dielectric architectures keeping the ratio of solid dielectric to air cavities volume constant and therefore an expected
similar Young’s modulus magnitude. However, within these architectures, we have demonstrated that it is possible to engineer the Young’s modulus to vary by over 50% and the capacitive sensitivity to vary by over 100%. This research therefore paves the path to designing sensors to suit very specific applications, including being able to have a higher elastic modulus and yet bring about a larger change in capacitance with the same pressure applied. We have also demonstrated the ability to engineer a non-linear Young’s Modulus - sought after by artificial skin researchers in robotics and prosthetics, since human skin has a non-linear elastic response. This work discusses the critical parameters that are to be focused on when designing the dielectric for a capacitive sensor and aims to aid in the development of custom design that fulfils desired specifications.

SESSION S.SM03.06: 3D Micro-Structured Stretchable Materials, Devices and Patternings
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
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5:00 AM *S.SM03.06.01
Graphene Oxide Liquid Crystal towards Functional Hybrid Carbon Assembled Nanostructures Sang Ouk Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Graphene Oxide Liquid Crystal (GOLC) is a newly emerging graphene based material, which exhibits nematic type colloidal discotic liquid crystallinity with the orientational ordering of graphene oxide flakes in good solvents, including water. Since our first discovery of GOLC in aqueous dispersion, this interesting mesophase has been utilized over world-wide for many different application fields, such as liquid crystalline graphene fiber spinning, highly ordered graphene membrane/film production, prototype liquid crystal display and so on. Interestingly, GOLC also allow us a valuable opportunity for the highly ordered molecular scale assembly of functional nanoscale structures. This presentation will introduce our current status of GOLC research particularly focusing on the nanoscale assembly of functional nanostructures. Besides, relevant research works associated to the nanoscale assembly and chemical modification of various nanoscale graphene based materials will be presented particularly aiming at energy and catalytic applications

5:15 AM *S.SM03.06.02
Wearable Gas Sensors with Wireless Communication and RF Energy Harvesting Capabilities Huanyu (Larry) Cheng; The Pennsylvania State University, United States

Recent advances in electronics enable powerful biomedical devices that have significantly reduced therapeutic risks by monitoring vital signals and providing means of treatment. Small footprint deformable gas sensors that can be deployed on the skin surface to detect and distinguish multiple compounds in real-time are integral to accurate monitoring of health conditions. Low-dimensional nanomaterials or mixed metal oxides are state-of-the-art gas sensing materials that change their resistance upon binding of various important gases that require monitoring. However, it is challenging to integrate within a microscale footprint the numerous nanomaterials required to deconvolute signals from complex gaseous mixtures, as is necessary for deployment. The core innovation will be our ability to use laser writing to synthesize and pattern numerous low-dimensional nanomaterials and mixed metal oxides directly on laser-induced graphene gas sensing platform in order to facilitate the deconvolution of complex gas responses in mixtures. When combined with the stretchable antennas for wireless communication and rectennas for ambient RF energy harvesting, wearable gas sensors for health monitoring or toxic gas detection open new opportunities in epidermal electronic devices to enhance the operator and mitigate exposure.

5:30 AM S.SM03.06.03
3D Printing Flexible, Stimuli-Responsive and Shape Memory Polymers Rigoberto C. Advincula; Case Western Reserve University, United States

The use of 3D printing to create devices from elastomeric and polymeric materials has appended the design functionality for new materials including uses in biomedical devices enabling rapid development. While 3D printed polymers can be further classified into thermoplastics, thermosets, and elastomers based on their thermo-mechanical properties. The processability and functionality of flexible elastomers make it a challenge to employ 3D printing methods for additive manufacturing. The transition to a final phase or cross-linked structure results in new properties in combination with the processing method. This is more evident with the choices of 3D printing methodologies (FDM, SLA, SLS, VSP) which can make use of blended or
formulated compositions. We have demonstrated the 3D printing of biomedical grade thermoplastic polyurethanes (TPU), silicones, and rubberized epoxies. However, 4D printing allows the design of new materials and applications based on integrating the chemistry of conversion with the printing mode. In this talk, we demonstrate the fabrication of concept objects and elastomeric actuators based on the use of biomedical grade melts and extruded viscous solutions of nanocomposite elastomers as elastomeric actuating materials and shape memory devices.

5:40 AM *S.SM03.06.04
3D Stretchable Piezoelectric Materials Seungbum Hong; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Recently, the wearable devices combined with the internet of things (IoT) have become a vital part of our daily life. The trend of the wearable electronics is moving from small electronics to directly embedded ones. In this respect, fiber and fabric-based electronics have many advantages such as high wearability, ventilation through pores, and high durability by weave structures. Smart fibers and fabrics, which can generate electricity from human motions and monitor the motions of human body, can act as wearable energy harvesters and sensors. As such, they will be used as important components of IoT (Internet of Things) technology. Here, we present a smart fiber and an e-textile with piezoelectric poly[(vinylidenefluoride-co-trifluoroethylene) [P(VDF-TrFE)] for wearable energy harvester applications. We used dip coating and hot pressing to deposit P(VDF-TrFE) on fibers and fabrics. We found that our prototypes had high flexibility and high interfacial adhesion strengths between P(VDF-TrFE) and electrodes, indicative of high stability. We demonstrated that our prototypes could generate piezoelectric output voltage and current from human mechanical energies with low frequencies. We envision that our fiber and fabric-based piezoelectric devices are promising as energy harvesters for supplying energy source to low power wearable devices.

5:55 AM S.SM03.06.06
Highly-Sensitive Flexible Piezoelectric Acoustic Sensors for Speaker Recognition Young Hoon Jung, Jae Hyun Han and Keon Jae Lee; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Herein, we demonstrate a new concept of flexible piezoelectric acoustic sensors (f-PAS) using mechanical sequential multi-resonance in membrane. The flexible piezoelectric film of f-PAS fabricated by sol-gel method and inorganic laser lift-off (LLO) exhibits high sensitivity to nanometer scale vibration and multiple frequency resonances in human voice frequency range. The self-powered f-PAS mimicked the mechanism of basilar membrane in the human cochlear that has multiple response to different frequencies depending on the width of membrane. The f-PAS exhibits maximum -42dB of relative sensitivity, which is four to eight times higher than the conventional condenser sensor without any amplification circuit. The f-PAS acquired abundant voice information from the multi-channel electrodes and read the frequency domain characteristics. The standard records dataset (TIDIGITs) were utilized to excite the piezoelectric membrane of the f-PAS, which converts the original analog speech sound to the electrical signal. The voltage-time data was subsequently analyzed by a Fast Fourier Transform (FFT) and a Short-Time Fourier Transform (STFT) to convert to the frequency component. The machine learning algorithm was designed by using the most highest and second highest sensitivity data among multi-channel outputs, exhibiting outstanding speaker recognition rate of 97.5% with error rate reduction of 75%, compared to the reference condense-type MEMS microphone.
dispersion of fillers in matrix. In this talk, a highly-enhanced piezocomposite energy harvesters (PCEH) is representatively developed using a three-dimensional (3D) interconnected electroceramic skeleton by mimicking and reproducing the sea porifera architecture (although the speaker will introduce other research examples and achievements). This new mechanically reinforced PCEH is demonstrated to resolve the problems of previous reported conventional piezocomposites, and in turn induces stronger piezoelectric energy harvesting responses. The generated voltage, current density and instantaneous power density of the biomimetic PCEH device reach up to few tens times higher power output than that of conventional randomly-dispersed particle-based PCEH. This work broadens the further developments of high-output elastic piezocomposite energy harvesting and sensor application with biomimetic architecture.

5:15 AM S.SM03.07.02

Inkjet-Printed Soft Resistive Pressure Sensor Patch for Wearable Electronics Applications Li-Wei Lo1,1, Hongyang Shi2, Haochuan Wan3, Zhihao Xu4, Xiaobo Tan2 and Chuan Wang1,1; 1Washington University in St. Louis, United States; 2Michigan State University, United States

Soft pressure sensors may find a wide range of applications in soft robotics, biomedical devices, and smart wearables. In this paper, an inkjet-printed resistive pressure sensor that offers high sensitivity and can be fabricated using a very simple process is reported. The device is composed of a conductive silver nanoparticle (AgNP) layer directly printed onto a polydimethylsiloxane substrate and encapsulated by a VHB tape. The pressure is measured through change in electrical resistance caused by pressure-induced strain in the printed AgNP thin film. The influence of substrate stiffness and thickness on the sensitivity and achieved sensors with an optimized configuration that exhibit highly repeatable response with a sensitivity of up to 0.48 kPa⁻¹ is systematically studied. It is further demonstrated that such a printed soft sensor patch is capable of measuring arterial pulse waveforms or detecting acoustic vibrations under various sound pressure levels. With its simple and low-cost fabrication process and high sensitivity, the inkjet-printed resistive pressure sensor is promising for future biomedical and smart wearable device applications.

5:25 AM S.SM03.07.04

Dynamic Protein Hydrogels with Reversibly Tunable Stiffness Regulate Human Lung Fibroblasts Spreading Reversibly Linglan Fu, Amanda Haage, Na Kong, Guy Tanentzapf and Hongbin Li; University of British Columbia, Canada

Protein-based hydrogels can be utilized for extracellular matrices (ECM) by providing biocompatible and dynamic local microenvironment. Through cell-ECM interactions, these external mechanical signals are transduced to the cell’s interior, triggering biochemical signaling cascades that determine a wide variety of cellular behaviors, ranging from cell adhesion, cell spreading to cell differentiation. However, only a limited number of such hydrogels have been engineered allowing for investigating cell response to the change of hydrogel stiffness. Moreover, the stiffness of these hydrogels can only be switched unidirectionally and irreversibly. Here we report an entirely protein-based hydrogel that allows for a cyclic, reversible modulation of hydrogel mechanics in a relatively large range of Young’s modulus, and used it to investigate the cell spreading behaviors of human lung fibroblasts (HLF) in response to the cyclic change of the hydrogel Young’s modulus. This protein-based dynamic hydrogel as an ECM, was fabricated by using mutually exclusive protein (MEP, GL5CC/I27) as building blocks. MEP is a specially designed, redox-responsive protein folding switch. In the oxidized state, the host domain GL5CC is folded; in the reduced state, the GL5CC unfolds and the effective chain length of the MEP changes from 2.6 to 26 nm, leading to a change in the polymer chain length between two crosslinking points. Building upon this approach, we engineered the dynamic protein hydrogel based on TNfn3-GB1-resilin-(GB1-GL5CC/I27-resilin)2. TNfn3 contains a RGD motif for cell adhesion and resilin provides covalent crosslinking residues. We found that this dynamic hydrogel could be reversibly tuned between a stiff and soft state via a redox reaction. Moreover, this protein hydrogel supports cell adhesion and proliferation. In response to a cyclic change of the hydrogel’s Young’s modulus between ~6 kPa and 20 kPa, HLF dynamically change their morphology in a fully reversible fashion, demonstrating the great potential utility of such dynamic protein hydrogels in mechanochemical studies.
The recently developed laser induced graphene (LIG) process allows scribing electrically conductive circuits directly on a polyimide film. Its versatility is enabling a variety of designs, suitable for a broad range of electro-mechanical applications [1]. Silicone rubber layers incorporating LIG patterns were proposed to produce strain responsive devices such as strain gauges [2]. Nevertheless, the sensors had an overall thickness in the mm range, which makes challenging their use for thin, wearable, biointegrated devices. Here conformability plays a main role in determining a seamless interface with skin [4]. In this work we report the results on new LIG-based composites with low thickness and enhanced conformability to skin. The fabricated materials were used to develop various stretchable electrical devices.

Various silicone as well as polyurethane (PU) materials were investigated as the elastic carriers for LIG patterns. The latter were produced either in the form of a porous flat structure or as bundles of graphene fibers, by fine tuning of laser rastering parameters. The research included thin films with/without acrylic adhesives of various compositions and types of finish (including spin coating, blown film extrusion, etc.). The influence of laser rastering direction on the final functional properties of the composites was also investigated. One of the main challenges addressed in this work was an optimization of the transfer process of an electrically integer LIG circuit onto the investigated film. That was done in order to preserve low sheet resistance (100-1000 Ω/sq) and to achieve replicability among specimens. Developing a proper electrical connection suitable for flexible applications was another part of the work. A comprehensive electro-mechanical testing of composites has been carried out.

PDMS-based LIG devices have shown fully recoverable linear elastic behaviour and linear electrical resistance response up to 25% strain, as well as maximum stretchability up to 70%. These results allowed us to develop highly responsive thin strain sensors. A thin and soft (~30 µm, E ~ 15 MPa) wearable respiratory sensor based on biofriendly and medically approved flexible PU film served as another example for the proposed future applications. The spectrum of patterned LIG applications can be further enhanced by designing compact energy efficient power storage devices such as microsupercapacitors (MSCs) [5] which could be suitable for sports and medical applications, among others. To this aim we worked on creating thin flat electrodes with high surface area for electrochemical applications. These could be integrated into the last generation of bio- and environmentally friendly electrochemical micro supercapacitors (MSCs), based on a low-cost and skin-friendly aqueous electrolyte. Since the surface area of the electrode material plays a crucial role in the charge storage processes, LIG material in form of a scribed powder was investigated by means of BET technique in order to confirm its remarkably high surface area of ~400 m²/g. Thin and soft LIG electrodes integrating electrical contacts were tested for MSC application. The obtained results of electrochemical measurements (cyclic voltammetry, galvanostatic charge/discharge curves) have shown high potential for further applications of the developed devices in the form of miniaturized power suppliers.


Soft and Electrically-Active Redox-Active Polymeric Ionic Liquids
Saejin Oh¹, Andrei Nikolaev¹, Kan Tagami¹, Dongwook Lee¹², Rachel A. Segalman¹¹, Songi Han¹¹, Javier Read de Alaniz⁷ and Michael L. Chabinyc¹; ¹University of California, Santa Barbara, United States; ²California NanoSystems Institute (CNSI), United States

Polymeric ionic liquids (PILs) are promising candidates for soft electronics. They are amorphous polymers and with ionic functionalities on the backbone that are paired with a counterion that leads to a low glass transition temperature (Tg). Here, we present our work to design redox-active polymers that allow charge transport while maintaining the behavior of PILs. Developing soft redox polymers is challenging because of their relatively high Tg. There have been efforts to decrease Tg of redox-active polymers by increasing the length of the aliphatic chains in between tethered charge-conducting groups on the side chains and the backbone. However, this structure can harm charge transport properties because of the spatial separation of the redox active groups. In this work, we have synthesized the PIL with redox-active phenothiazine-bis(trifluoromethanesulfonyl)imide (TFSI) ionic liquid side chains placed very close to the backbone. By placing the side chains closer to each other, enhanced charge transport was successfully demonstrated upon oxidation and with increasing amounts of the TFSI anion. At the same time, the Tg was significantly lowered by addition of a short ethylene glycol units on...
the phenothiazine. In this presentation, we will demonstrate that both enhanced electrical and mechanical properties could be attained with our novel polymeric design for future applications.

S.SM03.08.09

*In Situ* Phase Transition of Peptide Side Chains Regulates Thermo-Responsive Properties of Protein-Based Hydrogels Tianyu Duan, Akash Panjabi and Hongbin Li; University of British Columbia, Canada

Protein-based hydrogels have emerged as promising biomedical materials thanks to the precisely controllable structures, mono-dispersity and biocompatibility of genetically engineered proteins. However, many protein-based hydrogels lack the ability to controllably change their biological, physical or mechanical properties in response to temperature variations, which limits their practical applications in clinical injection, pain relief, hyperthermia treatment, and drug delivery. Here we report a method to fabricate protein-based hydrogels with regulable thermo-responsive properties. By fusing an elastin-like polypeptide chain (Vn) to an elastomeric poly-(GB1-resilin) protein (YR), we synthesized a series of block co-polymers, Vn-YRs. With Vn blocks that exhibit a lower critical solution temperature (LCST) behavior, Vn-YRs become di-block amphiphiles and form micelles above the transition temperature (Tt) of Vn blocks in aqueous media. When Tyr-rich YR-blocks are cross-linked into a hydrogel network through a photo-induced di-Tyr reaction, the non-Tyr-containing Vn blocks are dispositioned into the side chains with one end attached to the network. These Vn side chains do not pronouncedly alter the mechanical properties of YR-based hydrogel networks at temperature below their Tt. By contrast, above Tt, Vn side chains undergo phase transitions within the hydrogel networks, similar to their micellization in solution. Such temperature-triggered *in situ* phase transition of the Vn side chains is reversible and bestows reversible modulus reinforcement and deswelling to the hydrogel materials. Furthermore, the amplitude of such property changes can be tuned by factors including side chain length and composition. The results demonstrate that *in situ* phase behaviors of side chains can regulate thermo-responsiveness of protein-based hydrogels. We anticipate that this reported method can be applied to various biomedical applications, as well as inspire the potential development of other stimuli-responsive hydrogels.

S.SM03.08.11

High-Performance, Low Haze Silver Grid Embedded Flexible Transparent Electrode Ziyu Zhou and Paul Leu; University of Pittsburgh, United States

The higher demanding for the clarity and flexibility limit the current-leading materials such as indium tin oxide (ITO) further development in optoelectronics. Polymer substrate embedded with metal mesh has recently drawn increased attention for various flexible and transparent display devices because of their high electrical conductivity, optical transparency and robustness. However, for some commercial ITO/PET substrates applied in devices are still not satisfied the performance requirement.

Our study has investigated a low-temperature, particle-free silver ink formed multi-layer micro/nano structured transparent conductor to achieve a higher light management with a lower loss of electrical properties. Ag microgrid embedded into a nanostructured polyethylene terephthalate (PET) substrate shows a high transparency, low haze as well as a low sheet resistance. An anti-reflection nanostructured fabrication is also applied to the back side of PET to further suppress the reflection, thus mostly enhanced transparency. This work focused on minimizing the optical transmittance loss and shadowing losses: (i) Small size feature for linewidth to 3 um; (ii) improve the T-Rs trade-off, making T > 90% with a Rs less than 4 ohm/sq, (iii) reducing the cost-effectiveness of fabrication method. Mechanical reliability is also demonstrated by bending and folding test comparing to ITO/PET. The sheet resistance only increased 5% under 500 bending cycles and still effectively conductive after 10-times completely folding. The mechanism of highly flexible even foldable properties resulting from lowering stress within metal grid is also discussed.

S.SM03.08.14

Exfoliated Black Phosphorus as an Active Material for High Energy Nanogenerator Application Sachin K. Singh1, Subas Muduli1, Dipti Dhakras1, Richa Pandey2, Rohit Babar1, Ankur Singh1, Dinesh Kabra2, Mukul Kabir1, Ramamoorthy Boomishankar1 and Sathishchandra Ogale1; 1Indian Institute of Science Education Research, India; 2Indian Institute of Technology Bombay, India

2D materials are at the focus of scientific attention in recent years in view of their several unique and interesting physical properties. The initial research on 2D materials was centred on their novel synthesis and property characterizations, and now the applications of these materials are being sought in different fields. Since clean and renewable energy research has acquired immense prominence lately, applications of 2D materials for energy harvesting are being keenly pursued at this time; mechanical energy harvesting being currently a rapidly developing field with several opportunities to harvest different forms of mechanical energy such as flexing, vibration, friction etc. using device systems known as nanogenerators (NGs) and
triboelectric nanogenerators (TENGs) which are based on different principles. While some very interesting research using 2D materials has already appeared in the literature, many innovative design possibilities are still open for evaluations on the use of these materials for enhanced mechanical energy harvesting performance.\textsuperscript{1,2} Thus, in this work, we have explored the high mechanical energy harvesting possibility of the uniquely puckered structured elastically and electronically interesting 2D material, namely black phosphorous (BP). Nanogenerator device was fabricated by homogenously and densely embedding BP Nanosheets in Polydimethylsiloxiane (PDMS) matrix forming a composite film at different concentrations. The BP-PDMS based Nanogenerator displays an exceptionally high voltage output of maximum peak-to-peak voltage output of the order of ±350 V (maximum current density of 12.8 mA m\textsuperscript{-2} under an applied impact force of 40 N, at a frequency of 20 to 25 Hz. In terms of output power performance, the NG exhibits a power density of 1400 mW m\textsuperscript{-2} and a volume power density of 2 kW m\textsuperscript{-3}, with active material (BP) contribution of 0.35 W g\textsuperscript{-1}. By using Piezoresponse force microscopy (PFM), we have calculated the piezoelectric coefficient value (d\textsubscript{33}) which is 20 pm/V. DFT calculations suggest the presence of strain-induced polarization via deformation-induced redistribution of intra-layer electron charge density. Demonstration of three real life applications namely wheel motion, tap water flow, and bending/flexing movements demonstrate that BP-PDMS NG is indeed a high powering capability device.\textsuperscript{3}

References:

S.SM03.08.16
Adaptable Ionic Liquid-Containing Supramolecular Hydrogel with Multiple Sensations for Intelligent Robot at Subzero Temperatures Bo Li\textsuperscript{1,2} and Ning Ma\textsuperscript{1}; 1Harbin Engineering University, China; 2Tufts University, United States

There is a challenge to prepare the hydrogel that hold a high stretchability and conductivity in below zero temperature. In this work, we demonstrate a supramolecular ionic liquid hydrogel, wherein quadruple hydrogen bonding ureidopyrimidinone (UPy) units cross-linked polyethylene glycol (PEG) polyurethane was employed as networks with aqueous solution of imidazolium ionic liquid as free phase. Owing to the hydrophilic PEG segments, the hydrophobic UPy moieties, and the green molten imidazolium ionic liquid, this hydrogel exhibited high water content (~600%), swelling ratios (~400%), elongation (~750%), low resistivity (~0.51 kΩ\textcdot cm), excellent transparency (~98%), especially, the most striking characteristic could be maintain outstanding mechanical and thermal sensitivity at -20°C. The supramolecular ionic liquid hydrogel was utilized to fabricate E-skin for intelligent robot to realize pressure feedback and thermal recognition. This line of research not only demonstrates the anti-freezing stimuli-responsive hydrogel are a promising candidate for E-skins used in harsh condition, but also enrich the design of supramolecular polymers-based hydrogel sensors for future artificial intelligence applications. (This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.)

S.SM03.08.18
Self-Healing, High-Elongation Polysiloxanes with Soft-Tissue Compatibility Barry Arkles, Allison Phillips, Santy Sulaiman and Jonathan Goff; Gelest Inc., United States

Ultra-high elongation siloxane nanocomposites that rely on mechanically interlocked polymer chains that result from high degrees of entanglement and knot formation. In a first step, living anionic ring opening polymerization techniques are employed in the synthesis, yielding monodisperse heterobifunctional polydimethylsiloxanes with a hydrido-, omega vinyl-functionality. Composites are formed in a second step in which a step-growth polymerization is conducted in the presence of surface modified silica nanoparticles yielding a regularly ethylene interrupted polydimethylsiloxane structure. High elongations, as great as 6000%, and self-healing properties appear to be dependent on the degree of polymerization of the linear step-growth polymers. The polymer chemistry, physical properties and practical examples of high-elongation and self-healing behavior will be presented.

S.SM03.08.19
Soft, Smart Contact Lenses for Human Disease Monitoring Using Mobiles through NFC Communications Funkyung Cha, Joohee Kim, Minjae Ku and Jang-Ung Park; Yonsei University, Korea (the Republic of)
In order to monitor a person’s health condition and diagnose disease, it is important to continuously monitor the vital physical signals or metabolites in body fluids. Especially, eyes provide various physiological signals, thus being a promising site for non-invasive wearable sensing. Therefore, the contact lens provides a unique wearable sensing platform for monitoring various signals from the wearer’s eye. However, in the conventional smart contact lenses, the components were opaque, rigid, and brittle, so they could obstruct the wearer’s vision and damage the eyes. Moreover, to supply power and receive signals from the smart contact lens, a bulky and expensive external equipment was needed, which might restrict the wearer’s movements.

In this talk, we fabricated a transparent and stretchable soft, smart contact lens for quantitative monitoring using a smartphone. One of the diseases that can be diagnosed through eyes is glaucoma, and the only known controllable risk factor of glaucoma is intraocular pressure (IOP). For monitoring the IOP, this smart lens is composed of a strain sensor, a strain-concentrating layer, a transparent and stretchable antenna, and an integrated circuit chip, and each component is electrically connected with three-dimensional structures of stretchable metals. This smart lens can operate without battery through NFC communications with a mobile phone. The in-vivo test using live rabbits and the human pilot experiment demonstrated the real-time monitoring of IOP using the fabricated smart contact lens without blocking the wearer’s view. Another biomarker that can be analyzed from the eye is glucose concentration, which is a crucial factor to the diabetics. The correlation between blood glucose and tear glucose concentration was investigated by using a smart contact lens integrated with the electrochemical glucose sensor.

S.SM03.08.20
Blood-Vessel Mimicking Sensors for Deformation-, Pressure- and Chemical- Detections Weiheng Xu, Dharmeedar Ravichandran, Sayli Jambhulkar and Dr. Kenan Song; Arizona State University, United States

Polymer nanocomposite-based piezoresistive sensors have broad applications in physiology monitoring, soft robotics, and human-machine interfaces. In this work, we developed a bio-inspired, blood-vessel-like thermoplastic polyurethane (TPU), graphene nanoplatelets (GnPs), multi-walled carbon nanotubes (MWCNTs) based fibers capable of detecting strains, high pressures, gas/liquid flow, and chemicals. Two-dimensional GnPs contributed to the formation of pores and the one-dimensional MWCNTs contributed to the electrical sensitivities of the compressible piezoresistive middle-layer, which was sandwiched by inner and outer TPU support layers. Continues fibers were manufactured via dry-jet wet spinning with a 3D laser sintered triaxial spinneret. Due to the pores generated during solvent exchange and each layer’s unique thermal stability, a hollow core is observed after undergoing hot isostatic pressing (HIP). Performances of the hollow-core multi-phase sensor were tested for gas/liquid flows at varied pressure and geometry orientations. The smallest detectable pressure is observed at ~ 200 mmHg, similar to pressures in the human arteries. A mapping of the pressure distribution in various geometries is constructed using multiple sensors and the results were confirmed by mechanical analysis. The sensor also shows a linear piezoresistive response for strain smaller than 80%, and is stable for over 1000 cycles at 10% strain. The pores of the piezoresistive-layer also enhance the sensitivity towards different types of solvents and gas vapors as they were guided through the sensor. Mechanical and thermal properties of the sensors were characterized using dynamic mechanical analyzer (DMA), differential scanning calorimetry (DSC) and thermogravimetric analyzer (TGA), demonstrating improvements of mechanical durability and thermal stability during the sensing cycles. This blood vessel-based design showed a high potential to be used in fluid pressure monitoring, 3D organ prototyping, and medical/biological educations.

S.SM03.08.26
High-Resolution, Flexible Retinal Prosthesis Based on Three-Dimensional Soft Stimulation Electrodes Hyo-beom Kim, Jiuk Jang and Jang-Ung Park; Yonsei University, Korea (the Republic of)

Loss of sight is one of the most severe problems that degrade the quality of human life, rather than any other disorders. Various methods for restoring the vision have been studied. Among them, electronic prosthetic devices for the visually-impaired person allows the individual to recognize the phase and movement of an object. It is based on the principle of converting an external light signal into an electric signal that is transmitted to the human optic nerve, which allows a person to perceive the electric signal as light. This retinal prosthesis has undergone considerable development over the last few decades; however, there are several challenges to be solved. First, the resolution is too low to visualize the information from the outside to the human eye. This problem is mainly originated from the high impedance of the electrodes. Second, the mechanical modulus of the material within the device is a mismatch to the modulus of the retina tissues, followed by severe inflammation and permanent damage to the retina. Finally, since this device is planned to be implanted on the human eye, the reliable operation is important.

Here, we presented the high-resolution, flexible retinal prosthesis based on three-dimensional (3D) soft stimulation electrodes for blind people. The high-resolution phototransistor array with a stimulation electrode allows the patient to perceive the image clearly. 3D structure of the electrode reduces the impedance of each pixel so that the single-pixel can be integrated in
high density without any electrical breakdown. Since we formed 3D electrodes using soft, self-healable materials, this stimulation electrode hardly damages the retina surface and easily restore their electrical characteristics under various mechanical deformations, suggesting the reliable operation of the implanted retinal prosthesis. Furthermore, in-vitro and in-vivo animal experiments using mouse and rabbit provided enough biocompatibility for the human trial. This high-resolution, flexible retinal prosthetic device provides a substantial chance to step-up for next-generation implantable electronic devices.

S.SM03.08.27
Modulation of Mesenchymal Stem Cell Migration Using Programmable Polymer Sheet Actuators Zijun Deng1,2, Weiwei Wang1, Xun Xu1, Nan Ma1,2 and Andreas Lendlein1,2,3; 1Institute of Biomaterial Science and Berlin-Brandenburg Centre for Regenerative Therapies, Helmholtz-Zentrum Geesthacht, Germany; 2Institute of Chemistry and Biochemistry, Free University of Berlin, Germany; 3Institute of Chemistry, University of Potsdam, Germany

The therapeutic potential of mesenchymal stem cells (MSCs) in regenerative medicine is governed by multiple factors. Recruitment of MSCs to the damaged tissue, where they differentiate into the local components and release the bioactive substances, is a crucial step to initiate and support tissue regeneration.1 Stimulating MSC migration with pure physical cues presents attractiveness. In this study, MSC migration responding to thermal and mechanical stimuli was investigated using programmable shape-memory polymer actuator (SMPA) sheets. Changing the temperature repetitively between 10 and 37 °C, the SMPA sheets are capable of reversibly changing between two different pre-defined shapes like an artificial muscle.2 After the attachment of MSCs on the SMPA sheets, cell movement was recorded using a time-lapse microscope. Compared to non-actuating control sheets, the MSCs cultured on the programmed actuating sheets presented a higher migration velocity (0.45 ± 0.17 vs. 0.58 ± 0.17 µm/min). SMPA sheets can be applied as a platform to study the combinatorial and synergetic effects of thermal and mechanical stimuli as well as their interplay, which helps to understand the orchestration of microenvironmental complexity for regulating stem cell migration. The use of physical cues to increase the homing capacity of MSCs presents a promising approach to improve their therapeutic potential in regenerative medicine.

References:

S.SM03.08.28
Multifunctional Strain Sensor Based on Graphene-Hydrogel Yuting Cai1,2; 1The Hong Kong University of Science and Technology, Hong Kong; 2Southern University of Science and Technology, China

With the growing market for wearable and implantable electronics, strain sensors with exceptional performance in sensitivity, stretchability, biocompatibility, and tough adhesion between human/machine interfaces have become essential. Herein, a novel graphene-ions based strain sensor, whose structure contains a carefully selected graphene foam (GF) and polyacrylamide/calcium-alginate (PAM/CA) double network hydrogel coupled with chitosan, can meet the above requirements to the maximum extent. Taking advantage of the excellent electrical properties of graphene and super mechanical properties of double network hydrogel, this strain sensor can measure an exceptionally wide range of strain up to 500%, which allows us to monitor and distinguish almost all human body motions, with a gauge factor of ~1800, which is up to 3 orders of magnitude larger than the 0.1–10 value reported previously. The device also shows high stability and excellent durability for 1000 cycles. Most importantly, the chitosan-bridge and skin-like elastic modulus of 8–90 kPa achieve conformal adhesion between the skin and sensor, with the adhesion energy of ~200 Jm−2. Moreover, this structured sensor is highly biocompatible and can be implanted in vivo, and has further potential in clinical applications.

S.SM03.08.29
Reversible Shape-Memory Actuation of Individual Micro/Nanofibers Yue Liu1, Oliver Gould1, Karl Kratz1 and Andreas Lendlein1,2; 1Helmholtz Zentrum Geesthacht, Germany; 2University of Potsdam, Germany

Advances in the fabrication and characterization of polymeric nanomaterials has greatly advanced the miniaturization of soft actuators, creating materials capable of replicating the functional physical behavior previously limited to the macroscale. Techniques such as emulsion polymerization and electrospinning have enabled the realization of nano and microscale objects whose shape change can be controlled by ensemble programming methods to realize one-way shape-memory.1 Previously,
we reported that a universal atomic force microscopy (AFM) test platform enables the implementation and quantification of a thermomechanically induced one-way shape memory effect for individual polymeric micro- and nanosystems. Here, we demonstrate how a reversible shape-memory polymer actuation can be generated in a single micro/nano object, where the shape change during actuation of an individual fiber can be dictated by programming using AFM.

In this work, electrospinning was used to prepare poly(ε-caprolactone) micro/nano fibers, which were fixed and crosslinked on a structured silicon wafer. Using AFM, the programming as well as the observation of recovery and reversible displacement of the fiber were performed by vertical three point bending. A plateau tip was utilized to improve the stability of the fiber contact and working distance, enabling larger deformations and greater rbSMPA performance. Programming strains of 39 ± 1% or 46 ± 1% were realized for fibers with diameters of 1 ± 0.2 µm and 300 ± 50 nm, which were deformed at 80 °C and fixed at 10 °C. Values for the reversible elongation of εrev = 3.4 ± 0.1% and 10.5 ± 0.1% were obtained for a single micro and nanofiber in cyclic testing between the temperatures 10 and 60 °C. The reversible actuation of the nanofiber was successfully characterized for 10 cycles. An actuation induced pulling force of 0.2 ± 0.01 nN and pushing force of 0.5 ± 0.1 nN were measured on the tip. The demonstration and characterization of individual shape-memory nano and microfibers represents an important step in the creation of miniaturized robotic devices capable of performing complex physical functions at the length scale of cells and proteins.

References:

**SYMPOSIUM S.SM04**

Fundamental Materials, Devices and Fabrication Innovations for Biointegrated and Bioinspired Electronics
November 21 - November 30, 2020

**Symposium Organizers**
Huanyu (Larry) Cheng, The Pennsylvania State University
Pasqualina Sarro, Delft University of Technology
Zheng Yan, University of Missouri-Columbia
Jun Yao, University of Massachusetts Amherst

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SESSION S.SM04.10: Live Keynote I: Fundamental Materials, Devices and Fabrication Innovations for Biointegrated and Bioinspired Electronics
Session Chairs: Huanyu (Larry) Cheng, Zheng Yan and Jun Yao
Saturday Morning, November 28, 2020
S.SM04

8:15 AM OPEN SLOT

8:30 AM *S.SM04.02.03
Ultra-Thin Organic Photovoltaics and Sensors for Wearable Sensors Kenjiro Fukuda1, Tomoyuki Yokota2, Zhi Jiang1, Sunghoon Lee1, Wenchao Huang2, Hyunjae Lee1 and Takao Someya1,2; 1RIKEN, Japan; 2The University of Tokyo, Japan

One of an important target application of biointegrated electronics is wearable sensors that enable accurate and continuous detection of physiological signals. These devices require conformable and biocompatible sensors and power source to continuously supply electricity to health-monitoring systems. In this talk, we will report on recent progresses of ultraflexible organic photovoltaic cells as power sources and wearable sensors. First, the progresses of power conversion efficiency (PCE) and mechanical/long-term stability of ultraflexible organic photovoltaics have been achieved using new material and process engineering. The certified PCE of 12.3% for the ultra-flexible organic photovoltaic cell has been achieved with novel ternary blend active layer [1]. Second, long-term continuous monitoring using organic electrochemical transistors with nonvolatile gel electrolyte has been achieved with a high mechanical stability and high signal-to-noise ratio (24dB) [2]. Then, the integration of the ultra-flexible organic photovoltaic cells as power sources with OECT-based sensors has been demonstrated [3].

[1] W. Huang et al., Joule, Accepted.

8:45 AM *S.SM04.02.07
Fish-Eye-Inspired Wide Field-of-View Camera Dae-Hyeong Kim1,2; 1Institute for Basic Science, Korea (the Republic of); 2Seoul National University, Korea (the Republic of)

Although recent efforts in device designs and fabrication strategies have resulted in meaningful progresses to the goal of novel high-performance imaging devices, significant challenges still exist in developing a miniaturized and lightweight camera that enables the wide field-of-view (FoV) imaging. This is mainly due to bulky and heavy multiple lenses employed in the conventional wide angle camera. In this work, inspired by structural and functional features of the aquatic vision, we have developed a novel wide FoV camera by integrating a tailored monocentric lens and a hemispherical silicon nanorod photodetector array. This bioinspired camera offers the wide FoV, a miniaturized module size, minimal optical aberrations, the deep depth-of-field, and the enhanced light sensitivity in one simple integrated device. Theoretical analyses in conjunction with imaging demonstrations have corroborated the validity of the proposed concept. The fish-eye-inspired camera is expected to provides new opportunities for the advanced mobile electronics.

9:00 AM *S.SM04.03.01
Bioelectronics with Nanocarbons Tzahi Cohen-Karni; Carnegie Mellon University, United States

We focus on developing a new class of nanoscale materials and novel strategies for the investigation of biological entities at multiple length scales, from the molecular level to complex cellular networks. Our highly flexible bottom-up nanomaterials synthesis capabilities allow us to form unique hybrid-nanomaterials. Recently, we have demonstrated highly controlled synthesis of 3D out-of-plane single- to few-layer fuzzy graphene (3DFG) on a Si nanowire (SiNW) mesh template. By varying graphene growth conditions, we control the size, density, and electrical properties of the NW templated 3DFG (NT-3DFG). This flexible synthesis inspires formation of complex hybrid-nanomaterials with tailored optical and electrical properties to be used in future applications such as biosensing, and bioelectronics. For example, we have developed a unique bioelectrical platform based on 3DFG and have demonstrated, for the first time, recording of the electrical activity of excitable cells using ultra microelectrodes ranging from 10µm down to 2µm, without the need of any surface coatings. Currently, we target the limits of cell-device interfaces using out-of-plane grown 3DFG, aiming at electrical recordings with subcellular spatial resolution (<5µm) and µsec temporal resolution. In summary, the exceptional synthetic control and flexible assembly of nanomaterials provide powerful tools for fundamental studies and applications in life science and open up the potential to seamlessly merge either nanomaterials-based platforms or unique nanosensor geometries and topologies with cells, fusing nonliving and living systems together.

9:15 AM *S.SM04.03.02
Soft Tissue-Like Rubbery Electronics and Integrated Systems Cunjiang Yu; University of Houston, United States

While human organs and tissues are mostly soft; conventional electronics are hard. Seamlessly merging electronics with human is of imminent importance in addressing grand societal challenges in health and joy of living. However, the main challenge lies in the huge mechanical mismatch between the current form of rigid electronics and the soft curvy nature of biology. Here, I will present a new form of electronics, namely “rubbery electronics and bioelectronics”, with skin-like softness and stretchability, which is constructed all based upon elastic rubbery electronic materials. These rubbery electronic
materials are structured in the format of composites, which can be scalably manufactured from common and commercial available materials without dedicated and complicated synthesis. Specifically, we build nanofibril organic semiconductor and metallic nanowires percolated in the elastomeric polymer matrix in a composite format for the rubbery semiconductors and conductors, respectively. Employing these rubbery electronic materials, we have achieved fully rubber format devices, including transistors and sensors, logic gates, active matrices, elastic sensory skin systems, and biointegrated devices, etc. I will showcase a few examples including artificial skins, biomedical implants, and wearable applications.

9:30 AM *S.SM04.03.03
Wireless Modular E-Tattoos Chargeable On-the-Go Nanshu Lu; University of Texas at Austin, United States

Soft, noninvasive and multifunctional epidermal electronics (a.k.a. electronic tattoos or e-tattoos) have demonstrated many exciting applications in mobile health, athletic training, human-machine interface (HMI) and so on. However, e-tattoos are only practically useful when they are low cost and wireless. Previously, our group has invented a dry and digital manufacturing approach named the “cut-and-paste” method for the rapid prototyping of e-tattoo sensors using a paper/vinyl cutter plotter [1]. This method has been demonstrated to work for thin film metals [1, 2], various polymer sheets [1, 3], ceramics [4], as well as 2D materials such as graphene [5, 6]. The cut-and-pasted e-tattoos are low cost and can be used to measure a variety of physiological signals such as electrocardiogram (ECG), seismocardiogram (SCG), electrooculogram (EOG), skin hydration, skin temperature, respiratory rate and so on [1-3, 5, 6]. To make the e-tattoos go wireless, we now report the “cut-solder-paste” process to incorporate integrated circuits (ICs) for signal readout and processing, near field communication (NFC) [7], as well as Bluetooth transmission [8]. To overcome the limited patterning resolution of the cutter plotter and to recycle the tattoo layers with ICs, we propose a modular concept in which the wireless charging layer (NFC layer), the wireless communication layer (Bluetooth layer), the readout circuit layer, and the sensor/electrode layer are fabricated individually and stacked up at the final step of fabrication. The thickness of a fully assembled multilayer e-tattoo (excluding IC chips) is less than 300 um and the overall stretchability is still beyond 20%. In addition to already mentioned capabilities, such e-tattoos can also be wirelessly tracked, mechanoo-acoustic heart signals, and oxygen saturation (SpO2) [3, 7, 8]. The NFC-enabled e-tattoos can be wirelessly charged so no battery is needed but the sampling rate is limited to 25 Hz and the wireless communication distance is limited to 5 cm. The Bluetooth-enabled e-tattoos require on-tattoo batteries but the sampling rate can be up to 4 kHz and the wireless communication range can be up to 10 m. Combining the NFC layer and the Bluetooth layer in one e-tattoo, we demonstrate that such wireless e-tattoo can also be wirelessly charged on-the-go via stretchable fabric feeding coils [8], enabling long-term, ambulatory and continuous sensing. Moreover, we propose that different layers can be disassembled and reassembled multiple times. After disassembly, the electrode layer should be disposed but the other layers can be reassembled into new e-tattoos. The low-cost, rapid prototyping method together with the wireless and reconfigurable capabilities represent exciting advancement towards practically useful wireless e-tattoos.


9:45 AM *S.SM04.03.06
Memory and Learning in Biomolecular Soft Matter for Low-Power, Brain-Like Computing Joseph S. Najem; The Pennsylvania State University, United States

The brain carries out complex cognitive and computing tasks by optimizing energy efficiency, information processing, communication, and learning in massively parallel, dense networks of highly interconnected neurons. To cope with its
everchanging surroundings, the brain is able to grow neurons, synapses, and connections—owing to its plastic nature. At the molecular and cellular levels, synaptic plasticity and neuronal excitation are the main mechanisms underlying these processes. Therefore, the ability of next-generation computing devices, robots, and machines to autonomously sense, process, learn, and act in complex and dynamic environments while consuming very little power will require approaches to computing and sensing that are inherently brain-like. Reproducing these features using traditional electronic circuit elements is virtually impossible, requiring the design and fabrication of new hardware elements that can adapt to incoming signals and remember processed information. These elements should be scalable, biomimetic, and preferably ionic to achieve energy consumption levels approaching those in the brain. While a major effort is being invested in developing inorganic materials that could emulate synaptic and neural functionalities, I believe that an overlooked, yet high-reward, pathway to success is through the development of biomolecular materials with the composition, structure, and switching mechanisms of actual biological synapses and neurons. Here, I describe two-terminal, biomolecular memcapacitors and memristors, consisting of highly insulating 5 nm-thick lipid bilayers assembled between two water droplets in oil. These devices exhibit memcapacitance that is nonlinearly dependent on the applied voltage as well as hysteresis in the charge due to voltage-driven, reversible changes in the area and thickness of the bilayer membrane. This is the first demonstration of a memcapacitor in which capacitive memory results from geometrical changes in a lipid bilayer membrane. We also show that the incorporation of voltage-activated alamethicin and monazomycin peptides in these devices results in variable ionic conductance across the membrane and memristive behavior. We discuss how these devices exhibit learning through synaptic plasticity, and how to implement them in online learning applications. These results serve as a foundation for a new class of low-cost, low-power, soft mem-elements based on lipid interfaces and other biomolecules for applications in neuromorphic computing which could have major implications on the robotics and computing fields.

SESSION S.SM04.11: Live Keynote II: Fundamental Materials, Devices and Fabrication Innovations for Biointegrated and Bioinspired Electronics
Session Chairs: Huanyu (Larry) Cheng, Zheng Yan and Jun Yao
Sunday Afternoon, November 29, 2020
S.SM04

7:15 PM S.SM03.02.01
Three-Dimensional Curvy Electronics Created Using Conformal Additive Stamp (CAS) Printing Cunjiang Yu; University of Houston, United States

Electronic devices are typically manufactured in planar layouts but many emerging applications, from optoelectronics to wearables, require three-dimensional curvy structures. The fabrication of such structures has though proved challenging due, in particular, to the lack of an effective manufacturing technology. This presentation will show our development of conformal additive stamp (CAS) printing technology and its employment to reliably manufacture 3D curvy electronics. CAS printing employs a pneumatically inflated elastomeric balloon as a conformal stamping medium to pick up pre-fabricated electronic devices and print them onto curvy surfaces. To illustrate the capabilities of the approach, we will demonstrate various devices with curvy shapes: silicon pellets, photodetector arrays, electrically small antennas, hemispherical solar cells, and smart contact lenses. We also show that CAS printing can be used to print onto arbitrary 3D surfaces.

7:30 PM *S.SM04.05.03
From Functional Nanomeshes to Advanced Soft Microsystems Hui Fang; Northeastern University, United States

New form of materials can often enable new device and system applications. In this talk, I will highlight our group's recent work under this motivation in two synergistic areas. Firstly, by stacking individual layers of polymer, metal, and low-impedance coating reliably in a same nanomeshed pattern, the final multilayer multifunctional nanomeshes achieved system-level performance from all individual layers, in addition to nanomesh advantages. Compelling demonstrations from this multifunctional nanomesh approach include high-performance transparent and flexible neuroelectrode arrays, which has been recently validated in vivo. The second part of my talk will introduce our recent concept on semiconductor nanomeshes. By making a silicon film into homogeneous nanomeshes, we achieve high mobility semiconductor that is intrinsically stretchable to conventional microelectronic layouts. Together, our work demonstrates that nanomeshing is a unique way of transforming microelectronics for emerging applications.

7:45 PM *S.SM04.05.07
Insertion Mechanics of Microscale Devices into the Brain Nicholas Melosh and Abdul Obaid; Stanford University, United States

Microscale electrodes, on the order of 10-100 µm, are rapidly becoming critical tools for neuroscience and brain-machine interfaces (BMIs) for their high channel counts and spatial resolution, yet the mechanical details of how probes at this scale insert into brain tissue are largely unknown. Here, we discuss quantitative measurements of the force and compression mechanics together with real-time microscopy for insertion of a systematic series of microelectrode probes as a function of diameter (7.5–100 µm and rectangular Neuropixels) and tip geometry (flat, angled, and electrochemically sharpened), within phantoms, ex vivo and in vivo. Results from each model system elucidated the role of tip geometry, surface forces, and mechanical scaling with diameter. Surprisingly, real-time microscopy revealed that at small enough length scales (<25 µm), blood vessel rupture and bleeding during implantation could be entirely avoided. This appears to occur via vessel displacement, avoiding capture on the probe surface which led to elongation and tearing for larger probes. We propose a new, three-zone model to account for the probe size dependence of bleeding, giving a new conceptual framework for how blood vessels fail and provide guidance for probe design.

8:00 PM *S.SM04.06.03
Rehealable, Recyclable and Reconfigurable Electronics Based on Dynamic Covalent Thermoset Jianliang Xiao; University of Colorado, United States

Dynamic covalent thermosets show superior properties, including self-healability, recyclability, malleability/reprocessability, thanks to the molecular level bond exchange reactions. These properties promise bright future of dynamic covalent thermosets in broad applications. We here report our work on dynamic covalent thermoset-based electronic systems that are rehealable, recyclable and reconfigurable. A flexible multifunctional electronic device that integrates electrocardiograph (ECG), temperature, motion, and acoustic sensing capabilities was demonstrated. It was exhibited that the rehealed and recycled devices showed electronic performance comparable to the original ones. Bond exchange reactions in the polymer network effectively relaxes stresses induced by mechanical deformation, which made it possible to reconfigure the flexible device into different configurations that are suited for different applications. Such rehealable, recyclable and reconfigurable electronics provides an approach to address sustainability and environment issues associated with mass production of electronics. It can find broad applications in prosthetics, health care, and human-computer interface and other areas that are hard to be addressed by conventional approaches.

8:15 PM *S.SM04.06.04
3D Printing Electronics Directly on the Body Michael C. McAlpine; University of Minnesota, United States

The ability to directly print biomedical devices on the body could benefit patient monitoring, wound treatment, and even allow for the possibility of human augmentation. In reality, this concept requires the 3D printer to adapt to the various translations, rotations, and deformations of the biological surface. Conventional 3D printing technologies typically rely on open-loop, calibrate-then-print operation procedures. An alternative approach is adaptive 3D printing, which is a closed-loop method that combines real-time feedback control and direct ink writing of functional materials in order to fabricate devices on moving freeform surfaces. Here we demonstrate that the changes of states in the 3D printing workspace in terms of the geometries and motions of target surfaces can be perceived by an integrated robotic system aided by computer vision. This allow us to directly 3D print a wireless antenna based on a novel silver ink a free-moving human hand, to power a skin-mounted LED. Using this same approach, cell-laden hydrogels were also printed on live mice, creating a model for future studies of wound-healing diseases. Moreover, we developed an in situ 3D printing system that estimates the motion and deformation of the target surface to adapt the toolpath in real time. With this printing system, a hydrogel-based sensor was printed on a porcine lung under respiration-induced deformation. The sensor was compliant to the tissue surface and provided continuous spatial mapping of deformation via electrical impedance tomography. This adaptive 3D printing approach may enhance robot-assisted medical treatments with additive manufacturing capabilities, enabling advanced medical treatments, and autonomous and direct printing of wearable electronics and biological materials on and inside the human body.

8:30 PM *S.SM04.06.07
Exploring Bioelectric Dynamics at the Soft-Hard Interfaces Bozhi Tian; University of Chicago, United States

Although there are numerous studies on either hard or soft materials, our understanding of the fundamentals at hard/soft interfaces has been limited. As different types of energy (such as electrostatic, mechanical, thermal, and chemical energies) display diverse scaling behaviors and can converge, an appropriate selection of the length scale is critical for promoting new
scientific discoveries across these interfaces. Our group integrates material science with biophysics to study several hard/soft interfaces. We synthesize new materials and probe interfacial dynamics, with particular focus at the sub-micrometer and sub-cellular length scales. In this talk, I will focus on the interfaces that enabled non-genetic, freestanding, and semiconductor-based bioelectric modulation. I will also discuss some recent work that exploits the dynamic behaviors of granular materials in polymeric matrices toward bioelectronic and robotic applications. I will end the talk by proposing several new scientific and engineering approaches to improving our fundamental understanding of the (bio)chemical processes at soft/hard interfaces and to exploring new applications of these interfacial (bio)chemical processes.

SESSION S.SM04.12: Live Keynote III: Fundamental Materials, Devices and Fabrication Innovations for Biointegrated and Bioinspired Electronics
Session Chairs: Huanyu (Larry) Cheng, Zheng Yan and Jun Yao
Monday Afternoon, November 30, 2020
S.SM04

1:30 PM *S.SM04.07.02
Liquid Metal Embedded Polymers for Soft-Matter Electronics, Actuation and Energy Harvesting Carmel Majidi; Carnegie Mellon University, United States

Soft polymers that are embedded with nano- and microscale droplets of liquid metal (LM) can be tailored to exhibit a broad range of electrical, thermal, mechanical, and dynamic shape morphing properties. In contrast to lithographically-fabricated soft microfluidic architectures, these LM-embedded soft polymer (LMSP) composites are statistically homogenous and exhibit effective medium properties at the mesoscale. Depending on the choice of polymer matrix, LMSPs can be engineered to achieve a wide variety of properties – from thermally conductive rubber for heat management and thermoelectric energy harvesting in wearable electronics to shape memory materials that dynamically respond to electrical stimulation. Eutectic Ga-In (EGaIn) and Ga-In-Sn (Galinstan) alloys are used as the liquid metal due to their high electrical conductivity, low viscosity, non-toxicity, and the self-passivating formation of an oxide skin (Ga2O3) that enables emulsification and wetting to non-metallic materials. Because they are liquid-phase at room temperature, these alloys have virtually no influence on the mechanics of the surrounding elastomer medium. This allows the resulting composite to exhibit a unique and extraordinary combination of features not seen in other heterogeneous material systems. In this talk, I will review recent experimental and theoretical studies of this unique class of soft material architectures, with specific emphasis on LM-filled liquid crystal elastomers and soft polymers for stretchable electronics and energy harvesting. I’ll also highlight several applications in which LMSPs can have a potentially transformative impact, especially in the domains of wearable computing, physical human-machine interaction, and bioinspired soft robotics.

1:45 PM *S.SM04.06.08
Self-Powered Wearable and Implantable Electrical Stimulation Devices for Therapeutics Xudong Wang; University of Wisconsin--Madison, United States

Electrical stimulation (ES) is a widely used therapeutic treatment strategy. It showed significantly positive results in treating a variety of diseases, biological disorders, and neurological problems. Today, the emergence of wearable devices is rapidly reshaping the development of medical devices, pushing them from conventional bulky and rigid silicon electronics to flexible and primarily polymer-based systems. Among many types of functions, nanogenerators are developed as a unique device for converting biomechanical energy into electrical pulses. In addition to applying it directly as a power source, this pulsed electricity can be applied directly as a ES signal for therapeutic treatment. In our recent research, we successfully implemented such an electromechanical system for skin wound healing and vagus nerve stimulation for obesity control. An electrical stimulation bandage was developed by integrating a flexible nanogenerator and a pair of dressing electrodes on a flexible substrate. Rat studies demonstrated rapid closure of a full-thickness rectangular skin wound within 3 days as compared to 12 days of usual contraction-based healing processes in rodents. From in vitro studies, the accelerated skin wound healing was attributed to the electric field-facilitated fibroblast migration, proliferation and transdifferentiation. In another work, an implanted vagus nerve stimulation system was developed. The device comprises a flexible and biocompatible nanogenerator that is attached on the surface of stomach. It generates biphasic electric pulses in responsive to the peristalsis of stomach. The electric signals generated by this device stimulates the vagal afferent fibers to reduce food intake and achieve weight control. This strategy is successfully demonstrated on rat models. Within 100 days, the average body weight is controlled at 350 g, 38% less than the control groups. Both results bring a new concept in electrical
therapeutic technology that is battery-free, self-activated and directly responsive to body activities.

2:00 PM
*S.SM04.03.05*  
**Assembly of Nanoelectronics Via Tissue Development**  
Jia Liu; Harvard University, United States

Tissue-wide electrophysiology with single-cell and single-spike spatiotemporal resolution is critical for biological studies and biomedical applications. In this talk, I will discuss the creation of cyborg organisms: the three-dimensional (3D) assembly of soft, stretchable mesh nanoelectronics across the entire living organism by the cell-cell attraction forces from 2D-to-3D tissue reconfiguration during organogenesis. We demonstrate that stretchable mesh nanoelectronics can migrate with and grow into the initial 2D cell layers to form the 3D organ with minimal impact on tissue growth and differentiation. The intimate contact between the dispersed nanoelectronics and cells enables us to chronically and systematically observe the evolution, propagation and synchronization of the bursting dynamics in different organisms through their entire organogenesis and maturation. I will also discuss the potential applications of these cyborg organisms in biology and biomedicine.

2:15 PM
*S.SM04.02.04*  
**Bio-Derived, Green Electronics Made from Microbially Produced Protein Nanowires**  
Jun Yao; University of Massachusetts Amherst, United States

Protein nanowires harvested from microbes are a revolutionary green electronic material. They have unique properties for novel electronic devices with improved performance, for a broad range of applications from energy harvesting to neuromorphic computing and sensing. (1) Thin-film protein nanowire devices were shown to continuously harvest electricity from ambient humidity (*Nature* 578, 550-554 (2020)), enabled by the unique structural (e.g., nanopores at wire-wire interface) and chemical (e.g., a high density of hydroscopic groups) properties. This leads to a continuous energy harvesting mechanism from the ubiquitous and enormous ambient humidity, and hence a promising strategy to powering self-sustained systems. (2) The protein nanowires are cleverly designed and recruited by the microbe to facilitate charge exchange with environments (e.g., through redox metallization). Thus, protein nanowires can be assembled into bio-dielectrics to construct memristor devices, in which the protein nanowires catalytically reduce the energy barrier involved in memristive switching and enable ultralow operational voltage in the biological regime of <100 mV (*Nature Commun.* 11, 1861 (2020)). Neuromorphic components (e.g., artificial neuron, synapse) made from the protein nanowire memristors take a further step in bio-emulation from functional emulation to parameter matching, creating opportunities for future ultralow-power electronics and bioelectronic interfaces. (3) Protein nanowires have ultra-small diameters (3 nm) and an ultra-high density of surface functional groups (e.g., 10 per nm) that are advantageous for sensing applications. Electronic sensors made from protein nanowires were shown to have enhanced selectivity and sensitivity (*Nano Res.* 13, 1479-1484 (2020)) for ammonia detection compared to inorganic nanowire devices. These studies, combined with the advantages of renewability, biocompatibility, and eco-friendliness in protein nanowires, have provided the starting point for future green electronics based on synthetic protein nanowires.

2:25 PM OPEN DISCUSSION

2:35 PM
*S.SM04.07.01*  
**Polymerized Liquid Metal Networks for Stretchable Electronics**  
Carl Thrasher, Zachary Farrell, Nicholas J. Morris, Michelle C. Yuen and Chris Tabor; Air Force Research Laboratory, United States

Room-temperature liquid metals, such as nontoxic gallium alloys, show enormous promise to revolutionize stretchable electronics for next-generation soft robotic, e-skin, and wearable technologies. Core–shell particles of liquid metal with various surface-bound ligands can be synthesized and polymerized together to create cross-linked particle networks comprising >99.9% liquid metal by weight. When stretched, particles within these polymerized liquid metal networks (Poly-LMNs) rupture and release their liquid metal payload, resulting in a rapid transformation from insulating to conducting behavior. These networks autonomously form hierarchical structures that mitigate the deleterious effects of strain on electronic performance and give rise to emergent properties. Notable characteristics include nearly constant resistances over large strains, electronic strain memory, and increasing volumetric conductivity with strain to over 20 000 S cm-1 at >700% elongation. Furthermore, these Poly-LMNs exhibit exceptional performance as stretchable heaters, retaining 96% of their areal power across relevant physiological strains. Remarkable electromechanical properties, responsive behaviors, and facile processing make Poly-LMNs ideal for stretchable power delivery, sensing, and circuitry.

2:45 PM
*S.SM04.07.05*  
**Advanced Multimodal Optoelectronic Systems for Bio-Interfacing**  
Luyao Lu; The George Washington University,
Recent advances in new materials, electronics, and assembly techniques have allowed optoelectronic systems to interface with biology and contribute significantly to the progress in basic biological research as well as clinical medicine. In this talk, I will introduce a novel class of flexible, multimodal optoelectronic systems that combines high-performance nanoscale electrodes with microscopic optical components for simultaneous electrophysiological recording under optogenetic modulation. We envision this unique technology will open up new windows to understanding important biological processes by enabling mapping the dynamics of perturbed cell populations and correlating cellular responses to behavior.

SESSION S.SM04.01: Innovative Designs for Biointegrated and Bioinspired Electronics
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-SM04

5:00 AM S.SM04.01.04
Improved Capacitive Pressure Sensor Design Methodology Using Pyramidal Microstructures for Specialized Monitoring of Biosignals
Sara Ruth, Helen Tran, Levent Beker, Vivian R. Feig, Naoji Matsuhasha and Zhenan Bao; Stanford University, United States

There is an increasing demand for specialized pressure sensors in various biomedical applications, especially health monitoring. For example, cardiovascular monitoring, which has implications in early diagnosis of heart failure.[1] To date, there have been numerous reports on pressure sensor designs in order to meet the demands of specialized pressure sensors. However, in order to address the growing demand for tailored pressure sensors for such a diverse range of applications, it is important to understand how different sensor parameters impact performance. By quantifying these relationships, we aim to determine design parameters that will enable researchers to predict a priori the specific design needed to achieve the targeted performance. Previously, capacitive pressure sensors have been shown to have wide versatility in use, with a high degree of potential tuning possible through manipulating the geometry or material selection of the dielectric layer. One effective approach first reported by our group to tune the performance of capacitive pressure sensors is microstructuring the dielectric layer, which improves its compressibility and, consequently, its sensitivity.[2,3] As researchers seek to incorporate novel materials into sensors, there is also a need to understand how various intrinsic material properties, such as compressive modulus, impact sensor performance. Compressive modulus is qualitatively known to affect the sensitivity of the pressure sensor.[4] Quantifying the relationships between intrinsic material properties, dielectric geometry, and sensor performance will enable a design of pressure sensors and selection of materials to meet requirements for specific applications. Presented here is an improved fabrication method to achieve simple, tunable, consistent, and reproducible pressure sensors by using a pyramid microstructured dielectric layer along with an added lamination layer to improve consistency and reproducibility. The as-produced sensor performance matches predicted trends of parameters that can be explicitly controlled. Further, we develop a simple computational model using intrinsic properties of the elastic dielectric layer and experimentally confirmed its efficacy. We then use our model to predict other properties and a wider range within the tested properties to better understand the effect of material property and microstructure geometry on the sensor performance. This would allow us to anticipate trends and sensor performance. Finally, we demonstrate that we can more directly design sensors for a specific application, such as wrist pulse sensing, using our model and fabrication method.


5:10 AM S.SM04.01.05
Cable Bacteria as Living (Semi)Conductors with Record Intrinsic Electrical Properties—A New Paradigm for Bioelectronics?
Robin Bonné, Raghavendran Thiruvallur Eachembadi, Rob Cornelissen, Roland Valcke, Bart Cleuren and Jean V. Manca; Universiteit Hasselt, Belgium
In nature, fibre-like organisms such as Geobacter sulfurreducens [1], Shewanella oneidensis [2] and Cable Bacteria [3] demonstrate surprising electrical transport properties and could be considered as ‘living electrical (nano)wires’. Cable bacteria, a group of recently discovered filamentous, electroactive, multicellular bacteria, have developed a unique energy metabolism and parallel fibre structures demonstrating electron transport for conduction lengths up to 1 cm and with fibre conductivities exceeding 10 S/cm [4]. Conduction measurements carried out in high vacuum excluded the possibility of ionic conduction, but the fundamental charge transport mechanisms remain unknown. The observed electron transport in cable bacteria over distances in the order of centimeters is unprecedented in the biological world.

Cable bacteria as ‘champion living electrical wires’ are of fundamental interest to better understand the underlying biological processes, but are also potentially interesting as alternative organic electronic materials for the emerging field of bioelectronics as e.g. biocompatible electrical connections and circuits, conductive composite materials, (nano-) sensors, transistors,... In order to investigate the intrinsic electrical properties and underlying transport mechanisms, our approach is to study them with a range of solid state electrical characterisation techniques and prototype electrical circuits/devices [4,5]. These activities revealed an unique electrical network architecture [5] and intrinsic electrical properties very similar to for instance organic semiconductors, situating them in the context of electrical functional materials between semiconductors and conductors [4].

While for various so-called biological semiconducting materials (e.g. peptides, DNA,...) the studied semiconducting properties do not have a direct functionality as electron transporting channel in the occurring life processes, for cable bacteria they are expected to be of key importance. The exceptional intrinsic (semi)conducting electrical properties and extracellular electron transport behaviour of cable bacteria highlighted in this work are therefore worthwhile to be further studied in a cross-disciplinary manner at the nexus of (micro-)biology, (materials) physics and electronics and to be further explored in a variety of bioelectronic devices/circuits.

References :

SESSION S.SM04.02: Novel Devices for Biointegrated and Bioinspired Electronics
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-04

5:00 AM S.SM04.02.01
Highly Sensitive Electro-Chemical Sensor Based on Biomimetic Porous Structured Oxide Semiconductor for Detecting Nitric Oxide [Sak Lee, Hyung Tae Kim, Dong Hyun Choi, Sujin Jung and Hyun Jae Kim; Yonsei University, Korea (the Republic of)]

In recent years, as the number of patients with Alzheimer’s disease increases due to the advent of early-onset dementia, the social severity of Alzheimer’s disease is on the rise. Accordingly, there are increasing demands for various dementia diagnosis methods because Alzheimer's disease can be prevented from disease development by early detecting and treatment. Among these methods, biosensors are emerging as applications that enable point-of-care testing with low cost and fast response time. The interest in these technologies has mainly focused on field-effect transistor-based biosensor (bio-FET), where the conventional gate and gate insulator are replaced by a reference electrode and the electrolyte, respectively. In addition, the bio-FET uses receptors such as enzyme and aptamer on the sensing surface for detecting targeted bio-molecules. From then on, a lot of researches on the improvement of performance for bio-FET have been reported. However, the bio-FET suffered from low sensitivity and chemical instability. Therefore, oxide semiconductors have been attracted for leading candidates for bio-FET with high chemical resistance against the bio-materials compared to one- and two- dimensional (1D and 2D) materials. Also, oxide semiconductors based bio-FETs have been attracted much attention for high sensitivity due to low off current characteristics. The low off current (< 10⁻¹² A) of oxide FETs guarantee high signal-to-noise ratio in biosensor
because they have large changes before and after sensing. In this study, we suggest a facile approach to fabricate highly sensitive and durable biosensors based on a bio-mimetic structure (i.e. spongia officinalis) of the oxygen plasma-treated porous indium–gallium–zinc oxide (IGZO):polytetrafluoroethylene (PTFE), which is PIP, thin–film layer. The PIP layer could be easily deposited by co-sputtering process and oxygen-plasm etching. Through this fabrication process, we were able to discuss two effects of the technique on the PIP film: 1) It is possible to drastically higher the surface area of the PIP layer utilizing the oxygen-plasma because the PTFE was selectively etched by oxygen-plasma process, which results in a porous of the PIP surface. 2) Improvement of hydrophilicity through the oxygen-plasma process of the PIP layer with free radical species formed by chemical etching. Due to the two effects mentioned above, the PIP layer could more easily be functionalized for surface silanization compared to conventional IGZO layer. In conclusion, to test the IGZO with the PIP layer for bio-FET, we investigated molecular detection of the pH and the neurotransmitter nitric oxide, which is known to induce in dementia, using an aptamer. As a result, the pH sensor with ultra-high sensitivity (1 pH−1) as well as a small limit of detection (0.001 pH) was demonstrated. Furthermore, specific detection of nitric oxide also was demonstrated, and an extremely low limit of detection (< 10fM) was achieved in 0.1× phosphate-buffered saline solution.

5:10 AM S.SM04.02.02
Chemical to Electrical Transduction Using Floating Gate Organic Electrochemical Transistors Siew Ting Melissa Tan, Alexander Giovannitti and Alberto Salleo; Stanford University, United States

Organic Electrochemical Transistors (OECTs) have been investigated as biosensors and logic circuitry due to their biocompatibility and large transconductance [1]. Minute perturbations in gate potentials enable significant changes in channel conductance, allowing OECTs to transduce weak potential changes in biological systems into large current modulations. They can additionally be used in sensing of metabolites enabled by enzymatic reactions [2]. While simple in design, the operation of OECTs still requires independent power and synchronized control of the gate and source-drain voltages, hindering the simplification of supporting control circuits. Furthermore, performing a chemical reaction within the electrolyte of the OECT can be challenging due to effects arising from electrochemical side reactions with both the gate and channel materials.

We demonstrate the development of an OECT that transduces a chemical signal (e.g. oxidation reaction) into an electrical signal (e.g. change of the conductivity of the channel material). To achieve this, the chemical reaction is isolated on a floating-gate, which acts as the chemical-to-electrical transducer for the electrochemical redox-reaction in the OECT. This approach eliminates the need for controlling the gate potential externally, simplifying device operation. We utilize a redox-active polymer on the floating-gate that is sensitive to hydrogen peroxide, intentionally produced by Oxidase enzymatic reactions, to generate a concomitant potential change on the gate of the OECT that modulates the conductivity of the channel material. Investigating different redox-active polymers, we elucidate several design criteria for the floating-gate and OECT channel to optimize the current moduluation and amplification of these chemically gated OECTs. Adopting this approach, we achieve large changes in OECT source-drain current of up to three orders of magnitude and demonstrate its versatility by detecting a diverse range of biomolecules spanning glucose to lactate or alcohol. This approach can be further generalized to other Oxidase enzymatic reactions that produce hydrogen peroxide. By harvesting the chemical potential energy of abundantly available biomolecules, the control circuitry and operation of next generation OECT biosensors can be simplified by solely supplying a single source of power.


5:20 AM *S.SM04.02.03
Ultra-Thin Organic Photovoltaics and Sensors for Wearable Sensors Kenjiro Fukuda1, Tomoyuki Yokota2, Zhi Jiang1, Sunghoon Lee1, Wenchao Huang2, Hyunjae Lee1 and Takao Someya1,2; 1RIKEN, Japan; 2The University of Tokyo, Japan

One of an important target application of biointegrated electronics is wearable sensors that enable accurate and continuous detection of physiological signals. These devices require conformable and biocompatible sensors and power source to continuously supply electricity to health-monitoring systems. In this talk, we will report on recent progresses of ultraflexible organic photovoltaic cells as power sources and wearable sensors. First, the progresses of power conversion efficiency (PCE) and mechanical/long-term stability of ultraflexible organic photovoltaics have been achieved using new material and process engineering. The certified PCE of 12.3% for the ultra-flexible organic photovoltaic cell has been achieved with novel ternary blend active layer [1]. Second, long-term continuous monitoring using organic electrochemical transistors with nonvolatile
Bio-Derived, Green Electronics Made from Microbially Produced Protein Nanowires

Jun Yao; University of Massachusetts Amherst, United States

Protein nanowires harvested from microbes are a revolutionary green electronic material. They have unique properties for novel electronic devices with improved performance, for a broad range of applications from energy harvesting to neuromorphic computing and sensing. (1) Thin-film protein nanowire devices were shown to continuously harvest electricity from ambient humidity (*Nature* 578, 550-554 (2020)), enabled by the unique structural (*e.g.*, nanopores at wire-wire interface) and chemical (*e.g.*, a high density of hydroscopic groups) properties. This leads to a continuous energy harvesting mechanism from the ubiquitous and enormous ambient humidity, and hence a promising strategy to powering self-sustained systems. (2) The protein nanowires are cleverly designed and recruited by the microbe to facilitate charge exchange with environments (*e.g.*, through redox metallization). Thus, protein nanowires can be assembled into bio-dielectrics to construct memristor devices, in which the protein nanowires catalytically reduce the energy barrier involved in memristive switching and enable ultralow operational voltage in the biological regime of <100 mV (*Nature Commun*. 11, 1861 (2020)).

Neuromorphic components (*e.g.*, artificial neuron, synapse) made from the protein nanowire memristors take a further step in bio-emulation from functional emulation to parameter matching, creating opportunities for future ultraslow-power electronics and bioelectronic interfaces. (3) Protein nanowires have ultra-small diameters (3 nm) and an ultra-high density of surface functional groups (*e.g.*, 10 per nm) that are advantageous for sensing applications. Electronic sensors made from protein nanowires were shown to have enhanced selectivity and sensitivity (*Nano Res*. 13, 1479-1484 (2020)) for ammonia detection compared to inorganic nanowire devices. These studies, combined with the advantages of renewability, biocompatibility, and eco-friendliness in protein nanowires, have provided the starting point for future green electronics based on synthetic protein nanowires.
of NGF-β can then be employed to observe morphological change of PC12 cells.

In conclusion, we will discuss a system which may allow interfacing with electroactive tissue by adopting controlled electrical and biochemical cues.

5:55 AM *S.SM04.02.07
Fish-Eye-Inspired Wide Field-of-View Camera Dae-Hyeong Kim1,2; 1Institute for Basic Science, Korea (the Republic of); 2Seoul National University, Korea (the Republic of)

Although recent efforts in device designs and fabrication strategies have resulted in meaningful progresses to the goal of novel high-performance imaging devices, significant challenges still exist in developing a miniaturized and lightweight camera that enables the wide field-of-view (FoV) imaging. This is mainly due to bulky and heavy multiple lenses employed in the conventional wide angle camera. In this work, inspired by structural and functional features of the aquatic vision, we have developed a novel wide FoV camera by integrating a tailored monocentric lens and a hemispherical silicon nanorod photodetector array. This bioinspired camera offers the wide FoV, a miniaturized module size, minimal optical aberrations, the deep depth-of-field, and the enhanced light sensitivity in one simple integrated device. Theoretical analyses in conjunction with imaging demonstrations have corroborated the validity of the proposed concept. The fish-eye-inspired camera is expected to provides new opportunities for the advanced mobile electronics.

SESSION S.SM04.03: Fundamental Materials and Devices for Biointegraed and Bioinspired Electronics
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-SM04

5:00 AM *S.SM04.03.01
Bioelectronics with Nanocarbons Tzahi Cohen-Karni; Carnegie Mellon University, United States

We focus on developing a new class of nanoscale materials and novel strategies for the investigation of biological entities at multiple length scales, from the molecular level to complex cellular networks. Our highly flexible bottom-up nanomaterials synthesis capabilities allow us to form unique hybrid-nanomaterials. Recently, we have demonstrated highly controlled synthesis of 3D out-of-plane single- to few-layer fuzzy graphene (3DFG) on a Si nanowire (SiNW) mesh template. By varying graphene growth conditions, we control the size, density, and electrical properties of the NW templated 3DFG (NT-3DFG). This flexible synthesis inspires formation of complex hybrid-nanomaterials with tailored optical and electrical properties to be used in future applications such as biosensing, and bioelectronics. For example, we have developed a unique bioelectrical platform based on 3DFG and have demonstrated, for the first time, recording of the electrical activity of excitable cells using ultra microelectrodes ranging from 10µm down to 2µm, without the need of any surface coatings. Currently, we target the limits of cell-device interfaces using out-of-plane grown 3DFG, aiming at electrical recordings with subcellular spatial resolution (<5µm) and µsec temporal resolution. In summary, the exceptional synthetic control and flexible assembly of nanomaterials provide powerful tools for fundamental studies and applications in life science and open up the potential to seamlessly merge either nanomaterials-based platforms or unique nanosensor geometries and topologies with cells, fusing nonliving and living systems together.

5:15 AM *S.SM04.03.02
Soft Tissue-Like Rubbery Electronics and Integrated Systems Cunjiang Yu; University of Houston, United States

While human organs and tissues are mostly soft; conventional electronics are hard. Seamlessly merging electronics with human is of imminent importance in addressing grand societal challenges in health and joy of living. However, the main challenge lies in the huge mechanical mismatch between the current form of rigid electronics and the soft curvy nature of biology. Here, I will present a new form of electronics, namely “rubbery electronics and bioelectronics”, with skin-like softness and stretchability, which is constructed all based upon elastic rubbery electronic materials. These rubbery electronic materials are structured in the format of composites, which can be scalably manufactured from common and commercial available materials without dedicated and complicated synthesis. Specifically, we build nanofibril organic semiconductor and metallic nanowires percolated in the elastomeric polymer matrix in a composite format for the rubbery semiconductors and conductors, respectively. Employing these rubbery electronic materials, we have achieved fully rubber format devices,
including transistors and sensors, logic gates, active matrices, elastic sensory skin systems, and biointegrated devices, etc. I will showcase a few examples including artificial skins, biomedical implants, and wearable applications.

5:30 AM *S.SM04.03.03
Wireless Modular E-Tattoos Chargeable On-the-Go Nanshu Lu; University of Texas at Austin, United States

Soft, noninvasive and multifunctional epidermal electronics (a.k.a. electronic tattoos or e-tattoos) have demonstrated many exciting applications in mobile health, athletic training, human-machine interface (HMI) and so on. However, e-tattoos are only practically useful when they are low cost and wireless. Previously, our group has invented a dry and digital manufacturing approach named the “cut-and-paste” method for the rapid prototyping of e-tattoo sensors using a paper/vinyl cutter plotter [1]. This method has been demonstrated to work for thin film metals [1, 2], various polymer sheets [1, 3], ceramics [4], as well as 2D materials such as graphene [5, 6]. The cut-and-pasted e-tattoos are low cost and can be used to measure a variety of physiological signals such as electrocardiogram (ECG), seismocardiogram (SCG), electrooculogram (EOG), skin hydration, skin temperature, respiratory rate and so on [1-3, 5, 6]. To make the e-tattoos go wireless, we now report the “cut-solder-paste” process to incorporate integrated circuits (ICs) for signal readout and processing, near field communication (NFC) [7], as well as Bluetooth transmission [8]. To overcome the limited patterning resolution of the cutter plotter and to recycle the tattoo layers with ICs, we propose a modular concept in which the wireless charging layer (NFC layer), the wireless communication layer (Bluetooth layer), the readout circuit layer, and the sensor/electrode layer are fabricated individually and stacked up at the final step of fabrication. The thickness of a fully assembled multilayer e-tattoo (excluding IC chips) is less than 300 um and the overall stretchability is still beyond 20%. In addition to already mentioned capabilities, such e-tattoos can also wirelessly track motion, mechanono-acoustic heart signals, and oxygen saturation (SpO2) [3, 7, 8]. The NFC-enabled e-tattoos can be wirelessly charged so no battery is needed but the sampling rate is limited to 25 Hz and the wireless communication distance is limited to 5 cm. The Bluetooth-enabled e-tattoos require on-tattoo batteries but the sampling rate can be up to 4 kHz and the wireless communication range can be up to 10 m. Combining the NFC layer and the Bluetooth layer in one e-tattoo, we demonstrate that such wireless e-tattoo can also be wirelessly charged on-the-go via stretchable fabric feeding coils [8], enabling long-term, ambulatory and continuous sensing. Moreover, we propose that different layers can be disassembled and reassembled multiple times. After disassembly, the electrode layer should be disposed but the other layers can be reassembled into new e-tattoos. The low-cost, rapid prototyping method together with the wireless and reconfigurable capabilities represent exciting advancement towards practically useful wireless e-tattoos.


5:45 AM S.SM04.03.04
A Biohybrid Synapse with Neurotransmitter-Mediated Plasticity Scott T. Keene1, Claudia Lubrano1,3, Setareh Kazemzadeh4, Armantas Melianas1, Yaakov Tuchman1, Giuseppina Polino1,2, Lucio Ciná6, Alberto Salleo1, Yoeri van de Burgt1 and Francesca Santoro2; 1Stanford University, United States; 2Istituto Italiano di Tecnologia, Italy; 3Università degli Studi di Roma Tor Vergata, Italy; 4Cicci Research, Italy

Brain-inspired computing paradigms have led to substantial advances in automation of visual and linguistic tasks by emulating the distributed information processing of biological systems. The similarity between artificial neural networks (ANNs) and biological systems has inspired ANN implementation in biomedical interfaces including prosthetics and brain-
machine interfaces. While promising, these implementations rely on software to run ANN algorithms. Ultimately, it is desirable to build hardware ANNs that can directly interface with living tissue which adapt based on biofeedback. The first essential step towards biologically integrated neuromorphic systems is to achieve synaptic conditioning based on biochemical signaling activity.

Direct communication between artificial and biological neurons is of particular interest because of the vast utility that can be achieved by interacting with the nervous system. In this work, we bridge the gap between artificial and biological neurons by directly coupling an organic neuromorphic device with dopaminergic neuron-like cells to constitute a biohybrid synapse with neurotransmitter mediated plasticity. Voltage pulses at the pre-synaptic electrode drive the oxidation of the excitatory neurotransmitter dopamine, leading to both a short-term potentiation of the channel from ionic drift as well as a long-term potentiation due to the redox reaction with dopamine at the interface.

We elucidate the working principle of the biohybrid synapse by characterizing the electrochemical response of the organic neuromorphic device to dopamine signaling both in solution and in vitro. Furthermore, we use focused-ion beam and scanning electron microscopy to visualize the interface between the living cells and organic postsynaptic electrode. We utilize microfluidic flow across the channel to mimic the dopamine recycling machinery of biological synapses to demonstrate both long-term conditioning and recovery of the synaptic weight. Finally, we report direct translation of dopamine secreted by PC12 neuron-like cells to long-term modulation of the biohybrid synapse memory state, paving the way towards combining neuromorphic systems with biological neural networks.

5:55 AM *S.SM04.03.05
Assembly of Nanoelectronics Via Tissue Development Jia Liu; Harvard University, United States

Tissue-wide electrophysiology with single-cell and single-spike spatiotemporal resolution is critical for biological studies and biomedical applications. In this talk, I will discuss the creation of cyborg organisms: the three-dimensional (3D) assembly of soft, stretchable mesh nanoelectronics across the entire living organism by the cell-cell attraction forces from 2D-to-3D tissue reconfiguration during organogenesis. We demonstrate that stretchable mesh nanoelectronics can migrate with and grow into the initial 2D cell layers to form the 3D organ with minimal impact on tissue growth and differentiation. The intimate contact between the dispersed nanoelectronics and cells enables us to chronically and systematically observe the evolution, propagation and synchronization of the bursting dynamics in different organisms through their entire organogenesis and maturation. I will also discuss the potential applications of these cyborg organisms in biology and biomedicine.

6:10 AM *S.SM04.03.06
Memory and Learning in Biomolecular Soft Matter for Low-Power, Brain-Like Computing Joseph S. Najem; The Pennsylvania State University, United States

The brain carries out complex cognitive and computing tasks by optimizing energy efficiency, information processing, communication, and learning in massively parallel, dense networks of highly interconnected neurons. To cope with its everchanging surroundings, the brain is able to grow neurons, synapses, and connections—owing to its plastic nature. At the molecular and cellular levels, synaptic plasticity and neuronal excitation are the main mechanisms underlying these processes. Therefore, the ability of next-generation computing devices, robots, and machines to autonomously sense, process, learn, and act in complex and dynamic environments while consuming very little power will require approaches to computing and sensing that are inherently brain-like. Reproducing these features using traditional electronic circuit elements is virtually impossible, requiring the design and fabrication of new hardware elements that can adapt to incoming signals and remember processed information. These elements should be scalable, biomimetic, and preferably ionic to achieve energy consumption levels approaching those in the brain. While a major effort is being invested in developing inorganic materials that could emulate synaptic and neural functionalities, I believe that an overlooked, yet high-reward, pathway to success is through the development of biomolecular materials with the composition, structure, and switching mechanisms of actual biological synapses and neurons. Here, I describe two-terminal, biomolecular memcapacitors and memristors, consisting of highly insulating 5 nm-thick lipid bilayers assembled between two water droplets in oil. These devices exhibit memcapacitance that is nonlinearly dependent on the applied voltage as well as hysteresis in the charge due to voltage-driven, reversible changes in the area and thickness of the bilayer membrane. This is the first demonstration of a memcapacitor in which capacitive memory results from geometrical changes in a lipid bilayer membrane. We also show that the incorporation of voltage-activated alamethicin and monazomycin peptides in these devices results in variable ionic conductance across the membrane and memristive behavior. We discuss how these devices exhibit learning through synaptic plasticity, and how to implement them in online learning applications. These results serve as a foundation for a new class of low-cost, low-power, soft mem-elements based on lipid interfaces and other biomolecules for applications in neuromorphic computing which could have
major implications on the robotics and computing fields.

**6:25 AM S.SM04.03.07**

**Magnetic Nanoparticle Sensor for Longitudinal Biomarker Monitoring** Richard J. Murdock\(^1,2\) and Michael J. Cima\(^1,2\); \(^1\)Massachusetts Institute of Technology, United States; \(^2\)Koch Institute for Integrative Cancer Research, United States

Harnessing the diversity of sensing platforms for applications in complex biological and chemical environments has been a challenge in the field of biosensing for many years. Electrochemical, optical, and magnetic techniques have been proposed, most with limitations ranging from biocompatibility, sensitivity, and signal transduction through opaque media, to longevity under non-laboratory conditions. Through advances in core/shell nanobiotechnology, we have developed an implantable diagnostic device for the measurement of biomarkers using a magnetic particle assay. This assay behaves as a platform technology tunable for biochemical monitoring in health, manufacturing, security, agriculture, and veterinary care. Our current applications focus on medical diagnostics in subclinical, chronic, and transient cardiac and cancer disease models with low sampled concentrations or temporary spikes in biomarker presence frequently missed by serial sampling. **In situ** diagnostics offer continuous sentineling of critical biomarkers, providing a deeper understanding of the local biology in heterogeneous systems. This monitoring provides valuable timescale data to clinicians giving them insight into their patients’ lab results for early intervention and data collection throughout treatment. Nanoparticle science, NMR technology, and modern biomaterials are combined in a multidisciplinary approach in this study to improve the diagnostic paradigm in addressing biochemical sensing.

Layered core/shell particles have been designed to detect the presence of specific molecules. Magnetic contrast is made possible by careful selection of the core material while biological functionality is provided by tunable surface ligands (antibodies, complementary DNA, aptamers, etc.) for specific affinity toward multivalent targets. Reversible (current concentration), irreversible (dosimetric, cumulative exposure), and switch (on/off) systems have been tuned by varying the affinity properties of the functionalization layers. We have shown proof-of-concept of a system composed of nanostructured materials easily implantable in vivo for both local and systemic chemical monitoring. Colloidal suspensions are kept at a constant particle concentration within a depot, protected from their environment by a semi-permeable membrane. Target diffusion across the membrane induces a switch from a dispersed to an assembled state with a corresponding change in magnetic properties allowing for robust contrast. Devices are deployed within the subcutaneous space or locally at the site of disease and immediately begin tracking their milieu. Magnetic relaxation measurements taken by Magnetic Resonance Imaging (MRI) and single-sided NMR systems are compared to demonstrate the feasibility of implementation in clinic-based and point-of-care, resource-limited settings.

Depot usable lifetime and nanostructure degradation are key parameters in multi-month applications. Recent work in tuning surface chemistry and bioconjugation strategies has enhanced the performance of the switch-based system by an order of magnitude over prior studies, increasing the expected lifetime to over 29 weeks in elevated temperature experiments. Progress in biomaterial capsule development has also shown promise in the deployment of a controlled degradation system with the added benefit of minimally invasive implantation compared to previous surgical placement methods. Overall this implant has the potential to broaden diagnostics in personalized medicine by addressing the hurdles of longevity and robust sensor signal stability in complex environments.

**SESSION S.SM04.04: Novel Interfaces for Biointegrated and Bioinspired Electronics**

On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

**5:00 AM S.SM04.04.01**

**Elucidating and Replicating Topography-Based Chemical Crypsis in the Puff Adder and Related South African Snake Species Via Micron Scale 3D Printing and Multidimensional Fourier Analysis** Rachel Miller\(^1\), Stephen Lee\(^2\) and Robert Shepherd\(^3\); \(^1\)Cornell University, United States; \(^2\)U.S. Army Research Laboratory, United States

Humans have been studying and mimicking animals’ visual crypsis using wearable camouflage since the 18th century. Yet, only recently we have documented and attempted to understand the origins of chemical crypsis, the ability to become
imperceptible to olfaction. Specifically this work aims to elucidate the mechanism of chemical crypsis in the first vertebrate shown to exhibit this trait, a snake known as the puff adder (Bitis arietans). Extensive behavioral and ecological studies show that puff adders are well evolved to be chemically imperceptible to predators, prey, and even potential mates without the capability to modulate pheromone molecular weight, produce odorant counteracters, or eliminate skin odorant sources such as bacteria. Therefore we turned to the skin surface structure, the major feature distinguishing the puff adder from its non-cryptic brethren such as the night adder (Causus rhombeatus). The skin’s micron-scale, high aspect ratio, curved features known as ‘fingers’ create an array of wells for odorants to pool, significantly reducing odorant volatility and therefore rendering the puff adder imperceptible to smell. To study and quantify this phenomena independent of snakeskin material, snakeskin surface biomes, and environmental contaminants, we employ various imaging and 3D printing processes to create a variety of detailed and accurate scaled models of both the puff adder skin and night adder skins. Nano-focused computed tomography (nano-CT) is used to create three-dimensional renderings of skins. To maximize accuracy of replicas, nano-CT image segmentation is informed by focused ion beam (FIB) and scanning electron microscopy (SEM) images. These digitally rendered surfaces are printed in urethane methacrylate or other acrylic using 3D printing. 90:1 models are printed using projection stereolithography (SLA) for millimeter resolution while 1:1 models require the use of two photon polymerization for micron scale feature resolution. 2D Fourier transforms of 2D slices examined along the third axis in real space in addition to 3D Fourier transformes are used to pinpoint key frequencies present in cryptic versus non- cryptic snakes. This analysis is used as a means to quantify periodicity and investigate the degree of quasi-ordered orientation as a predictor for surface thermodynamic phenomena. Physical experiments on printed models and topographical analysis of digital renderings are used together to analyze the effects of structure periodicity and surface-area-to-volume ratio on adhesion, wetting, and evaporation.

5:10 AM S.SM04.04.02
Dry Sensor with Strong Self-Adhesion to Hairy Skin for Contact Mode Bio-Signal Recording Abhijith Balamuraleekrishna Shyam, Anan Zhang, Alexandra Cunningham, Marianna Kontopoulou, Aris Docoslis and Shideh K. Ameri; Queen’s University, Canada

One in four people are affected globally by mental and neurological disorders during their lives. There is a stigma towards mental disorders and therefore, most of such issues remain undetected. Electroencephalography (EEG) is noninvasive recording of brain signals. Numerous studies suggest the correlation between electroencephalography (EEG) signals, and mental state. Conventional EEG systems are bulky and stationary which make them unstable for continues ambulatory measurements. Further, accurate EEG measurements, used for diagnosis, requires medical experts and is done in medical centers, which makes it time consuming and costly. In order to overcome these challenges and make the mental health monitoring accessible and low cost, wearable sensors are highly desirable. Here, we report a novel long-term wearable, dry, miniaturized self-adhesive sensor (DSAS). It can firmly adhere to hairy scalp without the use of any adhesive, gel or mechanical support and be used for high quality EEG recording with low motion artifacts. DSAS is a reusable and soft sensor that can be simply attached and detached. It consists of the arrays of low-density tulip-like microstructures made of PDMS-conductive-filler composite (graphene and carbon nanotube) that deploy between the hairs and stick to the scalp. Each tulip-like microstructure consists of a long stem (400-450 µm) and a micro-suction cup head (200-300 µm diameter). DSAS adhere to any surface including hairy skin by accumulative work of adhesion force, generated by forming negative pressure in each micro-structure. Negative pressure is generated when microstructures in DSAS are pressed against a surface and the air is pushed out of micro-suction heads. DSAS is made by a novel scalable fabrication process and comprehensive theoretical studies were performed for the optimization of the fabrication process. Our results suggest that each tulip-like microstructure produces 12 mN adhesion force. The cups’ shell wall in the tulip-like microstructure head is 15 µm thick and ultra-soft which allows forming conformal contact to the rough surfaces such as skin and prevents leaking the air into the interface between sensor and surface after attaching it to skin. An array of just 100 per cm² microstructures in DSAS can hold 120 gm of weight for extended amount of time and maintains the adhesive properties up to 15 attach-detach cycles.

5:20 AM S.SM04.04.04
Epidermal Antenna-based Sensor for Pervasive Healthcare Zhibo Chen and Jie Hu; Hong Kong University of Science and Technology, Hong Kong

While individual epidermal sensors present a good compromise between comfortability, affordability, and functionality, the assembly of soft electronics adds a performance sacrifice and a cost overhead to the sensor system manufacturing process – especially when interfacing these with wireless communication and data processing. The more functionalities, the more rigid components involved. Therefore, it is a big challenge to compromise between soft individual components and rigid integrated circuits. Even though some reports have shown promising fundamental soft electronics solutions, such as transistor and diode, etc., the epidermal sensor system is still trapped in an early-stage analog level due to the sophisticated Von Neumann
A novel far-field wireless epidermal pressure sensor system is presented here. The sensor which changes in the antenna electrical parameter is mapped to the changes in the properties of the electromagnetic wave propagation. This mechanical – electrical conversion manifests itself as a controlled sensing method from the signal response of the antenna device. Signal processing is demodulated from the reader side, making the epidermal pressure sensor a passive parasitic component in the antenna. This allows the sensor to directly leverage and benefit from concurrent advancements in wearable antenna research and conductive elastomer development while seamlessly extending to the pervasive low-cost wireless sensing applications.

Besides, an example of this approach will be presented in detail, including the design of the PDMS-based on-body sensor antenna and the signal response of Sub 1 GHz microstructure-based epidermal pressure sensor, etc. All key processing parts share the same on-body packaging, therefore enabling a chip-scale technology that can be designed in different elastic packaging forms. This unique sensor concept can lead to new applications and lead the pervasive epidermal healthcare sensing to a new level.

SESSION S.SM04.05: Novel Devices for Biointegrated Electronics

On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

5:00 AM S.SM04.05.02

Unusually Conductive Organic-Inorganic Hybrid Nanostructures Derived from Bio-Inspired Mineralization of a Peptide/Pi-Electron Assembly Taein D. Lee, Sayak S. Panda, John D. Tovar and Howard E. Katz; Johns Hopkins University, United States

Highly efficient charge-transport phenomena in biological systems ignited researchers’ interest to investigate the conductivity of biologically relevant macromolecules processed from aqueous solution. Self-assembling peptides and proteins are of particular interest due to their ease of synthesis and tunable side chains. Polypeptides have been designed and synthesized for self-assembly and charge delocalization of organic pi-electron systems. Of these, peptide-π conjugated materials form robust 1D nanostructures with tunable electronic and photonic properties while retaining significant conductivity and mobility. Electronic and photonic properties of π-conjugated oligopeptides can be tuned by incorporation of electron withdrawing and electron accepting chromophores in the peptide chains. Oligothiophenes are also one of the standard organic semiconductor subunits investigated for semiconducting properties of π-conjugated peptides. However, peptide-based charge transporting materials still suffer from relatively low conductivities due to the large insulating peptidic regions, posing a challenge for characterization of electrical transport pathways in biologically relevant materials.

Here, we investigated 1D nanostructures and electrical properties of a peptide-π-peptide oligopeptide self-assembly composed of peptides, HCl, and KOH in aqueous solution. Using supramolecular systems, oligomers with central chromophore groups with non-polar amino acid side chains plus one glutamic acid were self-assembled into macrostructures via pH triggering. In order to decouple the amino acid side chains from the chromophores, 3- carbon spacers were added in between them on both sides. Using KOH to dissolve the oligomers and subsequently exposing them to HCl vapor triggered self-assembly via pH change leading to protonation of glutamic acid, as well as biomineralization of KCl, presumably initiating at the glutamic acid. Together, the self-assembly achieved by formation of β-sheets, π-orbital overlaps and biomineralization formed highly interconnected dendritic structure given conditions with well-balanced kinetic and thermodynamic contributions. The solution conditions with HCl exposure enabled biomineralization of KCl nanocrystals templated by the glutamic acid in the underlying oligopeptides prior to self-assembly, resulting in a synergy of self-assembled peptides and biomineralized KCl to form supramolecular structures.

Electrical measurements indicated that these interconnected dendritic structures were highly conductive systems with conductivities comparable to that of a metal at around 1800 S/cm for samples with robust dendritic pathways. About 50 mA current was measured for 0.5 V at drain. Varying the gate V, however, had no effect on the current levels indicating a conductive material instead of a semiconducting material. Various experiments showed the conductivity of these systems were derived from proton doping of chromophores in strong acid environment in addition to closely fixated chromophores from the biomineralized KCl leading to easily transferred π-electrons along the interconnected dendritic pathways. Shelf-life tests showed that the conductive pathways degraded about 90% after 6 weeks; the KCl crystals formed around the self-
assembled structures further functioned as a protective layer to dedoping of protons as well as preventing disintegration of the closely packed chromophores. Our findings suggest that in supramolecular systems, biomineralization triggered with appropriate amino acids combined with self-assembly can be used as a template to grow highly conductive dendritic macrostructures as well as control nanowire growth in specific directions.

5:10 AM *S.SM04.05.03
From Functional Nanomeshes to Advanced Soft Microsystems Hui Fang; Northeastern University, United States

New form of materials can often enable new device and system applications. In this talk, I will highlight our group's recent work under this motivation in two synergistic areas. Firstly, by stacking individual layers of polymer, metal, and low-impedance coating reliably in a same nanomeshed pattern, the final multilayer multifunctional nanomeshes achieved system-level performance from all individual layers, in addition to nanomesh advantages. Compelling demonstrations from this multifunctional nanomesh approach include high-performance transparent and flexible neuroelectrode arrays, which has been recently validated in vivo. The second part of my talk will introduce our recent concept on semiconductor nanomeshes. By making a silicon film into homogeneous nanomeshes, we achieve high mobility semiconductor that is intrinsically stretchable to conventional microelectronic layouts. Together, our work demonstrates that nanomeshing is a unique way of transforming microelectronics for emerging applications.

5:25 AM S.SM04.05.04
Flexible Carbon Nanotube Synaptic Transistor for Neurological Electronic Skin Applications Haochuan Wan, Li-Wei Lo and Chuan Wang; Washington University in St. Louis, United States

There is an increasing interest in the development of memristive or artificial synaptic devices that emulate the neuronal activities for neuromorphic computing applications. While there have already been many reports on artificial synaptic transistors implemented on rigid substrates, the use of flexible devices could potentially enable an even broader range of applications. In this talk, we report high performance synaptic thin-film transistors (TFTs) built on ultrathin flexible substrate using high carrier mobility semiconducting carbon nanotubes (CNTs). The synaptic characteristics, including spike amplitude-dependent plasticity, long-term/short-term plasticity (LTP/STP), spike-number dependent plasticity (SNDP), spike-timing dependent plasticity (STDP) have all been systematically characterized on the flexible synaptic CNT TFT. Moreover, we have demonstrated an individual pixel circuit that may be used to construct a flexible neurological electronic skin in the future. The circuit comprises a flexible ferroelectret nanogenerator (FENG) serving as the sensory mechanoreceptor that generates action potentials to be processed by the artificial synapse. In such a system, the flexible FENG sensor converts the tactile input (the magnitude and frequency of force) into presynaptic action potential pulses, which are then passed to the gate of the synaptic transistor to induce change in its drain current (post-synaptic current), mimicking the modulation of synaptic weight in biological synapses. The single pixel circuit closely emulates the behavior of actual human skin and it allows for instantaneous detection of force stimuli and offers biological synapse-like behavior to relay the stimuli signal to the next stage. It could be further integrated into an array to achieve a neurological electronic skin with synaptic behavior and memory capabilities, which could potentially be used to interface with skeletal muscle fibers for applications in neuroprosthetic devices.

5:35 AM S.SM04.05.05
Selective Eradication of Bacteria by a Flexible Bacterial-Imprinted Electronic Chip Liwei Hui, Parmila Kafley and Haitao Liu; University of Pittsburgh, United States

Pathogen invasion not only release toxins to attack mammalian cells, but also colonize and disturb the balance of healthy microbiome. Therefore, it is desirable to develop antibacterial methods that target specific bacteria. Here we show a strategy to selectively immobilize bacteria on surface to allow its eradication by electricity. We designed a flexible PDMS chip that has been imprinted with bacteria and with integrated electrodes. The chip could selectively capture the target bacteria to the surface by shape complementarity. Upon applying a low voltage, we observed a fast killing of bacteria in real time. The work suggests a new approach to design intelligent antimicrobial devices that are suitable for use on microbiota sites.

5:45 AM S.SM04.05.06
MXene Ink-Infused Bioelectronic Interfaces Enabled by Rapid Laser Machining Nicolette Driscoll1,1,2, Nicholas Apollo1,1,2, Brian Erickson1, Brendan B. Murphy1,1,2, John Medaglia2 and Flavia Vitale3,1,2; 1University of Pennsylvania, United States; 2Corporal Michael J. Crescenz VA Medical Center , United States; 3Drexel University, United
In recent years, there has been tremendous interest in developing new technologies enabling the seamless integration of electronics with soft biological tissues. This has required significant innovation in materials and fabrication strategies to develop bioelectronic interfaces which are soft, biocompatible, and highly conformable to the tissue of interest. Many of the most successful technological advances in this realm so far have leveraged traditional metal and silicon materials along with thin-film microfabrication strategies to create highly flexible and conformable bioelectronic interfaces. While these thin-film technologies have been shown to achieve exquisite tissue conformability, one of their primary limitations to achieving clinical translation and widespread use is the high cost and low scalability of the materials and fabrication methods. Here, we present a novel process for rapid, low-cost, and highly scalable manufacturing of flexible bioelectronic interfaces by leveraging the electronic, physical, and chemical properties of Ti$_3$C$_2$ MXene. In this process, a laser-patterned cellulose-polyester blend substrate is infused with a water-based ink of Ti$_3$C$_2$ MXene to generate a bulk conductive composite which is subsequently encapsulated in thin layers of flexible silicone elastomer. This method is highly customizable, and allows manufacturing of electrode arrays of different scales and geometries for recording a wide range of bioelectronic signals, including scalp electroencephalography (EEG), electromyography (EMG), electrocardiography (EKG), and electrocorticography (ECoG). We have thoroughly characterized the electrochemical and mechanical properties of the MXene-textile electrodes at varying diameters, and validated their impedance and recording properties in vivo in a range of biosensing and stimulation applications. Enabled by the high conductivity and capacitance of Ti$_3$C$_2$ MXene, as well as the high effective surface area of the porous MXene interface, these electrodes show remarkably low electrochemical impedance both in saline (1 kHz |Z| 205.6 ± 11.1 Ω, 3mm MXene vs. 287.3 ± 7.8 Ω, 2.3mm Pt) and on human skin (1 kHz |Z| 6.2 ± 4.1 kΩ, 3mm MXene vs. 3.62 ± 0.6 kΩ, 1cm gelled commercial electrodes, Natus Inc.). Particularly interesting for epidermal sensing applications, our mm-scale dry MXene electrodes achieve comparable electrode-skin interface impedance and recorded signal quality compared to cm-scale gelled electrodes, which enables recording with higher spatial resolution as well as improving subject comfort and long-term recording capabilities by avoiding the need to use conductive gels. We demonstrated this advantage through EEG recording on a healthy human subject, where our mm-scale electrodes produced signals which were indistinguishable in signal-to-noise ratio, spectral content, or magnitude from a standard cm-scale gelled Ag/AgCl EEG electrode placed next to the MXene array. The MXene electrodes also exhibit extremely high cathodal charge storage capacities (901.5 ± 38.4 mC cm$^{-2}$, 500μm MXene vs. 105.2 mC cm$^{-2}$, 200μm PEDOT:PSS on Pt) and charge injection capacities (2.4 ± 0.5 mC cm$^{-2}$, 500μm MXene vs. 1.4 mC cm$^{-2}$, 200μm PEDOT:PSS on Pt), which make them a promising candidate for delivering electrical stimulation. Finally, we have demonstrated the compatibility of the MXene electrodes with both MRI and CT imaging, due to the low magnetic susceptibility and low density of the electrode materials. The work presented here is a platform technology, enabling rapid and low-cost manufacturing of bioelectronic interfaces by leveraging the unique properties and solution-processability of Ti$_3$C$_2$ MXene.

**5:55 AM *S.SM04.05.07**

**Insertion Mechanics of Microscale Devices into the Brain** Nicholas Melosh and Abdul Obaid; Stanford University, United States

Microscale electrodes, on the order of 10-100 μm, are rapidly becoming critical tools for neuroscience and brain-machine interfaces (BMIs) for their high channel counts and spatial resolution, yet the mechanical details of how probes at this scale insert into brain tissue are largely unknown. Here, we discuss quantitative measurements of the force and compression mechanics together with real-time microscopy for insertion of a systematic series of microelectrode probes as a function of diameter (7.5–100 μm and rectangular Neuropixels) and tip geometry (flat, angled, and electrochemically sharpened), within phantoms, ex vivo and in vivo. Results from each model system elucidated the role of tip geometry, surface forces, and mechanical scaling with diameter. Surprisingly, real-time microscopy revealed that at small enough lengthscales (<25 μm), blood vessel rupture and bleeding during implantation could be entirely avoided. This appears to occur via vessel displacement, avoiding capture on the probe surface which led to elongation and tearing for larger probes. We propose a new, three-zone model to account for the probe size dependence of bleeding, giving a new conceptual framework for how blood vessels fail and provide guidance for probe design.

**6:10 AM S.SM04.05.08**

**Biodegradable, Wireless Electroceutical for Accelerated Regenerative Medicine** Jio Kim, Sung-Geun Choi and Seung-Kyun Kang; Seoul National University, Korea (the Republic of)

Biodegradable systems are critically important in regenerative medicine since complete systems must be replaced by new tissues and organs. Biodegradable or transient electronics provide the electrical functionalities for typical biodegradable
regenerative materials that are generally used in tissue engineering like scaffolds and metal joints. The wireless electrical stimulator made of completely biodegradable materials proposed here can accelerate the regeneration of injured nerve and dissolve away. Passive electrode and capacitors were constructed using biodegradable metal Mg and dielectric SiO2 on a flexible PLGA substrate. Doped Si nanomembranes were used as diodes to rectify the stimulating pulse into monophasic form. Animal demonstrations showed the functional recovery of transected peripheral nerves by monitoring the EMG, muscle mass and force for up to three months.

SESSION S.SM04.06: Fabrication Innovations and Devices for Biointegrated and Bioinspired Electronics
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-SM04

5:00 AM S.SM04.06.01
PVDF-TrFe/PDMS Composite with Inkjet Printed PEDOT:PSS Electrodes for Flexible Sensing Andrew Closson, Lin Dong, Haley C. Richards and John X. Zhang; Thayer School of Engineering, United States

The development of soft and highly flexible electronics enables seamless interfaces with biology, with applications ranging from implantable medical devices to wearable sensors for health monitoring. Piezoelectric polymers have demonstrated superior performance compared to standard ceramic piezoelectric materials however, these polymer-based devices still require metallic electrodes, patterned through photolithography techniques which are time and resource intensive. Here we aim to fill this gap with inkjet printing, an iterative, low-cost, and scalable fabrication method for patterning polymer electrodes. Specifically, we developed an inkjet printing process, with over 500cm² printable area and linewidth resolution of 100 µm, able to print a patterned 5 cm² polymer electrode layer in minutes. The polymer electrodes showed a layer dependent conductivity with a high conductivity of 5.4*10⁻³ S/cm at 10 layers. Utilizing this technology, we developed a flexible piezoelectric PVDF-TrFEPDMS composite, with inkjet-printed patterning of a conductive PEDOT:PSS electrodes on either side of the piezoelectric material. Further, we are able to create a flexible sensor array. For a single 1 cm² element, voltage peak-peak output was measured over a range of forces giving a sensitivity of 258 mV/N, which outperforms many PVDF based force sensors in the literature. The 2x2 piezoelectric array is able to detect localized force, with a 12.5x greater output on the pressed element versus the output from adjacent untouched elements, even though they share the same substrate. This result is significantly higher than that seen in Piezoelectric-OSFET arrays for tactile sensing in the literature. For wearable health monitoring applications, we have shown the ability to detect a resting heart rate of 55 bpm from the carotid artery. This study develops a promising scalable method for high-throughput fabrication of polymer-based piezoelectric sensors on a laboratory scale that can be selectively patterned with inkjet technology.

5:10 AM S.SM04.06.02
Rapid Prototyping of Microfluidic Devices With Versatile Geometries and Functionalizations by Aerosol-jet Printing Nordin Catic and Sohini Kar-Narayan; University of Cambridge, United Kingdom

Microfluidic devices can be used as powerful analytical tools for biology, ranging from drug discovery to medical diagnostics, requiring only small sample volumes for testing. Such devices enable the scaling down of reaction volumes so that a small amount of material is required and the time for testing is reduced. The ability to perform a suite of diagnostic tests on a single device, with minimal reagents, is a major goal of ‘lab-on-a-chip’ research. For more than 20 years, microfluidic technology has promised to deliver such devices and thereby revolutionize biological and chemical research.

However, the impact of this technology has yet to be fully realized, with plenty of room for innovation[1]. Currently, the microfluidic channels in most devices play a passive role and are simply used to direct flow. The ability to “functionalize” the channels would impart greater use of these channels, by incorporating functional materials directly within the channels that can partake in, guide or facilitate the reactions taking place. Integrating functional materials could also serve to introduce new sensing functionalities within the channels themselves. At the same time, rapid prototyping of microfluidic devices is beneficial in a research environment, yet the high cost, slow turnaround and wasteful nature of the current techniques severely impede the development process. Finally, the lack of portability of the associated detection mechanisms, such as the complex optical microscopes typically employed, makes the ‘lab-on-a-chip’ aspect a moot point. The requirement of complex microscopes and equipment to drive and detect changes within microfluidic channels limits the range of applications of such devices.
Here, we demonstrate for the first time, the use of Aerosol Jet Printing (AJP) to produce bespoke molds for microfluidic devices, as well as functionalized microfluidic channels. We show that such an advanced microscale additive manufacturing method can be used to rapidly design cost-efficient and customized microfluidic devices, and add “functional” coatings while simultaneously embedding sensors and active elements on the same platform for electrical detection. Such functionalized microfluidic biosensors could become a transformative tool in biological and bio-medical research, with potential impact in areas such as drug screening, point-of-care diagnostics, and pharmacology. By using an AJP, these sensors can be localized to specific parts of the microfluidic device for constant monitoring and feedback using integrated electrical detection methods, without the need for complex equipment.


5:20 AM *S.SM04.06.03
Rehealable, Recyclable and Reconfigurable Electronics Based on Dynamic Covalent Thermoset Jianliang Xiao;
University of Colorado, United States

Dynamic covalent thermosets show superior properties, including self-healability, recyclability, malleability/reprocessability, thanks to the molecular level bond exchange reactions. These properties promise bright future of dynamic covalent thermosets in broad applications. We here report our work on dynamic covalent thermoset-based electronic systems that are rehealable, recyclable and reconfigurable. A flexible multifunctional electronic device that integrates electrocardiograph (ECG), temperature, motion, and acoustic sensing capabilities was demonstrated. It was exhibited that the rehealed and recycled devices showed electronic performance comparable to the original ones. Bond exchange reactions in the polymer network effectively relaxes stresses induced by mechanical deformation, which made it possible to reconfigure the flexible device into different configurations that are suited for different applications. Such rehealable, recyclable and reconfigurable electronics provides an approach to address sustainability and environment issues associated with mass production of electronics. It can find broad applications in prosthetics, health care, and human-computer interface and other areas that are hard to be addressed by conventional approaches.

5:35 AM *S.SM04.06.04
3D Printing Electronics Directly on the Body Michael C. McAlpine; University of Minnesota, United States

The ability to directly print biomedical devices on the body could benefit patient monitoring, wound treatment, and even allow for the possibility of human augmentation. In reality, this concept requires the 3D printer to adapt to the various translations, rotations, and deformations of the biological surface. Conventional 3D printing technologies typically rely on open-loop, calibrate-then-print operation procedures. An alternative approach is adaptive 3D printing, which is a closed-loop method that combines real-time feedback control and direct ink writing of functional materials in order to fabricate devices on moving freeform surfaces. Here we demonstrate that the changes of states in the 3D printing workspace in terms of the geometries and motions of target surfaces can be perceived by an integrated robotic system aided by computer vision. This allow us to directly 3D print a wireless antenna based on a novel silver ink a free-moving human hand, to power a skin-mounted LED. Using this same approach, cell-laden hydrogels were also printed on live mice, creating a model for future studies of wound-healing diseases. Moreover, we developed an in situ 3D printing system that estimates the motion and deformation of the target surface to adapt the toolpath in real time. With this printing system, a hydrogel-based sensor was printed on a porcine lung under respiration-induced deformation. The sensor was compliant to the tissue surface and provided continuous spatial mapping of deformation via electrical impedance tomography. This adaptive 3D printing approach may enhance robot-assisted medical treatments with additive manufacturing capabilities, enabling advanced medical treatments, and autonomous and direct printing of wearable electronics and biological materials on and inside the human body.

5:50 AM *S.SM04.06.05
Flexible Self−Powered Systems Based on Functional Polymers Ruiyuan Liu1, Zhong Lin Wang2 and Takao Someya1,3; 1Center for Emergent Matter Science (CEMS), RIKEN, Japan; 2Georgia Institute of Technology, United States; 3The University of Tokyo, Japan

Growing demand in advanced portable and wearable electronics raises requirements for the composed materials to be stretchable, conducting or even healable, for which functional polymers are ideal choices. Flexible devices (triboelectric nanogenerators and solar cells) using organic materials for effectively energy harvesting will be firstly presented (1-3). An integration with flexible energy storage components is followed to enable a self–powered system which can simultaneously harvest solar/mechanical energy and store electricity (2-4). These work pave a new direction for functional polymers in the
field of energy harvesting, storage and mechanosensing for potential applications in areas such as soft robotics, biomedical devices, and wearable electronics.


6:00 AM *S.SM04.06.07
Exploring Bioelectric Dynamics at the Soft-Hard Interfaces Bozhi Tian; University of Chicago, United States

Although there are numerous studies on either hard or soft materials, our understanding of the fundamentals at hard/soft interfaces has been limited. As different types of energy (such as electrostatic, mechanical, thermal, and chemical energies) display diverse scaling behaviors and can converge, an appropriate selection of the length scale is critical for promoting new scientific discoveries across these interfaces. Our group integrates material science with biophysics to study several hard/soft interfaces. We synthesize new materials and probe interfacial dynamics, with particular focus at the sub-micrometer and sub-cellular length scales. In this talk, I will focus on the interfaces that enabled non-genetic, freestanding, and semiconductor-based bioelectric modulation. I will also discuss some recent work that exploits the dynamic behaviors of granular materials in polymeric matrices toward bioelectronic and robotic applications. I will end the talk by proposing several new scientific and engineering approaches to improving our fundamental understanding of the (bio)chemical processes at soft/hard interfaces and to exploring new applications of these interfacial (bio)chemical processes.

6:15 AM *S.SM04.06.08
Self-Powered Wearable and Implantable Electrical Stimulation Devices for Therapeutics Xudong Wang; University of Wisconsin--Madison, United States

Electrical stimulation (ES) is a widely used therapeutic treatment strategy. It showed significantly positive results in treating a variety of diseases, biological disorders, and neurological problems. Today, the emergence of wearable devices is rapidly reshaping the development of medical devices, pushing them from conventional bulky and rigid silicon electronics to flexible and primarily polymer-based systems. Among many types of functions, nanogenerators are developed as a unique device for converting biomechanical energy into electrical pulses. In addition to applying it directly as a power source, this pulsed electricity can be applied directly as a ES signal for therapeutic treatment. In our recent research, we successfully implemented such an electromechanical system for skin wound healing and vagus nerve stimulation for obesity control. An electrical stimulation bandage was developed by integrating a flexible nanogenerator and a pair of dressing electrodes on a flexible substrate. Rat studies demonstrated rapid closure of a full-thickness rectangular skin wound within 3 days as compared to 12 days of usual contraction-based healing processes in rodents. From in vitro studies, the accelerated skin wound healing was attributed to the electric field-facilitated fibroblast migration, proliferation and transdifferentiation. In another work, an implanted vagus nerve stimulation system was developed. The device comprises a flexible and biocompatible nanogenerator that is attached on the surface of stomach. It generates biphasic electric pulses in responsive to the peristalsis of stomach. The electric signals generated by this device stimulates the vagal afferent fibers to reduce food intake and achieve weight control. This strategy is successfully demonstrated on rat models. Within 100 days, the average body weight is controlled at 350 g, 38% less than the control groups. Both results bring a new concept in electrical therapeutic technology that is battery-free, self-activated and directly responsive to body activities.

SESSION S.SM04.07: Fundamental Materials and Devices for Biointegrated and Bioinspired Electronics
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-SM04

5:00 AM S.SM04.07.01
Polymerized Liquid Metal Networks for Stretchable Electronics Carl Thrasher, Zachary Farrell, Nicholas J. Morris,
Room-temperature liquid metals, such as nontoxic gallium alloys, show enormous promise to revolutionize stretchable electronics for next-generation soft robotic, e-skin, and wearable technologies. Core–shell particles of liquid metal with various surface-bound ligands can be synthesized and polymerized together to create cross-linked particle networks comprising >99.9% liquid metal by weight. When stretched, particles within these polymerized liquid metal networks (Poly-LMNs) rupture and release their liquid metal payload, resulting in a rapid transformation from insulating to conducting behavior. These networks autonomously form hierarchical structures that mitigate the deleterious effects of strain on electronic performance and give rise to emergent properties. Notable characteristics include nearly constant resistances over large strains, electronic strain memory, and increasing volumetric conductivity with strain to over 20 000 S cm-1 at >700% elongation. Furthermore, these Poly-LMNs exhibit exceptional performance as stretchable heaters, retaining 96% of their areal power across relevant physiological strains. Remarkable electromechanical properties, responsive behaviors, and facile processing make Poly-LMNs ideal for stretchable power delivery, sensing, and circuitry.

**5:10 AM *S.SM04.07.02**

Liquid Metal Embedded Polymers for Soft-Matter Electronics, Actuation and Energy Harvesting [Carmel Majidi](#);
Carnegie Mellon University, United States

Soft polymers that are embedded with nano- and microscale droplets of liquid metal (LM) can be tailored to exhibit a broad range of electrical, thermal, mechanical, and dynamic shape morphing properties. In contrast to lithographically-fabricated soft microfluidic architectures, these LM-embedded soft polymer (LMSP) composites are statistically homogenous and exhibit effective medium properties at the mesoscale. Depending on the choice of polymer matrix, LMSPs can be engineered to achieve a wide variety of properties – from thermally conductive rubber for heat management and thermoelectric energy harvesting in wearable electronics to shape memory materials that dynamically respond to electrical stimulation. Eutectic Ga-In (EGaIn) and Ga-In-Sn (Galinstan) alloys are used as the liquid metal due to their high electrical conductivity, low viscosity, non-toxicity, and the self-passivating formation of an oxide skin (Ga2O3) that enables emulsification and wetting to non-metallic materials. Because they are liquid-phase at room temperature, these alloys have virtually no influence on the mechanics of the surrounding elastomer medium. This allows the resulting composite to exhibit a unique and extraordinary combination of features not seen in other heterogeneous material systems. In this talk, I will review recent experimental and theoretical studies of this unique class of soft material architectures, with specific emphasis on LM-filled liquid crystal elastomers and soft polymers for stretchable electronics and energy harvesting. I’ll also highlight several applications in which LMSPs can have a potentially transformative impact, especially in the domains of wearable computing, physical human-machine interaction, and bioinspired soft robotics.

**5:25 AM *S.SM04.07.03**

Spray-coated Graphene Oxide-Vitamin C Mixtures for the Safe and Efficient Production of Reduced Graphene Oxide Biomolecular Sensors [Brendan B. Murphy](#); Nicholas Apollo, Nicolette Driscoll, Tessa Posey, Nancy Rodriguez-Perez, Quincy Hendricks and Flavia Vitale; 1University of Pennsylvania, United States; 2Corporal Michael J. Crescenz Veterans Affairs Medical Center, United States; 3University of South Carolina, United States; 4Arizona State University, United States

Conductive carbon-based nanomaterials, such as graphene, carbon nanotubes (CNTs), and reduced graphene oxide (rGO), are flexible, corrosion-resistant, and exhibit high electrochemical capacitance, which are ideal properties for probing excitatory neural tissue. The realization of a high-fidelity, multi-modal electrochemical biosensor, which is capable of simultaneously monitoring the electrical and chemical signaling between neurons in a single platform, has been a focus of much research over the past 15 years. To enable such a technology, rGO has been extensively explored, because it can be handled using scalable, solutions-processing techniques starting from aqueous dispersions of its precursor structure, graphene oxide (GO). The oxygen moieties of dried GO films must be reduced in order to restore the film conductivity and a number of methods have been developed to achieve this goal, both in bulk and on an individual film basis. Exposure to hydrazine in vapor form, as well as high temperature annealing, typically at temperatures exceeding 1000 °C, are two of the most common methods to form rGO dried films. However, these methods pose toxicity and safety concerns, and are not compatible with flexible polymeric substrates that typically compose many bioelectronic devices. To address these issues, we have developed a novel, safe, low-temperature, and scalable method of direct GO film reduction using L-ascorbic acid, or Vitamin C, as the reducing agent. Room temperature aqueous mixtures of GO and Vitamin C were loaded into a spray-coating apparatus and deposited onto pre-heated substrates. The influence of Vitamin C concentration and substrate heating time on film conductivity were studied. Using 50 mM Vitamin C and a holding time of 15 minutes at 150 °C, we achieved our lowest sheet resistance value of 354.70 ± 20.52 kΩ sq-1. On average, rGO films were 2.20 ± 0.19 nm in thickness, and thus had conductivities as high as...
12.81 ± 1.75 S cm⁻¹. Using a rapid prototyping method, 3 mm diameter disc-shaped electrodes were made on glass substrates encapsulated in polyimide (PI). These PI electrodes allowed for direct comparison with size-matched glassy carbon (GC) and gold (Au) working electrodes in vitro. Electrochemical capacitances as high as 3.05 mF cm⁻² were achieved by spray-coating GO-Vitamin C onto thin film Au, which is an order of magnitude greater than the capacitances of either bare GC (0.29 mF cm⁻²) or bare Au (0.11 mF cm⁻²). Electrochemical impedance was also observed to decrease as the volume of spray-coated rGO increased, particularly in the frequency range from 0.1–100 Hz. The 10 Hz impedance of rGO electrodes was as low as 0.23 ± 0.15 kΩ, for example, compared to bare Au, which had impedance of 2.78 kΩ at the same frequency. At 1 kHz, the impedances of rGO/Au and Au were 0.13 ± 0.06 kΩ and 0.15 kΩ, respectively. To demonstrate the feasibility of using GO-Vitamin mixtures to realize high-fidelity electrochemical biosensors, the electrocatalytic activity of a handful of biologically relevant molecules was studied, including the direct voltammetric detection of dopamine, ascorbic acid, uric acid, and serotonin. Our novel approach to the production of rGO electrodes offers a safer alternative to chemical reduction using hydrazine or other strong acids, as well as a scalable method which is fully compatible with the soft, polymeric substrates used in state-of-the-art bioelectronic interfaces. Thus, this method enables the development of highly sensitive, biocompatible, and flexible conductive films for applications in fields of biosensors and bioelectronics.

5:35 AM *S.SM04.07.04
Flexible microLED for Bio-Integrated Electronics Keon Jae Lee; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

With the emergence of the internet of things (IoT) era, visual IoT platforms have attracted significant interest, which can offer sensing, collecting, and processing of optical information in hyperconnected society. Flexible displays are a potential candidate for bilateral visual communication, as they can be easily affixed anywhere, such as on the surfaces of human skin, clothes, automobiles and buildings. III-V Inorganic LEDs have superior characteristics, such as long-term stability, high efficiency, and strong brightness compared to OLED. However, due to the brittle property of inorganic materials, III-V LED limits its applications for the flexible electronics. This seminar introduces the flexible vertical GaAs/GaN microLED on plastic substrates using anisotropic conductive film (ACF), resulting high optical power density, The superb properties of the flexible inorganic LED enable the dramatic extension of flexible displays toward not only wearable devices of light source but also full color flexible microLED displays for consumer TV.

MicroLED stimulation of specific neural populations of the brain is one of the facile and reliable methods used in neuroscience for deduction of functional movement, complex behavior and even long-range connectivity. Recent advanced biomedical tools now employ flexible optoelectronic devices combined with optogenetic mouse models to activate small functional regions using blue-light driven channelrhodopsin. Here we introduce flexible vertical light-emitting diodes (VLEDs) for 2D perturbation of specific functional areas of mouse cortex, capable of stimulating motor neurons deep below layer III from the brain surface. Selective operation of pulsed red light from f-VLEDs induces mouse body movements and synchronized electromyogram (EMG) signals. These results show that the III-V based flexible LED can be used as the future flexible implantable biomedical applications such as skin research and phototherapeutic tool.

References (Prof. Lee’s corresponding authors in micro LED)
1. "Bio-Integrated Flexible Inorganic LED", Nanobiosensors in Disease Diagnosis, 1 , 5, 2012
5. "Optogenetic Control of Body Movements via Flexible Vertical Light-Emitting Diodes on Brain Surface", Nano Energy, 44, 447, 2018
10."Optogenetic Mapping of Functional Connectivity in Freely Moving Mice via iWEBS" ACS Nano, 10, 2791, 2016
Recently advances in new materials, electronics, and assembly techniques have allowed optoelectronic systems to interface with biology and contribute significantly to the progress in basic biological research as well as clinical medicine. In this talk, I will introduce a novel class of flexible, multimodal optoelectronic systems that combines high-performance nanoscale electrodes with microscale optical components for simultaneous electrophysiological recording under optogenetic modulation. We envision this unique technology will open up new windows to understanding important biological processes by enabling mapping the dynamics of perturbed cell populations and correlating cellular responses to behavior.

Capillary-Assisted Electrochemical Delamination for Wafer-Scale Fabrication of Ultrathin Flexible Electronics and Degradable Electronics

Constructing electronic systems on ultrathin polymer films is superior to render the system more flexible, conformable, and imperceptible. These characteristics are particularly beneficial for epidermal and implantable electronics. Generally, the system is processed with rigid supporting substrates during fabrication, followed by delamination and transfer to the targeted working areas. The challenge associated with an efficient and innocuous delamination operation is one of the major hurdles toward high-performance ultrathin flexible electronics at large scale. Here, a facile, rapid, damage-free approach is reported for detachment of wafer-scale ultrathin electronic foils from Si wafers by capillary-assisted electrochemical delamination (CAED) with a 100% success rate. Anodic etching and capillary action drive an electrolyte solution to penetrate and split the polymer/Si interface, leading to complete peel-off of the electronic foil. Such a process incurs neither mechanical damage nor chemical contamination; therefore, the delaminated electronic systems remain intact. Via this approach, carbon nanotube (CNT)-based CMOS technology has been realized on a 2.5 μm-thick plastic foil with high performance. The performances of both the p- and n-type CNT thin film transistors (TFTs) are excellent and symmetric on plastic foil with a low operation voltage of 2 V: width-normalized transconductances (gm/W) as high as 4.69 μS/μm and 5.45 μS/μm, width-normalized on-state currents reaching 5.85 μA/μm and 6.05 μA/μm, and mobilities up to 80.26 cm²V⁻¹s⁻¹ and 97.09 cm²V⁻¹s⁻¹, respectively, together with a current on/off ratio of approximately 10⁵. Based on CAED, we also developed a wafer-scale manufacturing process for degradable electronic platforms with an average yield of the transferred TFTs up to 96.6%. Great uniformity was achieved in the transferred TFTs and ICs on each chip and among different chips. Finally, real-time sunlight exposure and temperature monitoring and degradation of the system under artificial rain were successfully demonstrated in a simulated ecosystem outdoors with distributed sensor nodes consisting of TFTs, UV and temperature sensors.

References:

AUTHORS
Namho Kim¹, Junho Lee¹, Moon-Jung Yong¹, Un Yang¹, Ji Tae Kim², Jonghwan Kim¹, Byung Mook Weon¹, Chong Cook Kim¹ and Jung Ho Je¹; ¹Pohang University of Science and Technology, Korea (the Republic of); ²The University of Hong Kong, Hong Kong; ³Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of)

Quantifying humidity has long been an unavoidable task in science, industry, and society. Recent developments of
nanoscience and technology that deal with ultrasmall droplets have aroused interest in microscopic moisture. Utilization of nanomaterials has been emerging as a promising strategy to miniaturize hygrometers for high-sensitive, ultrasmall-area sensing. However, a lack of high-precision, on-demand position control of sensing nanomaterials makes it difficult to explore spatial distribution of humidity at the micro- and nanoscale. Here, we develop a scanning probe hygrometry (SPH) that enables not only micro/nano-resolution but also scalable spatial mapping of humidity distribution. The SPH is realized with an unprecedented scanning nanowire probe interferometer (NPI) that is produced by direct 3D nanoprinting of a moisture-sensitive polymer on a tapered optical fiber. We observe the interferometric response of the NPI probe in ultrasmall-areas quantitatively depends on humidity, arising from its refractive index change and volumetric swelling. By scanning the NPI probe and reading out the interferometric signals, we demonstrate not only multiscale spatial mapping of humidity distribution with versatile scanning steps from ~ $10^2$ nm to a few mm, but also local humidity in very small spaces. We expect our NPI to provide a new nanoscale metrology that could answer fundamental questions about evaporation-related science and engineering.

5:10 AM S.SM04.08.07 Non-Invasive Neuromodulation Using Ultrasound Aditya Vasan and James Friend; University of California, San Diego, United States

The discovery of light sensitive proteins led to the development of optogenetics and allowed the precise manipulation of neuronal and non-neuronal cells[1, 2]. This technique uses particular wavelengths of light to precisely manipulate cells that have been engineered to express this class of proteins. It has enabled the study of information processing in the brain and recent studies are looking into clinical translational applications of the technique[3]. Despite the advantages offered by optogenetics, it has the drawback of being invasive as light does not penetrate skin past a few millimeters. It is not possible to target deep tissue within the body using this technique and this limits the application in the context of diseases such as Parkinson's[5] or heart malfunction[4]. We are developing devices that can non-invasively manipulate cells using low-intensity ultrasound, in a technique termed "sonogenetics". This technique uses a combination of engineering cells to be more sensitive to a mechanical stimulus as well as developing ultrasound transducers capable of stimulating these cells. We demonstrate the development of miniature transducers made from non-hysteretic single crystal lithium niobate to be used for affecting behavior of freely moving, awake mice. In addition, we offer mathematical insights to the mechanism of action of ultrasound on neurons. Our analysis of membrane deflection enables us to predict cellular activity based on the applied ultrasound stimulus. By extension, we use this analytical framework to inform the development of transducers and stimulation parameters for achieving non-invasive stimulation of cells.

References

SESSION S.SM04.09: Poster Session: Fundamental Materials, Devices and Fabrication for Biointegrated and Bioinspired Electronics
On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
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S.SM04.09.02 Damage of CVD Graphene Layers in Contact with Electrolyte Solutions by Dissolved Oxygen Anastasia Svetlova1,2, Guillermo Beltramo1, Dirk Mayer1, Andreas Offenhäusser1 and Dmitry Kireev1; 1Forschungszentrum Jülich GmbH,
Chemical vapor deposited (CVD) graphene is considered a promising material for biomedical applications, namely in vitro and in vivo sensors. When the graphene sensor surface comes in contact with an analyte solution, electrochemical effects caused by a liquid aqueous environment start to take place and interfere with the material stability and detection of an analyte. Here we report our observations about two instances of such reactions. In the first system, fracturing of the graphene layer during anodization is recorded using a Quartz Crystal Microbalance (QCM) method combined with a 3-electrode electrochemical configuration. Positive biasing in a region of potentials that enable an oxygen oxidation reaction caused a layer fracturing and loss of the graphene film integrity. In the second system, origins of gate/leakage currents on an electrolyte-gated Graphene Field Effect Transistors (GFETs) are investigated. A potential-dependent reaction of oxygen is found to be responsible for these currents. Moreover, a surface activation towards this process is observed. As revealed by a complementary method, cyclic voltammetry with a redox probe Fe(MeOH)2+, more defects appear on the graphene transistor surface when extensive leakage currents are present during the GFET operation mode.

S.SM04.09.05
Impact of Gate Structure on Printed Electronic Biosensors for Detection in Whole Blood Nicholas Williams, Joseph B. Andrews, Faris Albarghouthi, Steven G. Noyce, James L. Doherty, Shiheng Lu, Daniel Y. Joh, Ashutosh Chilkoti and Aaron D. Franklin; Duke University, United States

As more hospitals close in rural America, healthcare in these areas has been pushed towards community- and home-care situations. To support this shifting market, new point-of-care (POC) diagnostic techniques are needed to fill the void left by the healthcare industry. Thin film transistor (TFT) -based electronic biosensors are ideally suited for POC applications due to their ability for miniaturization, low operating voltage, and high sensitivity. Yet, one significant hurdle in developing TFT biosensors is that the Debye length in complex fluids, such as serum or whole blood, is sufficiently small that electrical interactions between the analyte and the TFT are completely screened, rendering the device insensitive to changes in analyte concentration. Combining the TFT design with a non-fouling polymer brush layer, poly(oligo(ethylene glycol) methyl ether methacrylate) (POEGMA), has the potential to both extend the Debye length to support the measurement of analyte binding events and minimize nonspecific binding that could prove detrimental to the small electrical perturbations related to sensing low concentration analytes. In this work, we demonstrate the impact of the field-effect gating structure on the operation of a printed carbon nanotube (CNT) -TFT biosensing platform, harnessing the high sensitivity of the CNT thin film and the Debye length extension (in addition to non-fouling properties) of the POEGMA layer. As a demonstration, we print down capture and detection antibodies for the protein leptin on the POEGMA-coated CNT-TFT and measure leptin concentration in both phosphate buffered saline (PBS) and whole human blood. We demonstrate that, unlike optical techniques, no cumbersome wash procedure is required to enable concentration-dependent measurements. Furthermore, a comparison is made between substrate-gated and solution-gated approaches with the CNT-TFT, revealing the role of solution charge and leakage currents in the successful operation of these biosensors. Also explored is the impact of the solution gate stack for the CNT-TFT, where inclusion of a passivating buffer layer of Al2O3 over the entire device structure enhances yield without significantly compromising sensitivity and the addition of a secondary passivation from SU8 directly over the contacts increases measurement stability over longer duration tests. These results mark key progress towards realizing a printed CNT-TFT biosensing platform that can open the way for low-cost, biomedical sensors – a paradigm shift for POC electronic diagnostic systems.

S.SM04.09.06
Proton Conductivity Properties of Electrospun Chitosan Nanofibers Woo-Kyung Lee1, Jeremy J. Pietron2, David Kidwell1, Jeremy Robinson1, Christopher McGann1 and Shawn Mulvaney1; 1Naval Research Lab, United States; 2Lawrence Livermore National Laboratory, United States

A major challenge of the 21st century will be to establish meaningful two-way communication between biology and electronics. The study of protonics, devices that mimic electronics but pass protons instead of electrons, seeks to bridge this gap. Protonic conductive materials (PCMs) are essential elements of these devices and we have demonstrated significant improvement in conductivity for chitosan PCMs when deposited as electrospun nanofibers. The observed improvements stem from both enhanced molecular alignment and from chemical doping due to the electrospinning carrier fluid, trifluoroacetic acid (TFA). We deposited electrospun chitosan nanofibers over palladium protodes and then used the helium ion microscope to isolate single nanofibers for detailed study. We observed that single chitosan nanofibers are strongly doped by TFA with x-ray photoelectron spectroscopy demonstrating extensively protonated nitrogen functionality. With the isolated, single chitosan nanofibers we observed that water uptake, fiber/electrode contact area, and doping concentration are critical parameters of protonic device performance and lead to increased conductivity (i.e. low resistivity). The average resistivity of
single chitosan nanofibers is $6.2 \times 10^4 \ \Omega \cdot \text{cm}$, approximately two orders of magnitude lower than the resistivity of cast chitosan PCMs (cast from acetic acid solutions not TFA). We have observed excellent agreement between theoretical models and experiment results that explore each of the contributions to the improved conductivity. Finally, the fabrication and measurement of ionic field-effect transistor of single chitosan fiber using conductive atomic force microscope will be discussed.  


**S.SM04.09.07**

**Mimicking Signal Transmission in Single Neuron by Organic Electrochemical Transistors** Kwok Ki Chik and Paddy K. L. Chan; The University of Hong Kong, Hong Kong

Neuromorphic organic electrochemical transistors (OECTs) have been reported to demonstrate different synaptic plasticity features including short and long-term plasticity (STP & LTP) and spike-timing-dependent plasticity (STDP), which allows us to mimic synaptic transmission thus construct the neuromorphic circuits. Apart from the inherent advantages of neuromorphic circuits like low-power operations (~nW-pW) and learning capability, the operating mechanism of OECT has a high resemblance with the actual neurons: the movement of ions, which allows OECT to be a competent candidate for developing neuromorphic device. However, in order to build a comprehensive neuromorphic device, not only the synaptic transmissions, but also the signal propagations within single neuron should also be taken into consideration. In this study, a device mimicking signal transmission in single neuron based on a linear organic electrochemical transistors array featuring the regeneration of action potential at Nodes of Ranvier has been constructed. By utilizing the organic electrochemical transistors based on conducting polymer poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS), together with UV-cured poly(2-hydroxyethyl methacrylate) (PHEMA) hydrogel and PVC based ion-selective membrane (ISM), we attempt to fabricate a neuromorphic transistors device in mimicking the propagation of neuronal signals from dendrites to axon. The regeneration of action potentials at the Nodes of Ranvier is achieved by using the ion-sensing capability of OECT and the ion-selectivity of the ISM. In our devices, voltage as low as 0.2 V is enough for the operation, comparable with the ~0.1V of an actual action potential. This device can be incorporated with existing neuromorphic circuits and possibly bridges the future human–machine interfaces between biomimicking organic electronics and authentic neuronal systems.

**S.SM04.09.09**

**Needle-Shaped Micro-Electrodes for Tissue Structural Differentiation by Bioimpedance Spectroscopy** Timothy K. Leung and Paddy K. L. Chan; The University of Hong Kong, Hong Kong

Biopsy is a well-known minimal invasive technique to extract tissues from patients through a needle followed by performing histology to view cellular structures under the microscope. Biopsy studies of cancerous tissue is very common in surgical practice. To identify the cancer tissue, pathologists will usually examine the tissue features such as cell pattern, cytological atypia, mitotic activity, size and shape of cell nuclear. These structural features are highly correlated to the conductivity of the tissues which are composed of tightly packed cells. The cell walls are made of lipid which is a good insulator. When a D.C. current passes through the tissue, the cell wall stores the charges and prevent the current from passing through the cell. However, at high frequency, current can pass through the cell wall because the cell wall behaves as a capacitor. This difference of frequency response is often a characteristic for different tissue with different fluid composition. Currently, biopsy is still at the level for qualitative analysis and the measurements take a relatively long time around 20 minutes. There is a strong demand to develop a fast, localized biopsy tools which can provide quantitative characterizations of the tissue structures. In the current work, we will demonstrate a micro-scaled impedance sensing device developed on the tip of a glass capillary tube of 1mm diameter. Even the size of the electrodes is limited, we employed the organic semiconductor material, PEDOT:PSS (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)), to reduce interface impedance of microelectrodes. By adding this PEDOT:PSS layer on the bare gold electrode, the interface becomes highly capacitive and possess a lower impedance. It is important to point that many of the reported impedance measurement tools uses electrode with large surface area and therefore very inefficient in performing localized measurement. As the proposed needle diameter is only 1mm, the reduction of the electrode surface area will suffer from the effect of mass diffusion and data in the low frequency spectrum will be masked. Our approach to modify the impedance allows us to reveal the impedance response of tissues at low frequency range for more precise equivalent circuit model fitting.

**S.SM04.09.11**
**Investigation of Structure and Composition of Laser Induced Graphene from Polymer Precursors for Bioelectronics Applications** Hana Hampel¹, Maria Jernej¹, Alexander Dallinger¹, Harald Schröttner²-¹ and Francesco Greco¹; ¹Graz University of Technology, Austria; ²Graz Centre for Electron Microscopy, Austria

*Laser Induced Graphene* (LIG) was first described in 2014 and ever since it has been a far-reaching field of research. Research has focused on fundamental understanding of LIG structure and properties, as well as on technological applications in flexible/stretchable electronics, energy, among others¹². LIG is a porous and conductive carbon material produced by laser-induced pyrolysis of various polymer precursors, including biologically derived ones (e.g. wood, paper, silk)³. An infrared laser, as typically used in commercial CO₂ laser cutter for manufacturing, is used for this purpose. This process allows for fast scribing of circuits onto insulating substrates in ambient condition. We investigated the LIG formation process on polyimide to get a better understanding of the boundary conditions for the formation of LIG and the tuning of its morphology and properties (especially conductivity). LIG conductors are prepared by varying the various process parameters affecting laser fluence (i.e. energy per scribed area).

In this way, either a flat porous LIG or a dense forest of long (100-200 µm) carbon fibres bundles (with single fibres having a diameter of around 50-100 nm) can be obtained. Composition, morphology and structure are characterized by optical, scanning and transmission electron microscopy, EDX, and correlative Raman-SEM spectroscopy. A variation of graphene content along the fibre growth direction was found. Variations in structure and morphology were correlated with conductivity. Due to the huge potential of LIG in stretchable and wearable bioelectronics, latest developments of this research include investigation of biologically derived precursors.

References


**S.SM04.09.12**

**Fabrication and Integration of a Novel Coupled Lead Free Perovskite Oxide and Halide Active Multi-Morph—Towards Development of a Flexible Wearable and Continuous Non-Invasive Glucose Monitoring System** Jodi Bishop¹, Faheem Shaikh¹, Noah Haworth¹, Riley Wells¹, Soumyasanta Laha¹, Saquib Ahmed² and Sankha Banerjee¹; ¹California State University, Fresno, United States; ²Buffalo State College, United States

A novel device architecture using a coupled media of an electro-active perovskite oxide (PO) and lead free photo active perovskite halide (PH) layer will be used to enhance signal strength through increased electron mobility, and the photoactive nature of the multimorph. Although, the optical and PA approaches have been studied individually in the past, there were no efforts to integrate the two approaches using perovskite layers and a flexible substrate to improve the wearable form factor, reliability and accuracy of the measurements. So far, all these studies conducted with PA system for non-invasive glucose monitoring used class-IV lasers and non-continuous and mostly in-vitro. This unique approach will integrate electro-active PO, and photoactive PH layers for signal conversion from acoustic and photoluminescence to electrical signals respectively. The following work involves the development of an integrated PO (BaTiO3-PMMA-Graphene) - PH (Tin Iodide active layer) multimorph with a P3HT hole transport layer as the coupled media and development of the device architecture for the wearable device.

**S.SM04.09.13**

**Stretchable Wideband Dipole Antennas and Rectennas for Wireless Communication and RF Energy Harvesting** Jia Zhu¹ and Chaoyun Song²; ¹The Pennsylvania State University, United States; ²University of Liverpool, United Kingdom

Bio-integrated electronic devices can pliably conform on the textured skin surface to continuously monitor the physiologically relevant parameters or biomarkers, with a huge impact on human health from preventative monitoring and early diagnostic confirmation to non-invasive and convenient therapeutic options. The ultimate application of this class of emerging electronics hinges on the indispensable modules of stretchable wireless transmission and power supplies. While near field communication (NFC) allows for wireless powering and communication with a working distance of ~ 3 cm, radio frequency (RF) antennas enable wireless transmission of data and energy in the far-field. Compared to the approaches that exploit stretchable conducting materials such as liquid metal or elastomers with conductive fillers, designing conventional metals in a serpentine or meshed geometry is still of high interest because of their high radiation efficiency. Although this structural design concept has resulted in various stretchable dipole and patch antennas, the narrow bandwidth still limits their applications in wireless communication and energy harvesting because of the frequency detuning from mechanical
deformations. While the efforts on wideband antennas could possibly overcome this challenge, the deformation-dependent radiation properties are yet to fully investigated. Here we demonstrate a stretchable wideband dipole antenna that consists of serpentine units for both main and parasitic arms created by exploiting the laser-induced graphene (LIG) pattern and maskless metal coating. Additionally, combining stretchable dipole antenna with a high-efficiency impedance matching network and rectifying circuit leads to a stretchable rectifying antenna (i.e., stretchable rectenna) that can continuously harvest electromagnetic radiation energies from various widely available RF sources (e.g., WI-FI, 4G, and upcoming 5G). As an added component into the clean energy portfolio for future energy supply, the ambient RF energy-harvesting solution could also contribute to integrated energy systems and enable self-powered systems and remote monitoring of the environment.

S.SM04.09.14  
Characterization of Glassy Carbon and Graphene Based Metamaterial as Electrocorticography Electrodes Transferred on Flexible Substrate  
Surabhi Nimbalkar and Sammuel Kassegne; San Diego State University, United States

Graphene is the gold-standard for electrical conductivity along with its high mechanical strength and excellent thermal conductivity. On the other hand, GC has exceptional chemical inertness, good electrical properties, high electrochemically stability (gold-standard for electrochemistry), purely capacitive charge injection, and fast surface electrokinetics coupled with lithography patternability. Therefore, to leverage the unique strength of these ‘gold-standard’ materials in electrode technology, we introduce a new material system that brings the best qualities of these materials in a single format joined through strong covalent bonds. In this preliminary study, we investigate fabrication methodology, transfer on flexible substrate, bonding between the two allotropes of carbon through FTIR (Fourier transform Infrared) spectroscopy, surface morphology through SEM (Scanning electron microscopy) and topography by AFM (atomic force microscopy), and application of metamaterial based microelectrodes for neural signal recording i.e. electrocorticography (ECoG).

S.SM04.09.15  
Lactic Acid Neurotransmitter Detection using Functionalized Glassy Carbon Microelectrodes  
Amish Rohatgi and Sammuel Kassegne; San Diego State University, United States

Neurotransmitters are often referred to as the body’s chemical messengers. They are the molecules used by the nervous system to transmit messages between neurons. Dopamine and serotonin are electroactive neurotransmitters and can be detected though conventional neural probes. However, lactic acid is a non-electroactive molecule that cannot be detected by these conventional probes. Lactic acid can be found in the brain as a byproduct of energy production and a buildup of lactic acid leads to lactic acidosis. Lactic acidosis can hamper normal mitochondrial functions and has been linked to seizures and can be caused by ischemia or hypoxia. To detect lactic acid our group at SDSU are functionalizing glassy carbon electrodes by immobilizing an enzyme to catalyze lactic acid into a molecule that is electroactive. By immobilizing lactate oxidase into a chitosan matrix, we aim to cause a reaction that will create hydrogen peroxide which is an electroactive molecule with a redox potential of 1.2. In addition to functionalizing glassy carbon with lactate oxidase, we aim to immobilize lactate dehydrogenase which will catalyze lactic acid into NADH and pyruvate and compare both enzyme detection efficacies. We will use electrochemical methods such as fast scan cyclic voltammetry (FSCV), FTIR, and potentiostat reading to characterize, understand the chemical reactions occurring, and qualify these functionalized glassy carbon electrodes. Preliminary characterization results show a slight increase in impedance values once the immobilization matrix has been applied, but despite the increase in impedance the limit of detection has not decreased. Preliminary looks at FTIR data show an increase in functional groups for chitosan on glassy carbon compared to bare glassy carbon showing the chance of adherence.

S.SM04.09.16  
New Platform for Detecting Non-Electroactive Neurotransmitters – Case of Glutamate  
Sandra Lara and Sammuel Kassegne; San Diego State University, United States

Glassy Carbon (GC) microelectrodes have shown to be a promising material in Neuroscience, specifically electrochemistry with a capability of detecting electroactive and non-electroactive species such as Glutamate. Here we demonstrate immobilization of glutamate oxidase on a probe with a four-electrode array and subsequently using fast scan cyclic voltammetry (FSCV) where we pass a current through each microelectrode to detect the presence of neurotransmitters. Electroactive species such as Dopamine and Serotonin oxidize when they come in contact with the electroactive surface. The detection of neurotransmitters will happen at specific voltages in-vitro. Here, we focus on some recent strategies for Glutamate probes immobilization on the surface of electrochemical transducer such as adsorption,
covalent bonding and Glutaraldehyde and GluOx interaction on the electrode surface for specific interaction with its complementary Glutamate target. Using Glutaraldehyde, BSA and Glutamate oxidase we were able to detect as an electrochemical reduction of O2 to H2O2. The immobilization matrix of GluOx on the GC electrode acts as a barrier that allows the electrode to give supporting electrons. By functionalizing bare glassy carbon electrodes we have shown detection of Glutamate, non-electrode molecule. Through the chemical reaction with an enzyme happening at the surface of the electrode and cyclic voltammetry we were able to show the chemical reduction of non-electroactive of molecules.

S.SM04.09.20
Absorption of the Solar Radiation with Arrays of Subwavelength Nonimaging Light Concentrators Ashish Prajapati;
Ben Gurion University of the Negev, Israel

Light trapping and the broadband absorption of the solar radiation is of interest to various solar energy harvesting applications. In the current work, we report a new paradigm for light trapping, that is light trapping based on arrays of subwavelength nonimaging light concentrators (NLCs). We numerically show that silicon NLC arrays provide >75% broadband absorption enhancement of the solar radiation compared with that of optimized nanopillar arrays. The paper focuses on free-floating arrays of subwavelength compound parabolic concentrators (henceforth CPC arrays) as a case study. The calculations reveal that CPC arrays function as anti-transmission layers as only few photons transverse the CPC arrays which is in contrast to nanopillar arrays that function as anti-reflection layers. We show that the absorption enhancement in CPC arrays is due to efficient occupation of Mie modes which is motivated by the unique CPC geometry, and we demonstrate light trapping at the Yablonovitch limit. Finally, we examine the performance of a photovoltaic cell based on CPC arrays with respect to base doping levels and surface recombination. We show that the short-circuit current density of the CPC-based cell is >75% higher than the short-circuit current density of a photovoltaic cell based on optimized nanopillar arrays. We believe that light trapping based on NLC arrays paves the way to various applications such as ultra-thin photovoltaic cells.

S.SM04.09.02
Damage of CVD Graphene Layers in Contact with Electrolyte Solutions by Dissolved Oxygen Anastasia Svetlova1,2,
Guillermo Beltramo1, Dirk Mayer1, Andreas Offenhäusser1 and Dmitry Kireev3; 1Forschungszentrum Jülich GmbH,
Germany; 2RWTH Aachen University, Germany; 3The University of Texas at Austin, United States

Chemical vapor deposited (CVD) graphene is considered a promising material for biomedical applications, namely in vitro and in vivo sensors. When the graphene sensor surface comes in contact with an analyte solution, electrochemical effects caused by a liquid aqueous environment start to take place and interfere with the material stability and detection of an analyte. Here we report our observations about two instances of such reactions. In the first system, fracturing of the graphene layer during anodization is recorded using a Quartz Crystal Microbalance (QCM) method combined with a 3-electrode electrochemical configuration. Positive biasing in a region of potentials that enable an oxygen oxidation reaction caused a layer fracturing and loss of the graphene film integrity. In the second system, origins of gate/leakage currents on an electrolyte-gated Graphene Field Effect Transistors (GFETs) are investigated. A potential-dependent reaction of oxygen is found to be responsible for these currents. Moreover, a surface activation towards this process is observed. As revealed by a complementary method, cyclic voltammetry with a redox probe Fe(MeOH)2+, more defects appear on the graphene transistor surface when extensive leakage currents are present during the GFET operation mode.

S.SM04.09.05
Impact of Gate Structure on Printed Electronic Biosensors for Detection in Whole Blood Nicholas Williams, Joseph B. Andrews, Faris Albarghouthi, Steven G. Noyce, James L. Doherty, Shiheng Lu, Daniel Y. Joh, Ashutosh Chilkoti and Aaron D. Franklin; Duke University, United States
As more hospitals close in rural America, healthcare in these areas has been pushed towards community- and home-care situations. To support this shifting market, new point-of-care (POC) diagnostic techniques are needed to fill the void left by the healthcare industry. Thin-film transistor (TFT)-based electronic biosensors are ideally suited for POC applications due to their ability for miniaturization, low operating voltage, and high sensitivity. Yet, one significant hurdle in developing TFT biosensors is that the Debye length in complex fluids, such as serum or whole blood, is sufficiently small that electrical interactions between the analyte and the TFT are completely screened, rendering the device insensitive to changes in analyte concentration. Combining the TFT design with a non-fouling polymer brush layer, poly(oligo(ethylene glycol) methyl ether methacrylate) (POEGMA), has the potential to both extend the Debye length to support the measurement of analyte binding events and minimize nonspecific binding that could prove detrimental to the small electrical perturbations related to sensing low concentration analytes. In this work, we demonstrate the impact of the field-effect gating structure on the operation of a printed carbon nanotube (CNT)-TFT biosensing platform, harnessing the high sensitivity of the CNT thin film and the Debye length extension (in addition to non-fouling properties) of the POEGMA layer. As a demonstration, we print down capture and detection antibodies for the protein leptin on the POEGMA-coated CNT-TFT and measure leptin concentration in both phosphate buffered saline (PBS) and whole human blood. We demonstrate that, unlike optical techniques, no cumbersome wash procedure is required to enable concentration-dependent measurements. Furthermore, a comparison is made between substrate-gated and solution-gated approaches with the CNT-TFT, revealing the role of solution charge and leakage currents in the successful operation of these biosensors. Also explored is the impact of the solution gate stack for the CNT-TFT, where inclusion of a passivating buffer layer of Al₂O₃ over the entire device structure enhances yield without significantly compromising sensitivity and the addition of a secondary passivation from SU8 directly over the contacts increases measurement stability over longer duration tests. These results mark key progress towards realizing a printed CNT-TFT biosensing platform that can open the way for low-cost, biomedical sensors – a paradigm shift for POC electronic diagnostic systems.

S.SM04.09.06
Proton Conductivity Properties of Electrospun Chitosan Nanofibers

Woo-Kyung Lee¹, Jeremy J. Pietron², David Kidwell¹, Jeremy Robinson¹, Christopher McGann¹ and Shawn Mulvaney¹; ¹Naval Research Lab, United States; ²Lawrence Livermore National Laboratory, United States

A major challenge of the 21st century will be to establish meaningful two-way communication between biology and electronics. The study of protonics, devices that mimic electronics but pass protons instead of electrons, seeks to bridge this gap. Protonic conductive materials (PCMs) are essential elements of these devices and we have demonstrated significant improvement in conductivity for chitosan PCMs when deposited as electrospun nanofibers. The observed improvements stem from both enhanced molecular alignment and from chemical doping due to the electrospinning carrier fluid, trifluoroacetic acid (TFA). We deposited electrospun chitosan nanofibers over palladium protodes and then used the helium ion microscope to isolate single nanofibers for detailed study. We observed that single chitosan nanofibers are strongly doped by TFA with x-ray photoelectron spectroscopy demonstrating extensively protonated nitrogen functionality. With the isolated, single chitosan nanofibers we observed that water uptake, fiber/electrode contact area, and doping concentration are critical parameters of protonic device performance and lead to increased conductivity (i.e. low resistivity). The average resistivity of single chitosan nanofibers is 6.2×10⁴ Ω●cm, approximately two orders of magnitude lower than the resistivity of cast chitosan PCMs (cast from acetic acid solutions not TFA). We have observed excellent agreement between theoretical models and experiment results that explore each of the contributions to the improved conductivity. Finally, the fabrication and measurement of ionic field-effect transistor of single chitosan fiber using conductive atomic force microscope will be discussed.¹


S.SM04.09.07
Mimicking Signal Transmission in Single Neuron by Organic Electrochemical Transistors

Kwok Ki Chik and Paddy K. L. Chan, The University of Hong Kong, Hong Kong

Neuromorphic organic electrochemical transistors (OECTs) have been reported to demonstrate different synaptic plasticity features including short and long-term plasticity (STP & LTP) and spike-timing-dependent plasticity (STDP), which allows us to mimic synaptic transmission thus construct the neuromorphic circuits. Apart from the inherent advantages of neuromorphic circuits like low-power operations (~nW-pW) and learning capability, the operating mechanism of OECT has a high resemblance with the actual neurons: the movement of ions, which allows OECT to be a competent candidate for
developing neuromorphic device. However, in order to build a comprehensive neuromorphic device, not only the synaptic transmissions, but also the signal propagations within single neuron should also be taken into consideration. In this study, a device mimicking signal transmission in single neuron based on a linear organic electrochemical transistors array featuring the regeneration of action potential at Nodes of Ranvier has been constructed. By utilizing the organic electrochemical transistors based on conducting polymer poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS), together with UV-cured poly(2-hydroxyethyl methacrylate) (PHEMA) hydrogel and PVC based ion-selective membrane (ISM), we attempt to fabricate a neuromorphic transistors device in mimicking the propagation of neuronal signals from dendrites to axon. The regeneration of action potentials at the Nodes of Ranvier is achieved by using the ion-sensing capability of OECT and the ion-selectivity of the ISM. In our devices, voltage as low as 0.2 V is enough for the operation, comparable with the ~0.1V of an actual action potential. This device can be incorporated with existing neuromorphic circuits and possibly bridges the future human–machine interfaces between biomimicking organic electronics and authentic neuronal systems.

S.SM04.09.09
Needle-Shaped Micro-Electrodes for Tissue Structural Differentiation by Bioimpedance Spectroscopy Timothy K. Leung and Paddy K. L. Chan; The University of Hong Kong, Hong Kong

Biopsy is a well-known minimal invasive technique to extract tissues from patients through a needle followed by performing histology to view cellular structures under the microscope. Biopsy studies of cancerous tissue is very common in surgical practice. To identify the cancer tissue, pathologists will usually examine the tissue features such as cell pattern, cytological atypia, mitotic activity, size and shape of cell nuclear. These structural features are highly correlated to the conductivity of the tissues which are composed of tightly packed cells. The cell walls are made of lipid which is a good insulator. When a D.C. current passes through the tissue, the cell wall stores the charges and prevent the current from passing through the cell. However, at high frequency, current can pass through the cell wall because the cell wall behaves as a capacitor. This difference of frequency response is often a characteristic for different tissue with different fluid composition. Currently, biopsy is still at the level for qualitative analysis and the measurements take a relatively long time around 20 minutes. There is a strong demand to develop a fast, localized biopsy tools which can provide quantitative characterizations of the tissue structures. In the current work, we will demonstrate a micro-scaled impedance sensing device developed on the tip of a glass capillary tube of 1mm diameter. Even the size of the electrodes is limited, we employed the organic semiconductor material, PEDOT:PSS (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)), to reduce interface impedance of microelectrodes. By adding this PEDOT:PSS layer on the bare gold electrode, the interface becomes highly capacitive and possess a lower impedance. It is important to point that many of the reported impedance measurement tools uses electrode with large surface area and therefore very inefficient in performing localized measurement. As the proposed needle diameter is only 1mm, the reduction of the electrode surface area will suffer from the effect of mass diffusion and data in the low frequency spectrum will be masked. Our approach to modify the impedance allows us to reveal the impedance response of tissues at low frequency range for more precise equivalent circuit model fitting.

S.SM04.09.11
Investigation of Structure and Composition of Laser Induced Graphene from Polymer Precursors for Bioelectronics Applications Hana Hampel1; Maria Jernej2; Alexander Dallinger1; Harald Fitzek3; Hartmuth Schrötter2;1 and Francesco Greco1; 1Graz University of Technology, Austria; 2Graz Centre for Electron Microscopy, Austria

Laser Induced Graphene (LIG) was first described in 2014 and ever since it has been a far-reaching field of research. Research has focused on fundamental understanding of LIG structure and properties, as well as on technological applications in flexible/stretchable electronics, energy, among others[1,2]. LIG is a porous and conductive carbon material produced by laser-induced pyrolysis of various polymer precursors, including biologically derived ones (e.g. wood, paper, silk)[3]. An infrared laser, as typically used in commercial CO2 laser cutter for manufacturing, is used for this purpose. This process allows for fast scribing of circuits onto insulating substrates in ambient condition. We investigated the LIG formation process on polyimide to get a better understanding of the boundary conditions for the formation of LIG and the tuning of its morphology and properties (especially conductivity). LIG conductors are prepared by varying the various process parameters affecting laser fluence (i.e. energy per scribed area). In this way, either a flat porous LIG or a dense forest of long (100-200 µm) carbon fibres bundles (with single fibres having a diameter of around 50-100 nm) can be obtained. Composition, morphology and structure are characterized by optical, scanning and transmission electron microscopy, EDX, and correlative Raman-SEM spectroscopy. A variation of graphene content along the fibre growth direction was found. Variations in structure and morphology were correlated with conductivity. Due to the huge potential of LIG in stretchable and wearable bioelectronics, latest developments of this research include
Towards Development of a Flexible Wearable and Continuous Non-Invasive Glucose Monitoring System

Fabrication and Integration of a Novel Coupled Lead Free Perovskite Oxide and Halide Active Multi-Morph—Towards Development of a Flexible Wearable and Continuous Non-Invasive Glucose Monitoring System Jodi Bishop¹, Faheem Shaikh¹, Noah Haworth¹, Riley Wells¹, Soumyasanta Laha¹, Saquib Ahmed² and Sankha Banerjee¹; ¹California State University, Fresno, United States; ²Buffalo State College, United States

A novel device architecture using a coupled media of an electro-active perovskite oxide (PO) and lead free photo active perovskite halide (PH) layer will be used to enhance signal strength through increased electron mobility, and the photoactive nature of the multimorph. Although, the optical and PA approaches have been studied individually in the past, there were no efforts to integrate the two approaches using perovskite layers and a flexible substrate to improve the wearable form factor, reliability and accuracy of the measurements. So far, all these studies conducted with PA system for non-invasive glucose monitoring used class-IV lasers and non-continuous and mostly in-vitro. This unique approach will integrate electro-active PO, and photoactive PH layers for signal conversion from acoustic and photoluminescence to electrical signals respectively. The following work involves the development of an integrated PO (BaTiO3-PMMA-Graphene) - PH (Tin iodide active layer) multimorph with a P3HT hole transport layer as the coupled media and development of the device architecture for the wearable device.

Stretchable Wideband Dipole Antennas and Rectennas for Wireless Communication and RF Energy Harvesting Jia Zhu¹ and Chaoyun Song²; ¹The Pennsylvania State University, United States; ²University of Liverpool, United Kingdom

Bio-integrated electronic devices can pliably conform on the textured skin surface to continuously monitor the physiologically relevant parameters or biomarkers, with a huge impact on human health from preventative monitoring and early diagnostic confirmation to non-invasive and convenient therapeutic options. The ultimate application of this class of emerging electronics hinges on the indispensable modules of stretchable wireless transmission and power supplies. While near field communication (NFC) allows for wireless powering and communication with a working distance of ~ 3 cm, radio frequency (RF) antennas enable wireless transmission of data and energy in the far-field. Compared to the approaches that exploit stretchable conducting materials such as liquid metal or elastomers with conductive fillers, designing conventional metals in a serpentine or meshed geometry is still of high interest because of their high radiation efficiency. Although this structural design concept has resulted in various stretchable dipole and patch antennas, the narrow bandwidth still limits their applications in wireless communication and energy harvesting because of the frequency detuning from mechanical deformations. While the efforts on wideband antennas could possibly overcome this challenge, the deformation-dependent radiation properties are yet to fully investigated. Here we demonstrate a stretchable wideband dipole antenna that consists of serpentine units for both main and parasitic arms created by exploiting the laser-induced graphene (LIG) pattern and maskless metal coating. Additionally, combining stretchable dipole antenna with a high-efficiency impedance matching network and rectifying circuit leads to a stretchable rectifying antenna (i.e., stretchable rectenna) that can continuously harvest electromagnetic radiation energies from various widely available RF sources (e.g., WI-FI, 4G, and upcoming 5G). As an added component into the clean energy portfolio for future energy supply, the ambient RF energy-harvesting solution could also contribute to integrated energy systems and enable self-powered systems and remote monitoring of the environment.

Characterization of Glassy Carbon and Graphene Based Metamaterial as Electrocorticography Electrodes Transferred on Flexible Substrate Surabhi Nimblekar and Samuel Kassegne; San Diego State University, United States

Graphene is the gold-standard for electrical conductivity along with its high mechanical strength and excellent thermal conductivity. On the other hand, GC has exceptional chemical inertness, good electrical properties, high electrochemically stability (gold-standard for electrochemistry), purely capacitive charge injection, and fast surface electrokinetics coupled with lithography patternability. Therefore, to leverage the unique strength of these ‘gold-standard’ materials in electrode technology, we introduce a new material system that brings the best qualities of these materials in a single format joined through strong covalent bonds. In this preliminary study, we investigate fabrication methodology, transfer on flexible

References
substrate, bonding between the two allotropes of carbon through FTIR (Fourier transform Infrared) spectroscopy, surface morphology through SEM (Scanning electron microscopy) and topography by AFM (atomic force microscopy), and application of metamaterial based microelectrodes for neural signal recording i.e. electrocorticography (ECoG).

S.SM04.09.15
Lactic Acid Neurotransmitter Detection using Functionalized Glassy Carbon Microelectrodes Amish Rohatgi and Sammuel Kassegne; San Diego State University, United States

Neurotransmitters are often referred to as the body’s chemical messengers. They are the molecules used by the nervous system to transmit messages between neurons. Dopamine and serotonin are electroactive neurotransmitters and can be detected though conventional neural probes. However, lactic acid is a non-electroactive molecule that cannot be detected by these conventional probes. Lactic acid can be found in the brain as a byproduct of energy production and a buildup of lactic acid leads to lactic acidosis. Lactic acidosis can hamper normal mitochondrial functions and has been linked to seizures and can be caused by ischemia or hypoxia. To detect lactic acid our group at SDSU are functionalizing glassy carbon electrodes by immobilizing an enzyme to catalyze lactic acid into a molecule that is electroactive. By immobilizing lactate oxidase into a chitosan matrix, we aim to cause a reaction that will create hydrogen peroxide which is an electroactive molecule with a redox potential of 1.2. In addition to functionalizing glassy carbon with lactate oxidase, we aim to immobilize lactate dehydrogenase which will catalyze lactic acid into NADH and pyruvate and compare both enzyme detection efficacies. We will use electrochemical methods such as fast scan cyclic voltammetry (FSCV), FTIR, and potentiostat reading to characterize, understand the chemical reactions occurring, and qualify these functionalized glassy carbon electrodes. Preliminary characterization results show a slight increase in impedance values once the immobilization matrix has been applied, but despite the increase in impedance the limit of detection has not decreased. Preliminary looks at FTIR data show an increase in functional groups for chitosan on glassy carbon compared to bare glassy carbon showing the chance of adherence.

1. NanoFab.SDSU, Department of Mechanical Engineering, College of Engineering, San Diego State University, 5500 Campanile Drive, CA 92182

S.SM04.09.16
New Platform for Detecting Non-Electroactive Neurotransmitters – Case of Glutamate Sandra Lara and Sammuel Kassegne; San Diego State University, United States

Glassy Carbon (GC) microelectrodes have shown to be a promising material in Neuroscience, specifically electrochemistry with a capability of detecting electroactive and non-electroactive species such as Glutamate. Here we demonstrate immobilization of glutamate oxidase on a probe with a four-electrode array and subsequently using fast scan cyclic voltammetry (FSCV) where we pass a current through each microelectrode to detect the presence of neurotransmitters. Electroactive species such as Dopamine and Serotonin oxidize when they come in contact with the electroactive surface. The detection of neurotransmitters will happen at specific voltages in-vitro. Here, we focus on some recent strategies for Glutamate probes immobilization on the surface of electrochemical transducer such as adsorption, covalent bonding and Glutaraldehyde and GluOx interaction on the electrode surface for specific interaction with its complementary Glutamate target. Using Glutaraldehyde, BSA and Glutamate oxidase we were able to detect as an electrochemical reduction of O2 to H2O2. The immobilization matrix of GluOx on the GC electrode acts as a barrier that allows the electrode to give supporting electrons. By functionalizing bare glassy carbon electrodes we have shown detection of Glutamate, non-electrode molecule. Through the chemical reaction with an enzyme happening at the surface of the electrode and cyclic voltammetry we were able to show the chemical reduction of non-electroactive of molecules.

S.SM04.09.20
Absorption of the Solar Radiation with Arrays of Subwavelength Nonimaging Light Concentrators Ashish Prajapati; Ben Gurion University of the Negev, Israel

Light trapping and the broadband absorption of the solar radiation is of interest to various solar energy harvesting applications. In the current work, we report a new paradigm for light trapping, that is light trapping based on arrays of subwavelength nonimaging light concentrators (NLCs). We numerically show that silicon NLC arrays provide >75% broadband absorption enhancement of the solar radiation compared with that of optimized nanopillar arrays. The paper focuses on free-floating arrays of subwavelength compound parabolic concentrators (henceforth CPC arrays) as a case study. The calculations reveal that CPC arrays function as anti-transmission layers as only few photons transverse the CPC arrays which is in contrast to nanopillar arrays that function as anti-reflection layers. We show that the absorption enhancement in
Continuous liquid phases. Bijels can be used as templates for fabricating bijels-derived bicontinuous structures having interconnected channels. These channels (“pores”) in bicontinuous structures can provide desired space for cell encapsulation, proliferation and migration in tissue engineering while enabling the transport of nutrients and bioactive molecules. However, pore sizes of bijels-derived bicontinuous structures are normally small. To realize their potential in tissue engineering, bijels-derived bicontinuous structures with larger pore sizes need to be made for cell encapsulation and delivery. Our research has developed new methods for fabricating bijels and bijels-derived structures. In this investigation, bijels-derived polymer-hydrogel hybrids with normal pore size (~30 μm) and large pore size (~60 μm) were produced, and human dermal fibroblasts (HDFs) and osteoblast precursor cell line (MC3T3 cells) were encapsulated in respective hybrid. The cells were encapsulated in the crosslinked alginate hydrogel (with different crosslinking degrees) of polymer-hydrogel hybrids. The hybrids were then cultured for different periods to study controlled cell release. SEM examinations showed successful fabrication of cell-encapsulated polymer-hydrogel bicontinuous structures and the degradation of alginate hydrogel during culture. The cell release process was studied using confocal microscopy and SEM. Live/Dead assay and MTT assay were also used in the studies. It was observed that live cells were locked in hybrid structures at the beginning and were gradually released since Day 1 during culture. Both HDFs and MC3T3 cells exhibited good cell viability and proliferation after their release and were able to migrate from the channels of hybrid structures to the surface of hybrids and to the outer culture plate. The two types of cells displayed different release behaviors. In the bijels-derived hybrids with small pore size (~30 μm), HDFs were released significantly slower than MC3T3 cells. The major release period of encapsulated HDFs was 24 h later than the major release period of encapsulated MC3T3 cells. For the bijels-derived hybrids with large pore size (~60 μm), the release rates of HDFs and MC3T3 cells were similar. A possible explanation for the differences is that the sizes of cells and pores in hybrids could affect cell release. HDFs have a larger cell size (~50 μm) than MC3T3 cells (20-30 μm), which may have caused slower release of HDFs in bijels-derived hybrids with small pore size. This investigation has demonstrated that bijel-derived bicontinuous hybrid structures are a good vehicle for cell delivery in tissue engineering. By controlling the pore size of hybrid structures, the release of different types of cells could be controlled. The released live cells could proliferate well and migrate in and outside the hybrid structures.

Optimizing Bicontinuous Structure of Bijels-Derived Polymer-Hydrogel Hybrids for the Controlled Release of Different Cells

Haoran Sun and Min Wang; University of Hong Kong, Hong Kong

Controlled cell release is an important strategy in tissue engineering which deliver live cells to the repair sites in human bodies with well-designed cell density and distribution that mimic targeted tissues and facilitate tissue regeneration. Bicontinuous interfacially jammed emulsion gels (“bijels”) are a new class of materials consisting of two interpenetrating continuous liquid phases. Bijels can be used as templates for fabricating bijels-derived bicontinuous structures having interconnected channels. These channels (“pores”) in bicontinuous structures can provide desired space for cell encapsulation, proliferation and migration in tissue engineering while enabling the transport of nutrients and bioactive molecules. However, pore sizes of bijels-derived bicontinuous structures are normally small. To realize their potential in tissue engineering, bijels-derived bicontinuous structures with larger pore sizes need to be made for cell encapsulation and delivery. Our research has developed new methods for fabricating bijels and bijels-derived structures. In this investigation, bijels-derived polymer-hydrogel hybrids with normal pore size (~30 μm) and large pore size (~60 μm) were produced, and human dermal fibroblasts (HDFs) and osteoblast precursor cell line (MC3T3 cells) were encapsulated in respective hybrid. The cells were encapsulated in the crosslinked alginate hydrogel (with different crosslinking degrees) of polymer-hydrogel hybrids. The hybrids were then cultured for different periods to study controlled cell release. SEM examinations showed successful fabrication of cell-encapsulated polymer-hydrogel bicontinuous structures and the degradation of alginate hydrogel during culture. The cell release process was studied using confocal microscopy and SEM. Live/Dead assay and MTT assay were also used in the studies. It was observed that live cells were locked in hybrid structures at the beginning and were gradually released since Day 1 during culture. Both HDFs and MC3T3 cells exhibited good cell viability and proliferation after their release and were able to migrate from the channels of hybrid structures to the surface of hybrids and to the outer culture plate. The two types of cells displayed different release behaviors. In the bijels-derived hybrids with small pore size (~30 μm), HDFs were released significantly slower than MC3T3 cells. The major release period of encapsulated HDFs was 24 h later than the major release period of encapsulated MC3T3 cells. For the bijels-derived hybrids with large pore size (~60 μm), the release rates of HDFs and MC3T3 cells were similar. A possible explanation for the differences is that the sizes of cells and pores in hybrids could affect cell release. HDFs have a larger cell size (~50 μm) than MC3T3 cells (20-30 μm), which may have caused slower release of HDFs in bijels-derived hybrids with small pore size. This investigation has demonstrated that bijel-derived bicontinuous hybrid structures are a good vehicle for cell delivery in tissue engineering. By controlling the pore size of hybrid structures, the release of different types of cells could be controlled. The released live cells could proliferate well and migrate in and outside the hybrid structures.

Poplar Reinforced Biocomposites Via Cellulose Nanofibril Modification

Xianhui Zhao, Kai Li, Daniel Rasmussen, Halil Tekinalp, Erin Webb and Soydan Ozcan; Oak Ridge National Laboratory, United States

A common material used for large-scale 3D printing is a composite consisting of acrylonitrile butadiene styrene (ABS) polymer compounded with carbon fiber (CF/ABS). However, the high cost of CF/ABS indicates a market for 3D printing with bioderived materials. Natural lignocellulosic fibers have the advantages of biodegradability, abundance, low density, low cost, and easy availability. In the present study, poplar fibers (Populus spp.) were modified using cellulose nanofibril (CNF) slurry (~3 wt% solid). The modified CNF/poplar fibers were used to reinforce ABS. The biocomposites obtained were characterized using techniques including tensile testing, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), rheometer, thermogravimetric analysis (TGA), and scanning electron microscope (SEM). The tensile strength and Young’s modulus of neat ABS were 36 MPa and 1,901 MPa, respectively. After the addition of CNF/poplar fibers into ABS, the tensile strength and Young’s modulus of the biocomposites increased by 19% and 143%, respectively. The physical treatment of doping CNF solution on poplar fibers was found to be an effective technique to improve the thermomechanical properties of biocomposites.
Tissue-engineered scaffolds play an important role in the repair or regeneration of tissues and organs. Scaffolds provide strength, stability, and support for cell and tissue development and growth. Common scaffold materials are natural and synthetic polymers, however, each one has its own limitations and different disadvantages. Interestingly, in order to promote the mechanical properties and increase the bioactivity, the composite systems comprised of various sources or types of polymers can retain the advantages of each material. Furthermore, composite polymer systems have the ability to allow stem cell adhesion and differentiation and to carry drug molecules and special biological molecules, like growth factor and enzyme. Research on composite scaffolds is focused on identifying composites with enhanced mechanical properties, sustained drug-releasing capabilities and the ability to support tissue development and growth.

In this study, we produced and characterized a novel nanocomposite polymer scaffold composed of poly-ethylene oxide (PEO), polycaprolactone (PCL) and halloysite clay nanotubes (HNTs). PGS, a polymer with repeating -O-CH2-CH2- units, and PCL, a hydrophobic aliphatic polyester with exceptional biodegradable and biocompatible properties, were used in combination with HNTs to form nanocomposite polymer scaffolds. The nanocomposite polymer scaffold thin films were prepared by solution blow spraying, which is an easy and convenient way to make fibers and films. We characterized the structural, morphological, thermal and functional properties of these novel nanocomposite polymer (PEO-PCL-HNT) scaffolds. The nanocomposite polymer scaffolds should be biocompatible and resorbable, maintain long-term cellular viability and functionality, have the ability to induce cellular differentiation leading to complex tissue formation, have the improved mechanical properties to support cell growth and have sustained-release capabilities.

S.SM06.08.08
Polysaccharide-Based Hybrid Hydrogels as Tissue Engineering Scaffolds and/or Drug Delivery System Jinku Kim and Byungduk Kim; Hongik University, Korea (the Republic of)

Introduction: Hydrogels have potential in many biomedical applications such as tissue engineering and drug delivery system.1 Among those, Polysaccharide-based hydrogels such as hyaluronic acid (HA) have been extensively studied for tissue engineering applications, for example cartilage tissue engineering, partly because they are involved in cellular processes such as proliferation, morphogenesis, and wound repair. A number of polysaccharide-based hydrogels were designed, synthesized by free radical polymerization and their properties were analyzed in vitro and in vivo. In this study, we hypothesized that the properties of polysaccharide-based hydrogels can be controlled and enhanced by combining with small molecules (e.g., proteins) or large molecules (e.g., PEG-based hydrogels). To test this hypothesis, novel biodegradable polysaccharide-based hydrogels were developed by combining polysaccharides (e.g., hyaluronic acid or HA) with PEG based macromers such as PEG sebacic acid diacrylates (PEGSDA) via free radical polymerization under mild conditions. Their physicochemical properties (e.g., swelling ratios) as well as biological properties were evaluated

Materials & Methods: Polysaccharide-based hydrogels were synthesized by free radical polymerization under mild conditions and their properties were controlled by incorporation of proteins (e.g., collagen or growth factors) or synthetic polymers such as polyethylene glycol (PEG). Physicochemical properties and in vitro and in vivo biological properties were investigated using mesenchymal stem cells (MSCs) and rat mandibular defect models.

Results: The chitosan-based hydrogels conjugated with collagen and/or growth factors were well synthesized under mild conditions. Growth factors were delivered from the hydrogel systems in a controlled manner. The encapsulated MSCs showed their potential of condrogenic differentiation in vitro. The physically crosslinked chitosan-based hydrogels revealed their capability of bone regeneration on the critical-sized defects (CSD) in rat mandibular. In addition, the physicochemical properties of hyaluronic acid-based polysaccharide hydrogels can be controlled by combining them with PEG-based hydrogels.

Conclusion: Polysaccharide-based hydrogels with well controlled their properties can be synthesized by incorporations of additives such as growth factors or synthetic hydrogels. These hybrid polysaccharide-based hydrogels can be useful as tissue engineering scaffolds and drug delivery systems to repair or regenerate the defects in organs or tissues, caused by injuries or diseases.

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References

S.SM06.08.10
A Screen-Printable Ph Sensor for Smart Textiles

Sooyoung Kim1, Jongwon Lee1, Minyoung Choi1, Ju-Hee So2 and Hyung-Jun Koo3; 1Seoul National University of Science and Technology, Korea (the Republic of); 2Korea Institute of Industrial Technology, Korea (the Republic of)

Recently, wearable sensors attract tremendous interest as real-time monitoring of physiological activities or environmental conditions becomes more important for many smart devices. Screen printing of sensing materials directly on fabric could not only enhance portability but also improve productivity by enabling a roll-to-roll process. Here, we present a solid-state pH sensor formed by a reliable screen printing technique. The pH sensor consists of two patterned electrodes. One is made of polyaniline(PANI)-carbon nanotube(CNT)-agarose composite. PANI, CNT, and agarose are a pH-sensing material, a conducting filler, and a binder and matrix material, respectively. For preliminary test, the composite in a paste state is deposited by doctor blade method with thickness of 150 µm. The film shows negative dependence on pH condition: e.g. higher potential at lower pH. The other electrode is a “reference” electrode, made of Ag/AgCl thin film with ion-selective solid membrane. The resulting electrode shows similar current-voltage curves with commercial Ag/AgCl reference electrode. Finally, the compositions of PANI film as well as the conditions for screen printing such as mesh thickness, printing temperature & speed, etc. are optimized, to establish the continuous, roll-to-roll process of a pH-sensor patterned directly on fabric by the screen printing.

S.SM06.08.11
Synthesis and Characterization of a New Antibacterial N-halamine Coating Based on Polydopamine. Nadia Nazi; Sorbonne Université, France

In the presence of moisture, surfaces are an ideal support for the development of biofilms containing bacteria that can be pathogenic. This poses a real public health, economic or even environmental problems in view of the use of biocides to eradicate this phenomenon. Due to the rise of multi-drug resistant microorganism, the investigation of new antibacterial coating is extremely requested.

The goal of this study is the development of a new regenerative antimicrobial coating based on polydopamine, containing haloamine (or N-halamine) functions (>N-Cl or/and >N-Br) that have oxidative properties due to the oxidation state +1 of Cl or Br1,2. Thus, the antimicrobial activity of N-halamines is attributable to halogen exchange reactions between N-halamines and microorganisms, leading to death of the microorganisms. N-halamines are broad-spectrum biocidal groups due to their mode of action, i.e. oxidation, bacteria should not develop resistance, unlike after repeated use of antibiotics.

The protection of surfaces with N-halamine compounds requires the immobilization of amine, amide or imine functions that will be transformed into haloamine either during synthesis or by post-treatment in the presence of NaOCl or NaOBr. The originality of this antibacterial coating is its regenerative proprieties. In fact, N-halamines, after contact with bacteria, can be regenerated by simple immersion of the coating in a diluted bleach recharge.

The purpose of this study was to investigate the synthesis and the antibacterial properties of a new N-halamine coating based on polydopamine (PDA). First the formation of the PDA coating by oxidative polymerization of dopamine in aqueous solution was studied and characterized. The thickness of the deposited layer reached a constant value around 50 nm after 24h of functionalization. Then this film was chlorinated by contact with a NaOCl solution in order to form and into the coating chloramine functions. An amount of 10^16 at/cm^2 of chlorine was successfully grafted into the surface. Finally, the antibacterial properties of the modified PDA coating were evaluated by testing its properties toward Escherichia coli. Bacterial viability in contact with the PDA-Cl film evaluated by epifluorescence microscopy revealed promising results.

References

S.SM06.08.12
Poly(lactic acid) with On-Demand Mechanical Properties Kai Li1, Denver Mcgrady1,2, Darby Ker1, Xianhui Zhao1, Reagan Newman1,3, Matthew Rowe1, Halil Tekinalp1 and Soydan Ozcan1,2; 1Oak Ridge National Laboratory, United States; 2Pellissippi State Community College, United States; 3University of Tennessee, United States
Stimuli-responsive materials, or smart materials, has been intensively studied for decades and numerous interesting materials have been developed. Among them, materials with controllable mechanical properties have found use in a wide variety of applications including aerospace, civil applications, and implantable medical devices. However, synthetic hydrogels are the most heavily investigated. Considering its sustainability, a biodegradable polylactic acid (PLA) based free-stand film with controllable mechanical properties was developed. It was found that through chain end modification with anthracene (AN), PLA experiences a 10-fold increase in toughness with no change in tensile strength. Interestingly, after 365 nm UV light irradiation, AN modified PLA became brittle and tensile strength increased by 20%. π-π* stacking of AN groups was proposed to be the mechanism behind the toughening, and light induced dimerization of two AN group resulted in the brittleness. Based on the light reversible dimerization nature of the AN group, light with different wavelengths (365 nm and 254 nm) can be used to control the mechanical properties of newly developed PLA+AN materials in solid state.

**S.SM06.08.13**

**NIR Triggered Upconversion Nanocomposites for Synergistic Photodynamic and Photothermal Therapy** Le Ma and Xiujun J. Li; The University of Texas at El Paso, United States

Development of near-infrared (NIR) laser triggered photo cancer therapy is highly desirable but still a big challenge. Herein, NaYF₄:Yb/Er Upconversion Nanoparticles (UCNPs) was rationally synthesized through a novel low-temperature hydrothermal method, exhibiting photoluminescence emissions at the wavelength of 538, 653 and 839 nm, under 980 nm laser radiation. The UCNPs were firstly surface-modified with silanization of tetraethyl orthosilicate (TEOS) and aminopropyltrimethoxysilane (APTMS) for water solubility improvement and amine terminals decoration. Subsequently, via a carbodiimide coupling reaction, UCNPs were grafted with benzoyloxy pyrrolidine based C₆₀ derivatives, as photosensitizers. Finally, gold nanorods (AuNRs) with localized surface plasmon resonance (LSPR) at 980 nm were synthesized, carboxylic polyethylene glycol (PEG) functionalized and covalently conjugated around the UCNPs-C₆₀ nanocomposite to obtain a multifunctional nanoplatform for photothermal therapy (PTT) and photodynamic therapy (PDT). Notably, under NIR laser irradiation, singlet oxygen was effectively generated from an upconverting photodynamic combination of UCNPs and C₆₀, while localized hyperthermia was simultaneously induced by LSPR activity of AuNRs. The therapeutic efficacy was validated in vitro on breast cancer cell lines MCF-7 and MDA-MB-231 by various microscopic and biochemical studies under a significantly mild NIR irradiation and low dosage of the nanoplatforms. Furthermore, according to cell viability comparative analysis, such nanocomposite presents a remarkable synergistic therapeutic effect by the combination of PTT and PDT. Overall, this work provides an innovative strategy for the design and understanding of clinical phototherapeutics.

**S.SM06.08.18**

**Synthesis and Surface Modification Effect of BaTiO₃ Nanoparticles by Sodium Oleate and Chitosan on Their Piezoresponse Force Microscopy (PFM)** Luis M. Angelats Silva¹, Jose Roldan Lopez¹, Nikita A. Emelianov², Henry León-León¹ and Rudy Céspedes-Vásquez¹; ¹Universidad Privada Antenor Orrego, Peru; ²Kursk State University, Russian Federation; ³Universidad Nacional de Trujillo, Peru

Spherical titanium barium nanoparticles with an average size about 100 nm in the tetragonal crystal phase were obtained by peroxide synthesis and then with formation of OH groups on its surface by hydrogen peroxide. To prevent their agglomeration and reduce the toxic effect, the surface of nanoparticles was chemically modified with sodium oleate and chitosan. Influence of surface modification by these compounds on piezoresponse force microscopy and their structure were investigated.

**S.SM06.08.19**

**Laser-Induced Strong Marangoni Effect in Deformation and Manipulation of Ferrofluid** Feng Lin¹, Talari Talari Vishal², Junyi Zhao³, John Schaibley², Dong Liu³, Zhiming M. Wang¹ and Jiming Bao²; ¹University of Electronic Science and Technology of China, China; ²University of Houston, United States; ³Washington University in St. Louis, United States; ⁴University of Arizona, United States

Optical manipulation of fluid or droplet has long been investigated for applications in microfluidics. The light-induced thermocapillary effect is one of the strategies in optical control of liquid. We demonstrate the laser-induced deformation of ferrofluid surfaces with ultra-violet to infra-red lasers. The surface deformation reaches the bottom and breaks the liquid, achieving the highest liquid deformation thickness for over 1000 μm. The deformation process and rupture are related to strong Marangoni effect, high laser absorption and low viscosity of ferrofluid. As applications of the laser-controlled ferrofluid, we show that a ferrofluid droplet in the capillary can be easily moved horizontally and vertically by the...
illumination of a laser beam. We also demonstrate that letters and patterns can be written on the black surface of ferrofluid thin film with a laser beam even with a common laser pointer. Laser manipulation of ferrofluid also makes it a controlling vehicle for varieties of liquid or droplets.

S.SM06.08.20
Preparation and Characterization of Nitroxide-Based Magnetic Nanoemulsions Directed toward MRI-Visible Targeted Delivery System Kota Nagura and Naoki Komatsu; Kyoto Univ, Japan

We have prepared various all-organic magnetic soft materials containing a cyclic nitroxide radical moiety as a spin source [1]. In this talk, we report the preparation of all-organic magnetic nanoemulsions composed of the non-ionic surfactant and the hydrophobic nitroxide radical compound [2]. The properties of the nanoemulsions have been investigated by small angle neutron scattering (SANS) and dynamic light scattering (DLS) analyses, EPR spectroscopy, and MRI method. The nanoemulsions showed high colloidal stability, high reduction resistance to ascorbic acid, low cytotoxicity and an enough contrast enhancement in the proton longitudinal relaxation time (T1)-weighted MR images in (-)-PBS in vitro and in vivo. Furthermore, an additional hydrophobic anticancer drug such as Taxol® was simultaneously encapsulated inside the nanoemulsions. We expect that the drug-loaded nanoemulsions can be used as a biocompatible magnetic drug carrier for MRI-visible targeted delivery system.


S.SM06.08.22
One-Pot Synthesis of Highly Water-Soluble Iron Oxide Nanoparticles with Functional Groups in Polyols for T1-Weighted MRI Pohlee Cheah, Paul Brown and Yongfeng Zhao; Jackson State University, United States

The direct synthesis of water soluble iron oxide nanoparticles with both controlled size and functional groups on the surface has gained intensive interests. In this study, ultrasmall iron oxide nanoparticles (IONPs) with different functional groups were successfully synthesized via one-pot synthesis. The IONPs are prepared by first thermal decomposition of iron acetylacetonate Fe(acac)3 precursor in diethylene glycol (DEG), followed by mixing the surface ligands at the end of the reaction. This facile synthesis method enabled binding of different surface materials such as dopamine hydrochloride (Dopa), polyethylene glycol with thiol end group (thiol-PEG), and polyacrylic acid (PAA) onto the IONPs. The size growth of IONPs can be well controlled as evidenced by transmission electron microscopy (TEM) studies. The high water stability of nanoparticles was correlated with the change of hydrodynamic size and zeta potential. While TEM results showed no significant change in the nanoparticles core size before and after surface modification, hydrodynamic size slightly increases due to the presence of ligands molecules on the surface. The attachment of surface ligands was studied by FTIR and TGA. FTIR results indicated the corresponding functional group for each surface ligands as a result of surface modification. In addition, we confirmed the introduce of functional groups by bioconjugation of fluorescence dyes on to the surface. The magnetic resonance phantom study show that the resulted nanoparticles can be used for T1-weighted MRI imaging. The effect of surface ligands on the relaxivities of IONPs were also studied.

S.SM06.08.26
Activation of Electrocured Bioadhesives Using DC and AC for Electroceutical Therapies Manisha Singh and Terry W. Steele; Nanyang Technological University, Singapore

Stimuli sensitive adhesives can be cured with temperature, UVA, and voltage. However, heat and light cured adhesives are limited to heat-sensitive and transparent substrates. Electrochemically mediated adhesive curing (i.e. electrocuring) can be utilized on a wide range of substrates including heat- sensitive and opaque surfaces. When an applied voltage potential is raised above a certain threshold, voltage activation initiates the diazirine groups to crosslink neighboring surfaces. Under the influence of direct current (1-3 mA), electrocuring progresses from the cathode to the anode but the maximum migration of the electrocuring is limited to 60-70% of the surface area. The application of alternating current (AC) is hypothesized to improve the electrocuring progression resulting in 100% surface activation, with a subsequent improvement in material properties. Structure-activity relationships of DC vs. AC currents are evaluated for the migration rate, shear modulus, gelation time, and adhesion strength of Voltaglue. Complete progression is achieved under AC stimulation and the maximum bioadhesion strength achieved for AC is 33 % higher than that for DC stimulation.
12:30 PM *S.SM06.06.04
Optical Control of Nerves Using Organic Electrolytic Photocapacitors (OEPCs) Marie Jakešová1, Malin Silverå-Ejneby1, Ludovico Migliaccio1, Oliya Abdullaeva1, Maciej Gryszie1, Vedran Derek1 and Eric D. Glowacki1,2; 1Linkoping University, Sweden; 2Warsaw University of Technology, Poland

A great demand exists for nongenetic optical neuromodulation technologies. We report on our developments of ultrathin organic optoelectronic devices for neurostimulation. All of these devices rely on far red/near infrared irradiation in the tissue transparency window to actuate nanoscale organic semiconductor components. Our flagship technology is the organic electrolytic photocapacitor (OEPC) – a device that mimics biphasic current-pulse neurostimulation and thus transduces an optical signal into directly-evoked action potentials in neurons. These devices are not only wireless, but also 100-1000 times thinner than most existing technologies. Making implants with as small as possible mechanical footprint improves the efficacy of bioelectronic medical treatments by minimizing the risk for inflammation and making surgical implantation less invasive. We will present our results on pushing the limits of efficiency and stability, with benchmarking of performance using in vitro and ex vivo models, and cover our developments of peripheral nerve stimulation implants.

1:00 PM *S.SM06.05.02
Multi-Modal Sensors and Actuators for Biointerfacing Ivan Minev; University of Sheffield, United Kingdom

Interfaces that link biological systems with machines are increasingly evolving beyond the electrical domain. Multi-modal bioelectronics aims to add chemical, optical, thermal or mechanical functionality to the capabilities of classical electrode arrays. When such systems are used in physical contact with tissues or cells, the need for overall mechanical compliance is crucial for their biointegration. This raises a question: how do we build multi-modal arrays of sensors and actuators with tissue-like softness?

In this talk I will present our efforts to adapt direct ink writing (multi-material 3D printing) for the purpose of fabricating elastic systems of electrodes, optrodes, thermotrodes, and chemotrodes. A palette of silicones, composites and hydrogels are used as inks, where each of the inks enables one interfacing modality. As an example of in vitro application, I will present multi-modal pacing and monitoring of stem cell derived cardiomyocytes. In vivo, I will present printed neuro-muscular implants tailored to specific anatomical niches and animal models. These developments are expected to contribute to the development of personalized platforms for bioelectronic medicine.
**SESSION S.SM06.10: Live Lightning/Flash: Soft Organic and Hybrid Materials for Biointerfacing—Materials, Processes and Applications**

Session Chairs: Mary Donahue, Martin Kaltenbrunner and Robert Shepherd

Sunday Afternoon, November 29, 2020

S.SM06

5:00 PM INTRODUCTION

**5:05 PM *S.SM06.06.01**

*Wireless Photovoltaic Neuroprostheses for Artificial Vision* Diego Ghezzi; École polytechnique fédérale de Lausanne, Switzerland

Neural prostheses are devices integrated with the neural tissue for diagnostic or therapeutic purposes, such as restoring impaired or lost functions. Despite a large variety of devices exists, a shared future is the presence of cables connecting the electrode-tissue interface to implantable electronic circuits for signal management. The presence of wires and connectors is a significant disadvantage for neural prostheses; in fact, they are weak points often leading to failure, they exert mechanical forces and tractions on the implant and the tissue, and they are often transcranial or transcutaneous connections that might lead to post-surgical complications, such as infection. Also, the use of implantable electronic units is another disadvantage. Several aspects limit their operation, such as power consumption, excessive heat generation, and high risk of failure in a wet environment due to leakage.

In neural prostheses, wireless electrodes are desirable. Retinal prostheses are a particular category of neural prostheses, in which wireless neuronal stimulation was achieved thanks to photovoltaic technology, that also avoids the need for active implantable electronic units. In the case of retinal stimulation, photovoltaic technology is intuitive since the retina is made to absorb light entering from the pupil naturally. Although photovoltaic retinal prostheses do not work with ambient and natural light, electrical stimulation is triggered by artificial light projected into the pupil and absorbed by semiconductor elements embedded into the stimulating pixels. This solution allows retinal prostheses to avoid a transscleral flat cable which limits the maximum number of stimulating pixels on the device and induce post-operative complications such as eye inflammation or leakage through the incision.

In the first part of this talk, the development and validation in-vitro and in-vivo of a wide-field, photovoltaic, and injectable retinal prosthesis will be reported. POLYRETINA is a wide-field epiretinal prosthesis which contains 10,499 photovoltaic electrodes (diameter of 80 µm and pitch of 120 µm) distributed with a pixel density of 80.33 pixels mm\(^{-2}\). The pixels cover an active area of 12.9 mm in diameter; thus, the prosthesis covers a visual angle of 46.3 °. Each pixel is composed by a conductive polymer (PEDOT:PSS) a bulk heterojunction (P3HT:PCBM) and a metallic cathode (Ti). The results obtained both in-vitro with retinal explants and in-vivo with large animal models will be reported.

In the second part of the talk, a novel visual prosthesis based on intra-neural stimulation of the optic nerve will be described. OpticSELINE is an intraneural 3D electrode array capable of selectively activating the optic nerve fibres to induce artificial vision. This technology is essential to overcome the exclusion criteria of retinal implants. The results from our in-vivo preclinical trial in large animals will be presented.

In conclusion, the use of photovoltaic technology to design novel neuroprostheses will be highlighted.

**5:13 PM S.SM06.01.04**

*Design and Patterning of Conductive PEDOT:PSS Hydrogels with Tissue-Like Mechanical Properties for Long-Term Bio-Electronic Interfacing* Vivian R. Feig\(^1\), Helen Tran\(^1\), Minah Lee\(^2\) and Zhenan Bao\(^1\); \(^1\)Stanford University, United States; \(^2\)Korea Institute of Science and Technology (KIST), Korea (the Republic of)

Bioelectronics are poised to revolutionize health care, providing exciting opportunities for therapeutics, health monitoring, prosthetics, and human augmentation. Yet, there remain significant barriers to long-term implantation of these technologies within the body. This is due in large part to inflammatory responses resulting from the severe mismatch in mechanical properties between conventional device components, which are rigid (E–GPa) and non-deformable, and biological tissues, which are significantly more soft (E–kPa) and dynamic. With their high water content (70-99 wt%), hydrogels are capable of achieving tissue-level elastic moduli, though existing strategies to render hydrogels electrically conductive involve incorporating stiff, conductive additives into inert and stretchable hydrogels, necessitating a tradeoff between electrical and mechanical properties. Here, we present a new materials design strategy for conductive hydrogels that overcomes this tradeoff by decoupling mechanical from electrical properties through the use of two distinct, interpenetrating polymer networks. We first leverage the gel-forming capabilities of the conducting polymer poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) to form a macroscopically connected conductive network at
remarkably low polymer concentrations (~1 wt%). The highly dilute yet interconnected conductive network enables us to orthogonally tune elastic modulus using a second, interpenetrating polymer network. Our unique design enables an unprecedented combination of mechanical tunability over 3 biologically-relevant orders of magnitude (8 kPa – 374 kPa), stretchability (up to 400%), elasticity, and electrical conductivity up to 23 S/m. To enable their integration into devices, we further introduce a novel method for patterning these materials with high resolution onto surfaces of planar and even curved objects. We overcome limitations precluding the use of conventional molding or lithographic methods by using a sacrificial metal pattern that can be oxidized in the presence of a PEDOT:PSS electrolyte to locally induce gelation only at the pattern interface. This materials design strategy and its corresponding new patterning method represent a significant step towards the development of next-generation bioelectronics that can seamlessly interface with biological targets over extended timescales.

5:21 PM S.SM06.02.03
Super-Soft Solvent-Free Bottlebrush Elastomers for Touch Sensing Veronica G. Reynolds¹,¹, Sanjoy Mukherjee¹,¹, Renxuan Xie¹,¹, Adam E. Levi¹,¹, Amalie Atassi², Takumi Uchiyama³, Hengbin Wang³, Michael L. Chabinyc¹,¹ and Christopher M. Bates¹,¹,¹; ¹University of California, Santa Barbara, United States; ²University of Florida, United States; ³Tokyo Institute of Technology, Japan

Pressure sensors with high sensitivity have uses ranging from pulse monitoring and plantar pressure measurement (10–100 kPa) to in vivo intraocular and intracranial pressure measurement (1–10 kPa). The sensitivity of capacitive pressure sensors is primarily determined by the modulus of a dielectric layer that reversibly deforms to produce an electrical signal. Crosslinked polymers provide a means to achieve good dielectric properties with low modulus relative to inorganic materials. Unfortunately, the mechanical properties of conventional linear polymer networks are constrained such that a lower limit on softness translates to poor capacitive pressure sensor performance. Here, we overcome this limitation by leveraging the intrinsic “super-soft” characteristic of bottlebrush polymers, which can be crosslinked to form solvent-free networks with moduli in a range matching that of biological tissues (1–100 kPa). A simple light-induced crosslinking strategy is introduced to facilitate device fabrication. Parallel plate capacitive pressure sensors constructed with these bottlebrush polymer networks exhibit up to a 53× increase in sensitivity compared to commonly used elastomers, e.g., PDMS (Sylgard 184). The sensors show pressure resolution on the order of 0.1 kPa, capable of differentiating subtle forces in the light touch regime. Transparent and flexible sensors fabricated using indium-tin-oxide (ITO)-coated poly(ethylene terephthalate) (PET) electrodes are shown to be functional in a bent configuration. This combination of contemporary synthetic chemistry and application-driven materials design accentuates the opportunities available at the intersection of science and engineering to advance soft, flexible, and biocompatible devices.

5:29 PM *S.SM06.02.02
Iontronics for Human-Machine Interactions Pooi See Lee; Nanyang Technological University, Singapore

Gel based iontronics are attractive for epidermal electronics due to their compatible and tunable mechanical properties. Many receptive interface for bidirectional human-machine interactions require tactile sensors that are intrinsically soft, skin conformable and dynamically deformable. While addressable touch input can be realized using capacitive, resistive, piezoelectric or triboelectric signals, the output signal often requires integrated lighting for visual detection or optoelectronic signal feedback on a transparent interface. In addressing these needs, ionic conductors provide the advantages of optically transparent, skin compliant, ease of processibility and added novel functionality in the presence of ions and electrons transport.

We have demonstrated the use of conductive hydrogel composites as versatile strain sensors for monitoring of human motion. In addition, hydrogel ionic conductor was shown to be effective current collector by harnessing the electrical double layer for triboelectric nanogenerators, allowing them to be mounted onto skin or machine. On the other hand, we have formulated inkjet printable ionic gels with precise control of the rheological characteristics of gels. As a result, transparent deformable touch panels have been realized using the microscale patterning of ionic gel. The transparent touch interface is capable of remarkable signal fidelity under dynamic human-machine interactive conditions. We have further prepared thermally stable gels with self-healing ability and found applications in dielectric actuators, potentially used in biostimulation applications.

5:37 PM *S.SM06.02.04
Direct Writing of 3D Conducting Polymer Microarrays for Biological Sensing and Cell Stimulation Jadranka Travas-Sejdić¹,¹, Peikai Zhang¹, Jeremy Crook² and Eva Tomaskovic-Crook³; ¹Polymer Electronics Research Centre, University of Auckland, New Zealand; ²MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand; ³University of Wollongong, Australia
Conducting polymers (CPs) have been widely used as electroactive biointerfaces in applications such as DNA sensors, in electrically-stimulated tissue engineering and more recently in stretchable and conformable organic bioelectronics. However, the majority of these applications are based on the electropolymerized or solution deposited 2D films of CPs, and as such cannot fully probe the actual 3D cell environment within tissues and organs. Our approach to address this is based on a precise fabrication of individually addressable, high aspect ratio, 3D CP-pillar microelectrode arrays by means of ‘micro-extrusion printing’ using our in-house constructed system. The ‘printing’ principle is simple ‘extrusion’ of CP ‘ink’ from a micro-pipette into ‘pillars’, accompanied by evaporation of solvent (water) during the process. CP pillars of different aspect ratios (from 2 to 7000) were successfully fabricated, with excellent stability, mechanical properties and electrochemical properties [1].

Such 3D CP-pillar microelectrode arrays could be employed in a variety of applications, from biological sensing to recording and electrically stimulating cells and tissues, with the design of the arrays being easily adjustable to a particular application. Our demonstrated examples include: exosome capture, sensing and release - where the CP pillars can be easily functionalized for capture/release of exosomes; and 3D electrical stimulation of human neural stem cells into high-density of mature neurons and functional neural networks[2].

Overall, the 3D CP microelectrodes provide promising versatile substrates for a variety of bioelectronics applications, including where spatiotemporal control of individually addressable microelectrodes is desired.


5:45 PM *S.SM06.03.03
Conformable Organic Photonic Systems Tomoyuki Yokota and Takao Someya; The University of Tokyo, Japan

In this talk, I will introduce our recent activity of conformable organic photonic systems. We have developed ultra-flexible and lightweight highly efficient, ultra-flexible, air-stable, three-color, organic light-emitting diodes (OLEDs). The total thickness of the devices, including the substrate and encapsulation layer, is only three micrometers, which is one order of magnitude thinner than the epidermal layer of the human skin. Due to the very thin substrate and neutral position, our device shows the highly flexibility and conformability. The OLEDs are directly laminated on the surface of skin and are used as indicators/displays. Furthermore, we have developed ultra-flexible organic imager which consists with a monolithically processed rectifying pixel and an organic photo diode. Our organic imager has pixel pitches as small as 50 µm, with resolutions of up to 262 ppi. Using our ultra-flexible organic imager, we succeed to measure the spatial photoplethysmography (PPG) mapping.

5:53 PM BREAK

5:59 PM *S.SM06.02.05
Remote, Non-Genetic Modulation Cellular Activity Using Hybrid-Nanomaterials Tzahi Cohen-Karni; Carnegie Mellon University, United States

Electrical stimulation of tissue and ultimately individual cells has not only played an essential role in our understanding of the structure and function of excitable tissue but continues to serve as the basis for a variety of therapeutic interventions for the treatment of disorders ranging from cardiac arrhythmias to Parkinson’s disease. Advances in technology have attempted to overcome barriers associated with the spatial resolution (i.e., who and where to stimulate) and the invasiveness of the process. Optogenetics has revolutionized the way we can record and affect the electrophysiology of cells and tissue, using light as the input/output (I/O) interface. Though optogenetics has developed at a great pace and is making profound scientific contributions, the core of the technique requires genetic modifications of the cells or organism. This presents challenges both in terms of achieving targeted gene expression and the potential deleterious consequences of the expression of foreign proteins, which have implications on clinical translation to humans and regulatory approval. We report our developed breakthrough hybrid-nanomaterial synthesis process to enable minimally invasive, remote and non-genetic light-induced control of targeted cell activity with high spatial-temporal resolution. We combine one-dimensional (1D) nanowires (NWs) and two-dimensional (2D) graphene flakes grown out-of-plane with tailor-made physical properties for highly controlled photostimulation. Photostimulation using NW templated 3D fuzzy graphene (NT-3DFG) is flexible due to its broadband absorption and does not generate cellular stress. Our light-based platform adds a powerful toolset to the basic scientists studying cell signaling within and between tissues. Last, this platform can be adapted to address challenges in tissue...
engineering, i.e. the much-needed non-genetic stimulation control of engineered tissues. By controlled delivery of the NT-3DFG we will be able to locally and selectively control cellular activity with high spatial and temporal resolution of 3D tissues.

6:07 PM S.SM06.03.09
Transparent Flexible Polymer Actuator with Enhanced Output Force Enabled by Conductive Nanowires Interlayer

Tony Fook1,2, Jin Han Jeon2 and Pooi See Lee1; 1Nanyang Technological University, Singapore; 2Robert Bosch (SEA) Pte Ltd, Singapore

As the role of flexible soft materials become more crucial for applications such as flexible displays in foldable mobile phones, compliant sensors and actuators in wearables, etc., new functional soft materials are needed to fill the roles previously fulfilled by rigid and bulky conventional materials. The field of haptic technology has recently seen emerging needs for integration into soft, flexible and even transparent interfaces. Since several decades ago, haptic feedback in electronic devices such as mobile phones, gaming controllers, are provided by bulky mechanical motors that vibrate the entire device upon application of an electric signal to give a tactile sensation to the users. In recent years, piezoceramics such as lead zirconate titanate are seen as a popular alternative due to its high performance and small form factor. However, their high stiffness, density and opacity prove to be a large obstacle in applications where flexibility, weight and transparency are crucial. In such applications, electroactive polymers (EAPs) serve as an excellent solution and have been a rapidly growing focus of research due to the wide range of potential applications such as energy harvesters, sensors and actuators, artificial muscles, etc. In reported methods to enhance the dielectric and electromechanical properties of EAPs, there is a compromise in at least one of these factors: electrical breakdown strength, transparency and flexibility.

In this work, we present an approach to enhance the output force of polymer actuators by increasing the dielectric permittivity and polarizability of the EAP, poly (vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) (P(VDF-TrFE-CTFE)), by incorporation of a conductive nanowire interlayer into the polymer matrix. The interlayer is formed by a network of highly conductive silver nanowires with high aspect ratio and enhances the dielectric permittivity and polarizability of the EAP over a broad range of frequencies including ultra low frequencies (e.g. 0.1 Hz) and the range of 200 to 300 Hz at which the mechanoreceptors in the human fingertips are most sensitive to. Through experiments and finite element modelling, the enhancement of dielectric properties were found to originate from charge accumulation at the nanowire/polymer interface and resulted in an output force double that of a neat EAP actuator. The higher output force can be used to improve tactile feedback perception of a human user and allows a 40% reduction in the actuator excitation voltage compared to that of a neat EAP actuator. Even with enhanced dielectric properties and output force, the composite actuator retains its transparency and flexibility without severe compromise in the electrical breakdown strength. The excellent transparency and flexibility of the modified EAP are promising for a wider range of possible applications such as direct and localized haptic feedback on flexible electronic displays, touch screens, etc.

6:47 PM CLOSING SUMMARY

SESSION S.SM06.11: Live Keynote II: Soft Organic and Hybrid Materials for Biointerfacing—Materials, Processes and Applications

Session Chairs: Mary Donahue and Jonathan Rivnay
Monday Afternoon, November 30, 2020
S.SM06

7:30 PM *S.SM06.04.01
Robotic Fabrics as Thin, Wearable, Fiber-Based Machines

Rebecca Kramer-Bottiglio; Yale University, United States

Robot function is largely determined by the structural platform upon which it is built. The field of soft robotics aims to expand the design space by introducing unconventional robotic materials and methods to the engineering toolkit. In this talk, it is proposed that this increasing repertoire of robotic platforms be extended to include fabrics, which are known for their extreme deformability, versatility, and customizability. Possible fiber-based forms to achieve actuation, sensing, and stiffness control will be presented, including: (1) shape memory alloy ribbon as a thin-body actuator, which is effective at pure-bending motion, in contrast with typical fiber actuators that rely on axial contraction alone; (2) An in-fabric sensor that changes in resistance as the fabric weave is stretched and the gaps present between fibers are enlarged; and (3) A stiffness-
changing fiber based on a glass-transition polymer epoxy with low-melting-point metallic alloy inclusions that is capable of a stiffness change of two orders of magnitude using Joule heating. By designing actuators, sensors, and structural components that conform to a fiber-based geometry, we show that simple fabrics can be functionalized to create damage-responsive tourniquets, self-deploying structures, and morphing airfoils.

8:00 PM *S.SM06.05.04
Brain Machine Interfaces Using Flex to Chip Bonding Eric Zhao, Marc Ferro, Tyler Chen, Pingyu Wang and Nicholas Melosh; Stanford University, United States

Enabled by new materials and device designs, a new generation of brain interface technologies is replacing bulkier, non-compliant systems with the aim of seamless electronic-biological interfaces with lower tissue damage, reduced immunogenicity, high-density, tunable spatial distribution, and long-term stability. Recent successful examples leveraging mechanically compliant materials have demonstrated major breakthrough in brain research using ultra-flexible systems for ECoGs recordings, and for depth electrodes.

However, connectorization of these ultra-flexible electrodes to traditional electronics remains a significant challenge. Current connectors, such as zero-insertion force (ZIF) devices, are limited to 64 or 128 channels at most. While these may then be stacked together this approach does not scale, limiting the maximum number of channels feasible.

Here, we demonstrate an easy to use, massively scalable connector technology. Rather than using traditional amplifier electronics, we couple thousands of flexible electrodes directly to a CMOS pixel array, such as typically found in a camera or OLED display. These devices have millions of available pixels, and by taking advantage of the small, flexible nature of the electrodes we are able to attach thousands of electrodes in seconds. These form robust Ohmic contact that can be extensively cycled. We demonstrate the simplicity of the process, and show how it can be used to perform massively parallel neural recordings.

8:30 PM *S.SM06.06.05
Organic Mixed Conductors—Fundamental Properties and Applications Alberto Salleo; Stanford University, United States

Organic mixed ionic/electronic conductors have elicited much interest lately as the enablers of a “new wave” of organic electronic devices in the biomedical space. In this talk I will start by exploring how the microstructure of the polymer interacts with the electrolyte and the effect of the electrolyte on the characteristics of electrochemical transistors. I will then show some applications of these materials in the sensor space ranging from flexible sensors to quantify electrolytes in sweat to biomimetic sensors to determine antibiotic activity of small molecules and detect the presence of pathogens. Finally I will show how devices based on these materials can be modulated by neuron-like cells where neurotransmitters elicit both short and long term potentiation in the device demonstrating a first building block of a new type of brain-machine interface.

SESSION S.SM06.01: Electronic Interfaces with Skin and Tissue
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-SM06

5:00 AM S.SM06.01.02
Bioadhesives for Clinical Applications and Biointegrated Devices Hyunwoo Yuk and Xuanhe Zhao; Massachusetts Institute of Technology, United States

Rapid and robust adhesion of wet tissues has critical importance for clinical applications such as wound closure and tissue repair as well as biointegrated devices for their stable yet functional operations and communications with the target tissues. For example, traumatic injuries and failure of prompt wound closure and hemostasis cause over 2 million deaths annually in the world; and the development of a broad range of biointegrated devices for therapeutic and diagnostic applications is one of the fastest growing fields in recent decades. However, conventional approaches such as sutures and staples have face numerous challenges including complications and problems caused by their non-continuous, tissue-damaging, and highly

2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
technical nature. While tissue adhesives and glues have been investigated as promising alternatives for sutures and staples, practical utility and impact of existing tissue adhesives and glues have been greatly dampened by several limitations including 1) incompatibility to wet tissues, 2) incompatibility to body fluids such as blood and mucus, 3) slow adhesion formation, 4) weak and brittle adhesion, and 5) inability to allow bioelectronic communication between tissue and adhered device. In this talk, we will introduce a set of novel bioinspired mechanisms and tissue adhesives capable of instant, strong, and conductive adhesion formation on various tissues covered by blood or mucus to address all abovementioned challenges. We will demonstrate a broad range of potential applications of these novel tissue adhesives and their implications in clinical, biomedical, and bioelectronic applications.

5:10 AM S.SM06.01.04
Design and Patterning of Conductive PEDOT:PSS Hydrogels with Tissue-Like Mechanical Properties for Long-Term Bio-Electronic Interfacing Vivian R. Feig1, Helen Tran1, Minah Lee2 and Zhenan Bao1; 1Stanford University, United States; 2Korea Institute of Science and Technology (KIST), Korea (the Republic of)

Bioelectronics are poised to revolutionize health care, providing exciting opportunities for therapeutics, health monitoring, prosthetics, and human augmentation. Yet, there remain significant barriers to long-term implantation of these technologies within the body. This is due in large part to inflammatory responses resulting from the severe mismatch in mechanical properties between conventional device components, which are rigid (E~GPa) and non-deformable, and biological tissues, which are significantly more soft (E~ kPa) and dynamic. With their high water content (70-99 wt%), hydrogels are capable of achieving tissue-level elastic moduli, though existing strategies to render hydrogels electrically conductive involve incorporating stiff, conductive additives into inert and stretchable hydrogels, necessitating a tradeoff between electrical and mechanical properties. Here, we present a new materials design strategy for conductive hydrogels that overcomes this tradeoff by decoupling mechanical from electrical properties through the use of two distinct, interpenetrating polymer networks. We first leverage the gel-forming capabilities of the conducting polymer poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) to form a macroscopically connected conductive network at remarkably low polymer concentrations (~1 wt%). The highly dilute yet interconnected conductive network enables us to orthogonally tune elastic modulus using a second, interpenetrating polymer network. Our unique design enables an unprecedented combination of mechanical tunability over 3 biologically-relevant orders of magnitude (8 kPa – 374 kPa), stretchability (up to 400%), elasticity, and electrical conductivity up to 23 S/m. To enable their integration into devices, we further introduce a novel method for patterning these materials with high resolution onto surfaces of planar and even curved objects. We overcome limitations precluding the use of conventional molding or lithographic methods by using a sacrificial metal pattern that can be oxidized in the presence of a PEDOT:PSS electrolyte to locally induce gelation only at the pattern interface. This materials design strategy and its corresponding new patterning method represent a significant step towards the development of next-generation bioelectronics that can seamlessly interface with biological targets over extended timescales.

5:20 AM S.SM06.01.05
Skin-Inspired Soft Electronic Materials and Devices for Biointerfacing Zhenan Bao; Stanford University, United States

In this talk, I will present our recent work on engineering soft electronic materials and their applications in biointerfacing

SESSION S.SM06.02: Soft Materials and Devices for Humans Interfaces
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-SM06

5:00 AM S.SM06.02.01
Structural Colored Bacterial Colonies as a Living Optical Material Silvia Vignolini; University of Cambridge, United Kingdom

Bright and vivid colours found in living organisms are often the result of hierarchical nanostructured materials. Here we show that in the case of Flavobacterium IR1 colonies, the complex organisation of the cells in polycrystalline twodimensional lattices is a distinctive fingerprint of the colony organisation. By combining an analytical analysis of the scattering response with numerical modelling, we obtain the exact inter-cells distance and cell diameter with a resolution comparable to conventional electron microscopy techniques. Such a precise understanding of the structure-to-function
relation allows not only to fully describe their optical appearance, but it enables to gather insights on the mechanisms used for communication and their biological function. Further, the ability to genetically modify them allowed us to modify their colouration and control their optical appearance on-demand, enabling us to use such colonies as novel photonic living materials.

5:10 AM *S.SM06.02.02
Iontronics for Human-Machine Interactions Pooli See Lee; Nanyang Technological University, Singapore

Gel based iontronics are attractive for epidermal electronics due to their compatible and tunable mechanical properties. Many receptive interface for bidirectional human-machine interactions require tactile sensors that are intrinsically soft, skin conformable and dynamically deformable. While addressable touch input can be realized using capacitive, resistive, piezoelectric or triboelectric signals, the output signal often requires integrated lighting for visual detection or optoelectronic signal feedback on a transparent interface. In addressing these needs, ionic conductors provide the advantages of optically transparent, skin compliant, ease of processibility and added novel functionality in the presence of ions and electrons transport.

We have demonstrated the use of conductive hydrogel composites as versatile strain sensors for monitoring of human motion. In addition, hydrogel ionic conductor was shown to be effective current collector by harnessing the electrical double layer for triboelectric nanogenerators, allowing them to be mounted onto skin or machine. On the other hand, we have formulated inkjet printable ionic gels with precise control of the rheological characteristics of gels. As a result, transparent deformable touch panels have been realized using the microscale patterning of ionic gel. The transparent touch interface is capable of remarkable signal fidelity under dynamic human-machine interactive conditions. We have further prepared thermally stable gels with self-healing ability and found applications in dielectric actuators, potentially used in biostimulation applications.

5:25 AM S.SM06.02.03
Super-Soft Solvent-Free Bottlebrush Elastomers for Touch Sensing Veronica G. Reynolds1,1, Sanjoy Mukherjee1,1, Renxuan Xie1,1, Adam E. Levi1,1, Amalie Atassi2, Takumi Uchiyama3, Hengbin Wang1, Michael L. Chabinyc1,1 and Christopher M. Bates1,1,1; 1University of California, Santa Barbara, United States; 2University of Florida, United States; 3Tokyo Institute of Technology, Japan

Pressure sensors with high sensitivity have uses ranging from pulse monitoring and plantar pressure measurement (10–100 kPa) to in vivo intraocular and intracranial pressure measurement (1–10 kPa). The sensitivity of capacitive pressure sensors is primarily determined by the modulus of a dielectric layer that reversibly deforms to produce an electrical signal. Crosslinked polymers provide a means to achieve good dielectric properties with low modulus relative to inorganic materials. Unfortunately, the mechanical properties of conventional linear polymer networks are constrained such that a lower limit on softness translates to poor capacitive pressure sensor performance. Here, we overcome this limitation by leveraging the intrinsic “super-soft” characteristic of bottlebrush polymers, which can be crosslinked to form solvent-free networks with moduli in a range matching that of biological tissues (1–100 kPa). A simple light-induced crosslinking strategy is introduced to facilitate device fabrication. Parallel plate capacitive pressure sensors constructed with these bottlebrush polymer networks exhibit up to a 53× increase in sensitivity compared to commonly used elastomers, e.g., PDMS (Sylgard 184). The sensors show pressure resolution on the order of 0.1 kPa, capable of differentiating subtle forces in the light touch regime. Transparent and flexible sensors fabricated using indium-tin-oxide (ITO)-coated poly(ethylene terephthalate) (PET) electrodes are shown to be functional in a bent configuration. This combination of contemporary synthetic chemistry and application-driven materials design accentuates the opportunities available at the intersection of science and engineering to advance soft, flexible, and biocompatible devices.

5:35 AM *S.SM06.02.04
Direct Writing of 3D Conducting Polymer Microarrays for Biological Sensing and Cell Stimulation Jadranka Travas-Sejdic1,2, Peikai Zhang1, Jeremy Crook3 and Eva Tomaskovic-Crook3; 1Polymer Electronics Research Centre, University of Auckland, New Zealand; 2MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand; 3University of Wollongong, Australia

Conducting polymers (CPs) have been widely used as electroactive biointerfaces in applications such as DNA sensors, in electrically-stimulated tissue engineering and more recently in stretchable and conformable organic bioelectronics. However, the majority of these applications are based on the electopolymerized or solution deposited 2D films of CPs, and as such cannot fully probe the actual 3D cell environment within tissues and organs. Our approach to address that is based on a precise fabrication of individually addressable, high aspect ratio, 3D CP-pillar microelectrode arrays by means of ‘micro-
extrusion printing’ using our in-house constructed system. The ‘printing’ principle is simple ‘extrusion’ of CP ‘ink’ from a micro-pipette into ‘pillars’, accompanied by evaporation of solvent (water) during the process. CP pillars of different aspect ratios (from 2 to 7000) were successfully fabricated, with excellent stability, mechanical properties and electrochemical properties [1].

Such 3D CP-pillar microelectrode arrays could be employed in variety of applications, from biological sensing to recording and electrically stimulating cells and tissues, with the design of the arrays being easily adjustable to a particular application. Our demonstrated examples include: exosome capture, sensing and release - where the CP pillars can be easily functionalized for capturer/release of exosomes; and 3D electrical stimulation of human neural stem cells into a high-density of mature neurons and functional neural networks[2].

Overall, the 3D CP microelectrodes provide promising versatile substrates for a variety of bioelectronics applications, including where spatiotemporal control of individually electrically addressable microelectrodes is desired.


5:50 AM *S.SM06.02.05
Remote, Non-Genetic Modulation Cellular Activity Using Hybrid-Nanomaterials Tzahi Cohen-Karni; Carnegie Mellon University, United States

Electrical stimulation of tissue and ultimately individual cells has not only played an essential role in our understanding of the structure and function of excitable tissue but continues to serve as the basis for a variety of therapeutic interventions for the treatment of disorders ranging from cardiac arrhythmias to Parkinson’s disease. Advances in technology have attempted to overcome barriers associated with the spatial resolution (i.e., who and where to stimulate) and the invasiveness of the process. Optogenetics has revolutionized the way we can record and affect the electrophysiology of cells and tissue, using light as the input/output (I/O) interface. Though optogenetics has developed at a great pace and is making profound scientific contributions, the core of the technique requires genetic modifications of the cells or organism. This presents challenges both in terms of achieving targeted gene expression and the potential deleterious consequences of the expression of foreign proteins, which have implications on clinical translation to humans and regulatory approval. We report our developed breakthrough hybrid-nanomaterial synthesis process to enable minimally invasive, remote and non-genetic light-induced control of targeted cell activity with high spatial-temporal resolution. We combine one-dimensional (1D) nanowires (NWs) and two-dimensional (2D) graphene flakes grown out-of-plane with tailor-made physical properties for highly controlled photostimulation. Photostimulation using NW templated 3D fuzzy graphene (NT-3DFG) is flexible due to its broadband absorption and does not generate cellular stress. Our light-based platform adds a powerful toolset to the basic scientists studying cell signaling within and between tissues. Last, this platform can be adapted to address challenges in tissue engineering, i.e. the much-needed non-genetic stimulation control of engineered tissues. By controlled delivery of the NT-3DFG we will be able to locally and selectively control cellular activity with high spatial and temporal resolution of 3D tissues.

6:05 AM S.SM06.02.06
Studying Human Cell Membrane Function Using Bioelectronic Technologies Anna-Maria Pappa1, Walther Traberg-Christensen1, Han-Yuan Liu2, Susan Daniel2, Alberto Salleo3, Quentin Tribuce3 and Roisin Owens1; 1University of Cambridge, United Kingdom; 2Cornell University, United States; 3Stanford University, United States

Despite their significance in the aetiology of many diseases, cellular membranes are still an underexplored target for studying the mechanisms of diseases or drug therapies. Supported lipid bilayers (SLB), are a preferred model membrane system for cell membrane studies, including ion channel recording and pharmaceutical screening. However, to date, cell-free commercially available technologies for plasma membrane studies have been limited to synthetic membranes that lack the inherent complexity found in the membrane of the cell.

Here, we use vesicles derived from live cells to create cell-free native membrane models on top of active bio-transducers. These vesicles fuse on top of the desired substrates forming an SLB. In this work we use human embryonic kidney 293 cells (HEK) and a hydrated polymer-based transducer, based on poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS), instead of inorganic solid supports. This provides a fluid environment close to the physiologically relevant one, thus facilitating mobility of the transmembrane proteins (TMPs), which is a prerequisite for protein membrane studies.
Moreover, the optical transparency of PEDOT:PSS ensures compatibility with standard optical methods allowing us to confirm the presence and correct orientation of TMPs as well as the mobility (fluidity) of the bilayer using fluorescent microscopy techniques, such as fluorescence recovery after photobleaching (FRAP) and total internal reflection fluorescence (TIRF). These features enhance the native structural and functional properties of the membrane and ensure the usefulness of our platform as a physiologically relevant and predictive mimic of membrane molecular interactions.

In this study we carry out electrical characterization of membrane properties and interactions using both PEDOT:PSS-based electrodes and transistors (the Organic Electrochemical Transistor). This is based on measuring the ionic flux through the membrane via electrical impedance spectroscopy and transistor-characteristics. In this way, we can monitor biological interactions quantitatively and in real time, revealing useful information regarding the dynamics of membrane fusion. This allows for sensitive detection of minute changes of membrane properties, e.g. receptor binding events, changes in membrane potential and ion channel activity. As an example, we can observe differences in the electrical properties between the native membrane derived from HEK cells and a native membrane derived from HEK cells overexpressing the potassium ion channel TREK-1. Our device allows us to measure the chemically-induced gating of TREK-1 ion channels with the ability to distinguish between general ion channel activity and that of TREK-1, specifically. Overall, our results highlight the suitability of this platform for drug screening against ion channel targets paving the way for a scalable and cost-efficient alternative method to using whole cells e.g. patch clamp assays.

6:15 AM *S.SM06.02.07
Graphene-Based Sensing of Oxygen Permeation through Pulmonary Membranes
Cecilia Leal; University of Illinois at Urbana-Champaign, United States

Lipid-protein complexes are the basis of pulmonary surfactants covering the respiratory surface and mediating gas exchange in lungs. Cardiolipin is a mitochondrial lipid overexpressed in mammalian lungs infected by bacterial pneumonia. In addition, increased oxygen supply (hyperoxia) is a pathological factor also critical in bacterial pneumonia. In this work we present the fabrication of a micrometer-size graphene-based sensor to measure oxygen permeation through pulmonary membranes. Combining oxygen sensing, X-ray scattering, and Atomic Force Microscopy, we discovered that mammalian pulmonary membranes suffer a structural transformation induced by cardiolipin. We observe that cardiolipin promotes the formation of periodic protein–free inter–membrane contacts with rhombohedral symmetry. Membrane contacts, or stalks, promote a significant increase in oxygen gas permeation which may bear significance for alveoli gas exchange imbalance in pneumonia.

5:00 AM *S.SM06.03.03
Conformable Organic Photonic Systems
Tomoyuki Yokota and Takao Someya; The University of Tokyo, Japan

In this talk, I will introduce our recent activity of conformable organic photonic systems. We have developed ultra-flexible and lightweight highly efficient, ultra-flexible, air-stable, three-color, organic light-emitting diodes (OLEDs). The total thickness of the devices, including the substrate and encapsulation layer, is only three micrometers, which is one order of magnitude thinner than the epidermal layer of the human skin. Due to the very thin substrate and neutral position, our device shows the highly flexibility and conformability. The OLEDs are directly laminated on the surface of skin and are used as indicators/displays. Furthermore, we have developed ultra-flexible organic imager which consists with a monolithically processed rectifying pixel and an organic photo diode. Our organic imager has pixel pitches as small as 50 µm, with resolutions of up to 262 ppi. Using our ultra-flexible organic imager, we succeed to measure the spatial photoplethysmography (PPG) mapping.

5:15 AM S.SM06.03.04
Efficient Ultra-Flexible Photo-Charging Systems for Simultaneous Solar Energy Conversion and Storage
Ruiyuan Liu1, Masahito Takakuwa1, Kenjiro Fukuda2 and Takao Someya1,2; 1Center for Emergent Matter Science (CEMS), RIKEN, Japan; 2The University of Tokyo, Japan
Integration of high performance ultra-flexible energy harvesters with energy storage units not only provides an efficient, stable self-powered source, but also realizes a volume miniaturization with reduced thickness and wiring requirements, which is an unprecedented demand for biomedical devices and wearable electronics. The main challenge for an efficient flexible self-powered system lies in the management between the stable operation with mechanical flexibility and long-term electrical performance, the proposed research task will focus on materials design, interface engineering, device configuration and reliable packaging technologies mainly based on organic components to tackle with the latent issues. Here we report flexible integrated photo-charging devices subsequently constructed based on ultra-thin efficient organic photovoltaics and supercapacitors via advanced design and power management, achieving high overall energy conversion and storage efficiency as well as maintaining superior system operation stability and mechanical flexibility for multifunctional wearable electronics.

5:25 AM S.SM06.03.05
A High-k, Stretchable and Self-Healing Dielectric for Electroluminescent Devices
Yu Jun Tan1,1, Hareesh Godaba1, Ge Chen1, Siew Ting Melissa Tan1,2, Guan Xiang Wan1, Guojingxiang Li1, Pui Mun Lee1, Yongqing Cai1, Si Li1, Robert Shepherd4, John Ho1 and Benjamin C. Tee1,1; 1National University of Singapore, Singapore; 2Stanford University, United States; 3University of Macau, China; 4Cornell University, United States

Stretchable and conformable optoelectronic devices enable exciting applications in wearable electronics displays, human-machine interfaces as well as emerging soft robotics. We have developed a low-field emission electroluminescent device using a solvent processable self-healing dielectric material that exhibits high relative dielectric permittivity. Our device can be assembled facilely, which can then be stretched to 800% strain. The device also exhibits opto-healing from punctures or bifurcations. We achieved very low turn-on threshold voltages as low as 23 V, and can achieve an unprecedented electroluminescent brightness of >1000 cd m⁻². We further demonstrate the use of our device in soft robotics applications. Our soft, repeatable autonomous self-healing electroluminescent devices will enable applications in electronic skins and stretchable display interfaces that are easily reconfigurable, and robust to mechanical damage.

Reference:

5:35 AM S.SM06.03.09
Transparent Flexible Polymer Actuator with Enhanced Output Force Enabled by Conductive Nanowires Interlayer
Tony Fook1,2, Jin Han Jeon2 and Pooi See Lee1; 1Nanyang Technological University, Singapore; 2Robert Bosch (SEA) Pte Ltd, Singapore

As the role of flexible soft materials become more crucial for applications such as flexible displays in foldable mobile phones, compliant sensors and actuators in wearables, etc., new functional soft materials are needed to fill the roles previously fulfilled by rigid and bulky conventional materials. The field of haptic technology has recently seen emerging needs for integration into soft, flexible and even transparent interfaces. Since several decades ago, haptic feedback in electronic devices such as mobile phones, gaming controllers, are provided by bulky mechanical motors that vibrate the entire device upon application of an electric signal to give a tactile sensation to the users. In recent years, piezoceramics such as lead zirconate titanate are seen as a popular alternative due to its high performance and small form factor. However, their high stiffness, density and opacity prove to be a large obstacle in applications where flexibility, weight and transparency are crucial. In such applications, electroactive polymers (EAPs) serve as an excellent solution and have been a rapidly growing focus of research due to the wide range of potential applications such as energy harvesters, sensors and actuators, artificial muscles, etc. In reported methods to enhance the dielectric and electromechanical properties of EAPs, there is a compromise in at least one of these factors: electrical breakdown strength, transparency and flexibility.

In this work, we present an approach to enhance the output force of polymer actuators by increasing the dielectric permittivity and polarizability of the EAP, poly (vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) (P(VDF-TrFE-CTFE)), by incorporation of a conductive nanowire interlayer into the polymer matrix. The interlayer is formed by a network of highly conductive silver nanowires with high aspect ratio and enhances the dielectric permittivity and polarizability of the EAP over a broad range of frequencies including ultra low frequencies (e.g. 0.1 Hz) and the range of 200 to 300 Hz at which the mechanoreceptors in the human fingertips are most sensitive to. Through experiments and finite element modelling, the enhancement of dielectric properties were found to originate from charge accumulation at the nanowire/polymer interface and resulted in an output force double that of a neat EAP actuator. The higher output force can be
used to improve tactile feedback perception of a human user and allows a 40% reduction in the actuator excitation voltage compared to that of a neat EAP actuator. Even with enhanced dielectric properties and output force, the composite actuator retains its transparency and flexibility without severe compromise in the electrical breakdown strength. The excellent transparency and flexibility of the modified EAP are promising for a wider range of possible applications such as direct and localized haptic feedback on flexible electronic displays, touch screens, etc.

SESSION S.SM06.04: New Approaches for Soft Robotics
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-0SM06

5:00 AM *S.SM06.04.01
Robotic Fabrics as Thin, Wearable, Fiber-Based Machines Rebecca Kramer-Bottiglio; Yale University, United States

Robot function is largely determined by the structural platform upon which it is built. The field of soft robotics aims to expand the design space by introducing unconventional robotic materials and methods to the engineering toolkit. In this talk, it is proposed that this increasing repertoire of robotic platforms be extended to include fabrics, which are known for their extreme deformability, versatility, and customizability. Possible fiber-based forms to achieve actuation, sensing, and stiffness control will be presented, including: (1) shape memory alloy ribbon as a thin-body actuator, which is effective at pure-bending motion, in contrast with typical fiber actuators that rely on axial contraction alone; (2) An in-fabric sensor that changes in resistance as the fabric weave is stretched and the gaps present between fibers are enlarged; and (3) A stiffness-changing fiber based on a glass-transition polymer epoxy with low-melting-point metallic alloy inclusions that is capable of a stiffness change of two orders of magnitude using Joule heating. By designing actuators, sensors, and structural components that conform to a fiber-based geometry, we show that simple fabrics can be functionalized to create damage-responsive tourniquets, self-deploying structures, and morphing airfoils.

5:15 AM S.SM06.04.05
A Tuneable Method of Nanostructuring Polymers as Surfaces for Tissue Growth Thomas Chalklen, Michael Smith, Matthew Sims and Sohini Kar-Narayan; University of Cambridge, United Kingdom

The biological world relies on a variety of stimuli: chemical, electrical and also mechanical. For the fields of regenerative medicine and tissue engineering, understanding these cues is an important pathway for directing tissue behaviour.

Currently however, our understanding of the effect of mechanical stimulation on cell behaviour is poor, but it is becoming clear that these cues play an important role in regulating phenotype, recently being used to direct stem cell differentiation, for example [1]. A major issue for this field remains that the stiffness of biological tissue is many orders of magnitude lower than that of bulk materials such as polymers or ceramics. Work is being done to address this stiffness imbalance, the majority through the use of hydrogels [2], but this approach has some drawbacks, as the stiffness of a hydrogel is directly correlated to its chemistry, so in order to change the stiffness we require a change in chemistry. In addition, hydrogels fail to provide routes to actively direct cell behaviour whilst in culture.

In this work we utilise template wetting to create a tuneable, low stiffness surface through the use of nanostructuring to alter the effective surface stiffness of a widely used piezoelectric bio-polymer, poly-l-lactic acid [3]. By altering the length of the resulting nanotubes, we have successfully shown a strong preference by induced Pluripotent Stem Cells (iPSCs) for higher aspect ratio, softer, surfaces, and furthermore demonstrated the long term viability of this surface for cell growth. It is concluded that this nanostructuring presents a viable, controllable route to providing appropriate mechanical stimuli. Moreover, by exploiting the piezoelectric properties of the polymer there is the opportunity for active mechanical stimulation in culture. The implementation of this mechanical control opens up new avenues for detection, characterisation and stimulation of cell mechanobiology, paving the way towards an externally addressable lab-on-a-chip device.

SESSION S.SM06.05: Bioelectronics for Tissue- and Neural-Interfacing
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S- SM06

5:00 AM *S.SM06.05.02
Multi-Modal Sensors and Actuators for Biointerfacing Ivan Minev; University of Sheffield, United Kingdom

Interfaces that link biological systems with machines are increasingly evolving beyond the electrical domain. Multi-modal bioelectronics aims to add chemical, optical, thermal or mechanical functionality to the capabilities of classical electrode arrays. When such systems are used in physical contact with tissues or cells, the need for overall mechanical compliance is crucial for their biointegration. This raises a question: how do we build multi-modal arrays of sensors and actuators with tissue-like softness?

In this talk I will present our efforts to adapt direct ink writing (multi-material 3D printing) for the purpose of fabricating elastic systems of electrodes, optrodes, thermotrodes, and chemotrodes. A palette of silicones, composites and hydrogels are used as inks, where each of the inks enables one interfacing modality. As an example of in vitro application, I will present multi-modal pacing and monitoring of stem cell derived cardiomyocytes. In vivo, I will present printed neuro-muscular implants tailored to specific anatomical niches and animal models. These developments are expected to contribute to the development of personalized platforms for bioelectronic medicine.

5:15 AM *S.SM06.05.04
Brain Machine Interfaces Using Flex to Chip Bonding Eric Zhao, Marc Ferro, Tyler Chen, Pingyu Wang and Nicholas Melosh; Stanford University, United States

Enabled by new materials and device designs, a new generation of brain interface technologies is replacing bulkier, non-compliant systems with the aim of seamless electronic-biological interfaces with lower tissue damage, reduced immunogenicity, high-density, tunable spatial distribution, and long-term stability. Recent successful examples leveraging mechanically compliant materials have demonstrated major breakthrough in brain research using ultra-flexible systems for ECoGs recordings, and for depth electrodes.

However, connectorization of these ultra-flexible electrodes to traditional electronics remains a significant challenge. Current connectors, such as zero-insertion force (ZIF) devices, are limited to 64 or 128 channels at most. While these may then be stacked together this approach does not scale, limiting the maximum number of channels feasible.

Here, we demonstrate an easy to use, massively scalable connector technology. Rather than using traditional amplifier electronics, we couple thousands of flexible electrodes directly to a CMOS pixel array, such as typically found in a camera or OLED display. These devices have millions of available pixels, and by taking advantage of the small, flexible nature of the electrodes we are able to attach thousands of electrodes in seconds. These form robust Ohmic contact that can be extensively cycled. We demonstrate the simplicity of the process, and show how it can be used to perform massively parallel neural recordings.

5:30 AM S.SM06.05.05
Sono-Optogenetics: A Circulation Delivered Rechargeable Light Source for Minimally Invasive Optogenetics Xiang Wu, Xingjun Zhu, Paul Chong, Junlang Liu, Louis Andre, Kyrystyn Ong, Kenneth Brinson Jr., Ali I. Mahdi, Jiachen Li, Lief E. Fenno, Huiliang(Evan) Wang and Guosong Hong; Stanford University, United States

Understanding the complex neural circuitry and its correlation to specific behaviors requires spatially and temporally precise
modulation of neuron subtypes in certain brain regions. For decades, neural stimulation has predominantly been achieved by traditional electrical stimulation electrodes. More recently, optogenetics, which utilizes visible light to achieve neural modulation by genetically expressing microbial opsins in mammalian cells, has gained great popularity due to its rapid and precise control of neural activities and its capability of dissecting neural circuitry by selectively modulating specific neuron subtypes. However, owing to the limited tissue penetration of visible light, invasive craniotomy and intracranial implantation of tethered optical fibers are usually required for in vivo optogenetic modulation. Here, we report a new method termed ‘sono-optogenetics’, which provides minimally invasive optogenetic neuromodulation in the brain without any scalp incision, craniotomy or brain implant. Sono-optogenetics delivers nanoscopic light sources—mechanoluminescent nanoparticles—via the endogenous blood circulation, and provides millisecond-timescale switching of 470 nm light emission for optogenetic neuromodulation via brain-penetrant focused ultrasound. Furthermore, the mechanoluminescent particles could be recharged by 400-nm photoexcitation light in superficial blood vessels during circulation, enabling repetitive through-scalp optogenetic stimulation. Unlike the conventional ‘outside-in’ approaches of optogenetics with fiber implantation, our method, which combines minimal-invasive ultrasound excitation and intravenous delivery of mechanoluminescent nanoparticles, provides an ‘inside-out’ approach to deliver nanoscopic light emitters via the intrinsic circulatory system and switch them on and off at any time and location of interest in the brain. We envisage that sono-optogenetics provides a unique tool of rapid screening of different target regions in the brain for optogenetic neural modulation, owing to the ease of changing the location of ultrasound focus in the brain by eliminating fiber optic implantation. Furthermore, sono-optogenetics can be used in other regions of the central and peripheral nervous systems, as well as in other organs such as the heart and lungs, which are usually refractory to fiber implantation due to structural and functional constraints, for precise modulation with optogenetic control of cell activity. In addition, reduction of the footprint and the weight of the ultrasound transducer, as well as the use of ultraflexible neural probes with neural-tissue-like mechanical compliance, may enable sono-optogenetic stimulation of deep-brain regions with simultaneous electrophysiology in a behavioral setting. We anticipate that this approach could also be extended to applications in much deeper brain regions in larger animals owing to the penetration depth of ultrasound reaching several centimeters. The manuscript based on this work “Sono-optogenetics: a circulation delivered rechargeable light source for minimally invasive optogenetics. Xiang Wu,1,3,5 Xingjun Zhu,1,3,5 Paul Chong,1,3,5 Junlang Liu,1,3 Louis N. Andre,1,3 Kyrsyn S. Ong,1,3 Kenneth Brinson Jr.,1,3 Ali I. Mahdi,1,3 Jiachen Li,1 Lief E. Fenno,4 Huiliang Wang4* and Guosong Hong1,3*” has been reviewed at PNAS and the revision has been returned for further evaluation.

5:40 AM S.SM06.05.07
Tissue Adhesive Nanofiber Membranes for pH-Responsive Delivery of Oral Therapeutics Sunil Kumar Boda and Conrado Aparicio; University of Minnesota Twin Cities, United States

INTRODUCTION
Tissue adhesive nanofiber membranes present a synchronous capability of oral tissue regeneration and bio-sensing. Natural polymers such as chitosan, pectin and their combinations have been previously characterized for mucoadhesion ex vivo [1]. On a similar note, the mucoadhesiveness of gecko-inspired synthetic elastomer nanopatterns was enhanced via surface coating with oxidized sugar/ polysaccharide [2]. Taking cue from the aforementioned studies, electrosyn nanopiber membranes of chitosan were modified by surface coating with oxidized pectin for oral tissue adhesion. Such tissue adhesive nanofiber membranes are employed for pH-responsive delivery of oral therapeutics.

EXPERIMENTAL METHODS
Chitosan nanofiber membranes were fabricated by electrospinning a 5 wt% of chitosan dissolved in trifluoroacetic acid-dichloromethane (TFA: DCM = 70:30 v/v) solvent system. The nanofiber membranes were spin coated with 0.05 and 0.5 wt% of periodate oxidized pectin. A texture analyzer (TA-XT-plus, Stable Micro Systems) was used for recording the adhesion properties of the nanofiber membranes ex vivo to porcine oesophagus and hydroxyapatite discs representing the mucosal and enamel surfaces, respectively. The nanofiber membranes loaded with oral antibiotics/ antimicrobial peptides were evaluated for pH-responsive release in 0.1 M acetate buffers of pH = 4.5, 5.5 and 6.5 and their consequent antimicrobial activity assessed against oral pathogens (Streptococci). The cytocompatibility of similar membranes was examined using human gingival fibroblasts.

RESULTS AND DISCUSSION
The 0.05 wt% oxidized pectin coating on chitosan nanofiber membranes elicited maximum detachment force and work of adhesion to porcine oesophagus suggesting enhanced muco-adhesion resulting from the synergistic interaction of the nanofiber topology and surface aldehydes from oxidized pectin with the mucosal proteins. A higher 0.5 wt% oxidized pectin coating only enhanced the detachment force, but reduced the work of adhesion to mucosal mimic. Overall, our ex vivo mucoadhesion results are in agreement with an earlier report of oxidized dextran coating mediated improvement of
mucoadhesion of elastomeric nanopatterns [2]. On the contrary, the uncoated chitosan nanofiber membrane exhibited the strongest adhesion to hydroxyapatite discs. The greater abundance of cationic amines (-NH$_3^+$) in pure chitosan promoted adhesion to negatively charged phosphates (-PO$_4^{3-}$) on hydroxyapatite surfaces. The in vitro cytocompatibility of the membranes was illustrated by co-culture with human gingival fibroblasts for 24 h. Lastly, the pH-responsive delivery of oral therapeutics was demonstrated via the antibacterial activity of antibiotic/antimicrobial peptide loaded membranes against *Streptococcus gordonii*, a primary colonizer of oral prosthesis.

CONCLUSIONS
A synergistic combination of surface topography and surface chemistry can promote the tissue adhesion properties of nanofiber membranes to hard, soft or hard-soft tissue interfaces. The pH-responsive adhesive nanofiber membranes can be utilized for pH-induced delivery of oral therapeutics.

REFERENCES

ACKNOWLEDGEMENTS
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5:50 AM S.SM06.05.09
Morphing Electronics for Growing Tissue Yuxin Liu, Jinxing Li, Shang Song, Paul George and Zhenan Bao; Stanford University, United States

Bioelectronics for modulating nervous system, such as the vagus nerve stimulator, demonstrate great promise in treating various neurological diseases. However, their fixed sizes and shapes cannot accommodate the rapid tissue growth and negatively influence normal developmental functions. For infants, children and adolescents, once the implanted devices are ‘outgrown’, additional surgeries are usually needed for device removal, followed by replacement. These tedious processes inevitably lead to repeated intervention and elevated complication rates. Although stretchable electronics with high elasticity is ideal for repeated motion and volumetric expansion of organs, they still cannot adapt to developmental tissue growth, which should not be restricted by any strain. Here, we address this limitation with Morphing Electronics (termed MorphE) which are designed and fabricated to suitably adapt to in vivo nerve tissue growth with zero strain. This is achieved by viscoplastic electronic materials (VEMs) that eliminate the stress and tissue constraint on growing tissue. In addition, water-insensitive self-healing property of the multilayered MorphE consisting of viscoplastic electrodes and a strain sensor allows fora reconfigurable platform for individualized implantation procedures. Animal study demonstrated that the soft and self-adapting MorphE showed no damage to the rat nerve after grown 2.4 times its initial diameter. This stable neural interface allowed chronic electrical stimulation and monitoring without disruption of functional behavior in developing rats. Our MorphE creates a new avenue for adaptive pediatric electronics medicine.

SESSION S.SM06.06: From Photostimulation to Mixed Conduction with Organic Semiconductors
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020 S-SM06

5:00 AM *S.SM06.06.01
Wireless Photovoltaic Neuroprostheses for Artificial Vision Diego Ghezzi; École polytechnique fédérale de Lausanne, Switzerland

Neural prostheses are devices integrated with the neural tissue for diagnostic or therapeutic purposes, such as restoring impaired or lost functions. Despite a large variety of devices exists, a shared future is the presence of cables connecting the electrode-tissue interface to implantable electronic circuits for signal management. The presence of wires and connectors is a significant disadvantage for neural prostheses; in fact, they are weak points often leading to failure, they exert mechanical
forces and tractions on the implant and the tissue, and they are often trancranial or transcutaneous connections that might lead to post-surgical complications, such as infection. Also, the use of implantable electronic units is another disadvantage. Several aspects limit their operation, such as power consumption, excessive heat generation, and high risk of failure in a wet environment due to leakage.

In neural prostheses, wireless electrodes are desirable. Retinal prostheses are a particular category of neural prostheses, in which wireless neuronal stimulation was achieved thanks to photovoltaic technology, that also avoids the need for active implantable electronic units. In the case of retinal stimulation, photovoltaic technology is intuitive since the retina is made to absorb light entering from the pupil naturally. Although photovoltaic retinal prostheses do not work with ambient and natural light, electrical stimulation is triggered by artificial light projected into the pupil and absorbed by semiconductor elements embedded into the stimulating pixels. This solution allows retinal prostheses to avoid a transscleral flat cable which limits the maximum number of stimulating pixels on the device and induce post-operative complications such as eye inflammation or leakage through the incision.

In the first part of this talk, the development and validation in-vitro and in-vivo of a wide-field, photovoltaic, and injectable retinal prosthesis will be reported. POLYRETINA is a wide-field epiretinal prosthesis which contains 10,499 photovoltaic electrodes (diameter of 80 µm and pitch of 120 µm) distributed with a pixel density of 80.33 pixels mm\(^{-2}\). The pixels cover an active area of 12.9 mm in diameter; thus, the prosthesis covers a visual angle of 46.3 °. Each pixel is composed by a conductive polymer (PEDOT:PSS) a bulk heterojunction (P3HT:PCBM) and a metallic cathode (Ti). The results obtained in-vitro with retinal explants and in-vivo with large animal models will be reported.

In the second part of the talk, a novel visual prosthesis based on intra-neural stimulation of the optic nerve will be described. OpticSELINE is an intraneural 3D electrode array capable of selectively activating the optic nerve fibres to induce artificial vision. This technology is essential to overcome the exclusion criteria of retinal implants. The results from our in-vivo preclinical trial in large animals will be presented.

In conclusion, the use of photovoltaic technology to design novel neuroprostheses will be highlighted.

References:
they have been studied intensively for various applications such as wearable electronics, micro-actuators, and micro-robots. However, there are few studies of implanted electronics using a hydrogel/elastomer bilayer. Here, we fabricated a bilayer system with polydimethylsiloxane (PDMS)/polyacrylamide (PAAm). While PDMS works as the passive layer defining the motion of hydrogel, the PAAm active layer can respond to water and change the shape of the bilayer by swelling and deswelling[1].

To fabricate the bilayer, benzophenone was used to bond the wet PAAm hydrogel and PDMS with good reliability[2]. The bilayer remained integral after 72 hours in water. To demonstrate the shape morphing ability, the bilayer was rolled up into a tube and then expanded into a curved film due to swelling in water. For implantation, the shape morphing ability will create a compact structure to minimize the incision during surgery. After implantation, the device will unfurl to increase the size of the neural interface. Furthermore, the permanent 3D shape of the bilayer is tunable. Initial results showed that varying the concentrations of crosslinkers of the PAAm hydrogel allowed different curvatures to be achieved. A 25 mm long bilayer strip (thickness of PAAm: 200 μm, thickness of PDMS: 840 μm), with high monomer concentration (33.4 wt. %) and low crosslinker density (0.5 wt. %), demonstrated a curvature of 0.230 mm⁻¹. Another strip with the same dimension and a higher crosslinker density (1.3 wt. %) demonstrated a smaller curvature of 0.110 mm⁻¹. In addition to the properties of the PAAm hydrogel, the curvature also depends on the thickness ratio between the hydrogel and the elastomer layer. A bilayer bending beam model developed by Timoshenko was used to predict the curvature with different thicknesses[3]. By using the expansion ratio and elastic modulus previously reported[4][1], the result of the model showed that 1000 μm thick PDMS with 175 μm thick PAAm could achieve a bending degree of 180°. The results from the model can guide the designing of the thicknesses of the two layers.

The shape morphable bilayer will serve as a substrate for a retinal stimulating array that maximizes the size of the implanted electronics while minimizing the surgical trauma.


5:35 AM *SM06.06.04

Optical Control of Nerves Using Organic Electrolytic Photocapacitors (OEPCs) Marie Jakešová1, Malin Silverå-Ejneby1, Ludovico Migliaccio1, Oliya Abdullaeva1, Maciej Gryszel1, Vedran Derek1 and Eric D. Glowacki1,2; 1Linkoping University, Sweden; 2Warsaw University of Technology, Poland

A great demand exists for nongenetic optical neuromodulation technologies. We report on our developments of ultrathin organic optoelectronic devices for neurostimulation. All of these devices rely on far red/near infrared irradiation in the tissue transparency window to actuate nanoscale organic semiconductor components. Our flagship technology is the organic electrolytic photocapacitor (OEPC) – a device that mimics biphasic current-pulse neurostimulation and thus transduces an optical signal into directly-evoked action potentials in neurons. These devices are not only wireless, but also 100-1000 times thinner than most existing technologies. Making implants with as small as possible mechanical footprint improves the efficacy of bioelectronic medical treatments by minimizing the risk for inflammation and making surgical implantation less invasive. We will present our results on pushing the limits of efficiency and stability, with benchmarking of performance using in vitro and ex vivo models, and cover our developments of peripheral nerve stimulation implants.

5:50 AM *SM06.06.05

Organic Mixed Conductors—Fundamental Properties and Applications Alberto Salleo; Stanford University, United States

Organic mixed ionic/electronic conductors have elicited much interest lately as the enablers of a “new wave” of organic electronic devices in the biomedical space. In this talk I will start by exploring how the microstructure of the polymer interacts with the electrolyte and the effect of the electrolyte on the characteristics of electrochemical transistors. I will then show some applications of these materials in the sensor space ranging from flexible sensors to quantify electrolytes in sweat to biomimetic sensors to determine antibiotic activity of small molecules and detect the presence of pathogens. Finally I will show how devices based on these materials can be modulated by neuron-like cells where neurotransmitters elicit both short
and long term potentiation in the device demonstrating a first building block of a new type of brain-machine interface.

6:05 AM S.SM06.06.07
A Wearable Organic Electrochemical Transistor Patch for Multiplexed Sensing of Calcium and Ammonium Ions from Human Perspiration Scott T. Keene1, Daragh Fogarty1,2, Ross Cooke1,2, Carlos Casadevall1,3, Alberto Salleo1 and Onur Parlak1,4; 1Stanford University, United States; 2Trinity College Dublin, Ireland; 3University of Florida, United States; 4Karolinska Institutet, Sweden

Wearable health monitoring has garnered considerable interest from the health care industry as an evolutionary alternative to standard practices with the ability to provide rapid, off-site diagnosis and patient-monitoring. In particular, sweat-based wearable biosensors offer a non-invasive route to continuously monitor a variety of biomarkers for a range of physiological conditions. Both the accessibility and wealth of information of sweat make it an ideal target for non-invasive devices that can aid in early diagnosis of disease or to monitor athletic performance.

Here, we demonstrate the integration of ammonium ($\text{NH}_4^+$) and calcium ($\text{Ca}^{2+}$) ion-selective membranes with a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) organic electrochemical transistor (OECT) for multiplexed sensing of $\text{NH}_4^+$ and $\text{Ca}^{2+}$ in sweat with high sensitivity and selectivity. The presented wearable sweat sensor is designed by combining a flexible and stretchable styrene-ethylene-butene-styrene substrate with a laser-patterned micropipillary channel array for direct sweat acquisition and delivery to the ion-selective OECT. The resulting dermal sensor exhibits a wide working range between 0.01 mM to 100 mM, well within the physiological levels of $\text{NH}_4^+$ and $\text{Ca}^{2+}$ in sweat. The integrated devices are successfully implemented with both ex-situ measurements and on human subjects with real-time analysis using a wearable sensor assembly.

SESSION S.SM06.07: Late Breaking News
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S.SM06

5:00 AM S.SM06.07.01
Self-Induced Hollow Chemiresistor Fiber With High Volatile Organic Compounds Sensitivity, Selectivity and Piezoresistivity Weiheing Xu, Dhameedar Ravichandran, Sayli Jambhulkar, Rahul Franklin and Kenan Song; Arizona State University, United States

The detection and monitoring of volatile organic compounds (VOCs) are vital to numerous applications, such as long-term exposure to health issues, environmental protection, and chemical process control. Many previous attempts have successfully demonstrated portable chemiresistive devices on either conductive nanoparticle polymer composites or metal oxide semiconductor-based thin films. Nevertheless, composite sensors suffer from low sensitivity while thin-film sensors have limited flexibility. In this work, a carbon nanotubes (CNTs) and graphene nanoplatelets (GnP) filled thermoplastic polyurethane (TPU) fiber sensor is investigated with engineered micro-scale multiple layers. Through controlling the solvent exchange process, a self-induced hollow core with high porosity is formed and is utilized to transport vapor flow with high VOCs/CNTs/GnP interactions. The sensitivity is greatly enhanced, up to 60 ppm for xylene, comparing to traditional polymer composite sensors, usually over 1000 ppm. Additionally, the highly flexible polymer matrix, similar to traditional piezoresistors, enables the detection of different deformations, such as vibration at 0.3% strain, under different VOCs concentrations with distinct signal patterns. The unique multi-layer structure also provides pressure sensing application to as low as 6.89 kPa (1 psi) with high reversibility. This work provides new insights on the design and fabrication of complex polymer composite structures that enable more sensitive chemiresistors with piezoresistivity behavior.

5:10 AM *S.SM06.07.02
Balancing Local, Regional and Global Interactions to Direct Assembly of Engineered, Patchy Protein Particles James J. De Yoreo1,2, Shuai Zhang3, Robert Alberstein4, Harley Pyles5,2, Jiajun Chen1,2, Faik A. Tezcan5,6 and David Baker2,2; 1Pacific Northwest National Laboratory, United States; 2University of Washington, United States; 3University of California, San Diego, United States

Self-assembly of nanocrystals to form superlattices and mesocrystals is typically thought of in terms of colloidal forces and
liquid crystal ordering. Considerations of shape and solvent entropy dominate the controls on organization while atomic-scale details are of lesser importance due to the fairly homogeneous nature of the building blocks. Proteins offer unique advantages over inorganic particles as nanoscale building blocks, including monodisperse structures and patchy interactions that are both atomically precise and tuneable. For this reason, ordered assemblies of protein building blocks exhibit a wide range of structural motifs including 1D nanofibers and tubes, 2D lattices and 3D capsids and frameworks. Protein-based systems have the further advantage that they are readily assembled in interrogated in mild aqueous conditions, making them amenable to molecular resolution imaging techniques that provide a unique window into the assembly process. Here we report on two systems of engineered proteins. The first consists of a highly patchy 4-fold symmetric protein building block (L-rhamnulose-1-phosphate aldolase; RhuA), whose self-assembly is driven at the shortest length scale by disulphide bonds designed into four corners of the protein. By introducing a charged, atomically patterned substrate and varying charge states via solution ionic strength, we achieve simultaneous control of four different classes of interactions (covalent bonding, electrostatic surface templating, dipole-dipole interactions and desolvation-induced complexation) to yield four distinct, precisely patterned 2D crystals. The second system consists of a de novo designed rod-shaped helical repeat whose length can be set arbitrarily in units of one repeat. These MicaN proteins are designed to interact in an epitaxial manner with the K⁺-sublattice of mica. Variation of the design created an end-to-end hydrophobic interactions that were either dimeric at both ends or trimeric interface at one end and dimeric at the other. As with RhuA, we show that the interplay of the specific intermolecular interactions, regional electrostatic interactions and global colloidal forces lead to a variety of distinct ordered phases. In all cases, in situ AFM reveals the development of order and its relationship to protein design and surface and solution interactions. The results provide a mechanistic picture of assembly by patchy protein building blocks that links pathways and outcomes to the influence of interactions over many length scales.

5:25 AM S.SM06.07.03
Robot-Assisted Synthesis of Alternating and Random Multiblock Copolymers Based on Oligo(ε-caprolactone)/Oligotetrahydrofuran and Their Phase Morphology Marc Behl1, Maria Balk1,2 and Andreas Lendlein1,2; 1Helmholtz-Zentrum Geesthacht, Germany; 2University of Potsdam, Germany

The design of polymeric materials like multiblock copolymers (MBCs) is guided by the requirements of specific applications but demands an understanding of structure-function relationships. MBC materials provide a complex hierarchical structure. The chemical nature, the number length of integrated building blocks, as well as their sequence structure (e.g. alternating or random) impact the phase morphology. This organisation level largely influences the macroscopic mechanical properties such as deformability and the modulus.

We hypothesized that a strictly alternating sequence should favour crystallization and in this way the elastic properties. Well-defined multiblock copolymers (MBCs) composed of two different hydrophobic, semi-crystalline blocks providing domains with well-separated melting temperatures (T_m)s were thought to differ e.g. in the elongation at break just controlled by the polymer architecture of the MBC designed as strictly alternating (MBCsalt) or random (MBCsran). Accordingly, two different types of MBCs (MBCalt and MBCran) were synthesized from the same type of precursor building blocks and compared. Three different series of MBCsalt or MBCsran were created by means of high-throughput synthesis by coupling oligo(ε-caprolactone) (OCL) of different molecular weights (2, 4, and 8 kDa) with oligotetrahydrofuran (OThF, 2.9 kDa) via Steglich esterification whereby the blocks were designed either as macrodiol or as macrodicarboxylic acid. The maximum of weight average molecular weight (M_w) of MBCsalt of the three different series were 70,000 g mol⁻¹, 160,000 g mol⁻¹, and 190,000 g mol⁻¹ and increased with increase of the chain length of the OCL block. This increase in the maximum M_w was also observed for the series of MBCsran, where maximum M_w of 100,000 g mol⁻¹, 130,000 g mol⁻¹, and 160,000 g mol⁻¹ were obtained.

While the average phase size between the domains of the amorphous phase increased from 100 nm to 600 nm for MBCsran when the M_w increased the strictly alternating structure limited the demixing between OCL and OThF blocks resulting in an almost constant average phase size between the amorphous phase domains with raising M_w. Comparing MBCsran a more pronounced amorphous phase separation was observed with increasing OCL block length size and was attributed to higher phase separation tendency of a mixed OCL and OTHF mixed amorphous phase. The increase in M_w of MBCs resulted in a reduced degree of crystallinity as detected by transmission electron microscopy and x-ray scattering experiments attributed a decreased phase separation tendency. When the chain length of OCL building blocks was increased, the tendency for phase separation was facilitated, which was attributed to the decrease in chain mobility within the MBCs. For MBCalt compared to MBCran the crystallinity was lower and decrease in crystallinity with raising M_w was lower, which both was attributed to the confined crystallization in MBCalt. For all MBCs a decrease of both T_mS associated to the melting of the OCL and OTHF domains was observed when the molecular weight increased. T_m (OTHF) of MBCsran was always higher than T_m (OTHF) of MBCsalt which was attributed to a confined crystalline lamella growth of OTHF incorporated in alternating copolymers. In addition, the complex modulus of MBCalt was almost half as high when compared to MBCsran.
In this way this study demonstrates the pronounced role of the block length and sequence structure in MBCs and enables a quantitative elucidation of the structure-function relationship when two semi-crystalline block segments are utilized for the design of block copolymers.


5:35 AM S.SM06.07.05

**Optoelectronic Nature of Ampicillin to Enhance the Performance of Organic Light-Emitting Diodes** Hassan Hafeez, Justin Jesuraj Periyanayagam, Dong Hyun Kim and Seung Yoon Ryu; Korea University, Korea (the Republic of)

With the exponential increase in the demand for flat-panel displays, portable electronics, and biomedical devices, considerable attention has been directed towards the fabrication of highly efficient organic light-emitting diodes (OLEDs). Several techniques and methods were presented but the single-unit phosphorescent OLEDs have demonstrated a maximum external quantum efficiency (EQE) limit of 25% without additional out-coupling aid. In order to overcome this efficiency barrier, new exotic materials are to be investigated with exceptional properties like an interfacial dipole, exciton generation, and charge balance.

Herein, we present the robust contribution of a widely used antibiotic; ampicillin in optoelectronics. The optimum fusion of ampicillin with Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) considerably improved the device efficiency of a single-unit green phosphorescent OLED. The charge distribution over ampicillin’s structure due to the presence of primary, secondary and tertiary amine along with the lactam ring was found to be the key parameter. The concentration-dependent analysis of the mixture (ampicillin-PEDOT:PSS) revealed that the addition of 25% ampicillin in PEDOT:PSS provided a horizontal interfacial dipole. The dipole suppressed the hole injection by lowering the work function of the anode and improved the charge balance. Moreover, the parallel arrangement of molecules facilitated the generation of J-aggregations which contributed extra excitons to the device. Consequently, the values of current efficiency (120 cd/A), EQE (35%) and power efficiency (70 lm/W) boosted by J-aggregated excitons were demonstrated, which to our knowledge are the highest reported efficiencies. The EQEs were analyzed using integrating sphere and variable-angle measurements, which demonstrated a Lambertian emission trend. The devices with penicillin-PEDOT:PSS were also fabricated for cross-evaluation, where the only difference in penicillin structure as compared to ampicillin is the absence of primary amine. The resulting EQE of the penicillin devices was found to be ~11% lesser than that of the ampicillin devices. This indicated that the specific molecular structure and interfacial dipole generated by ampicillin was the crucial aspect to obtain higher efficiency (EQE ~35.1%). Further, the concentration (25, 40, and 75%) and time (2 days, 1 month, and 2 years) dependent interactions of ampicillin with PEDOT:PSS, and their role in device performance was systematically investigated by analyzing the physical, chemical, electrical, and optical properties of the layers.

The investigation of dynamic properties using antibiotic materials such as ampicillin opens new horizons for the technical advancements in the field of optoelectronics. The work presented here provides a facile, cost-effective and nature-friendly method to enhance the efficiency of the OLED devices and has high potential to be applied in photovoltaic and biomedical devices.

5:45 AM S.SM06.07.06

**Eco-Friendly Flexible Nanogenerator Based on Biowaste Squid-Pens-Extracted b-Phase Dominant Chitin Nanofiber/Polyvinylidene Fluoride Nanocomposites** Pin-Yi Her and Jyh-Ming Wu; 1National Tsing Hua University, Taiwan; 2University of California, Los Angeles, United States

Chitin nanofiber (ChNF) is one of a promising eco-friendly material because it is non-toxic, biocompatible, robust, and sustainable. It is also the most abundant marine polysaccharide. The b-ChNF is known to show piezoelectric properties due to its intrinsic molecular polarization arising from the non-centrosymmetric crystal structure. This work, we demonstrate a b-phase dominant ChNF/poly(vinylidene fluoride) (PVDF)-based flexible piezoelectric nanogenerators (PENGs) that exhibit superior electrical output. The PVDF is incorporated with ChNF to significantly enhance its piezoelectric properties. This is primarily because of the electrostatic interaction between the α-ChNF and the CH2/CF2 dipoles, the crystallinity of the b-
ChNF and b-PVDF are increased. The ChNF/PVDF film is characterized by scanning electron microscopy (SEM), polarizing optical microscope (POM), and peak force TUNA (PF-TUNA), x-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy to investigate the optical and piezoelectric properties of the ChNF/PVDF film. The ChNF/PVDF film exhibits superior remnant polarization ~10.8 μC/cm².

5:55 AM S.SM06.07.08
High-Resolution 3D Printing of Soft Electrode Arrays for Electrophysiological Signals Yohan Cho1,2, Young-Geun Park1,2 and Jang-Ung Park1,2; 1Yonsei University, Korea (the Republic of); 2Yonsei-IBS Institute, Korea (the Republic of)

Electrophysiological signals of the body provide critical information to assess the functionalities of organs or to diagnose diseases. In order to detect minute biological signals effectively, three-dimensional (3D) electrodes are required to minimize the tissue-electrode impedance and to form conformal interfaces with tissues. However, conventional approaches to form 3D-structured electrodes are based on photolithographic patterning and etching, and these processes result in the low variety of 3D structures limited to certain crystallographic planes of materials. Also, the poor selectivity of materials and their high stiffness easily damage tissues and obstruct the effective signal recording. Herein, the 3D electrode arrays composed of tissue-compatible soft metals have been formed by high-resolution direct printing. Various form factors of 3D electrodes with different heights (20 to 100 μm), diameters (5 to 30 μm) and the tip morphologies (sharpness) are printed and studied in terms of the tissue-electrode interfaces. While conventional materials for 3D microelectrode arrays have compatibility problems such as inflammation or the detachment of tissues because of a modulus mismatch, our 3D electrodes based on soft metals have Young’s modulus at least five orders of magnitude lower than that of platinum and silicon which are conventional materials for bioelectrodes. When human dermal fibroblasts are directly seeded to test the viability of the soft 3D electrodes, over 80% of cells were viable after 7 days with adhesion to the surfaces of electrodes. The improvement of signal transfer, including the signal-to-noise ratio of biopotentials and the persistency of signals at the tissue-electrode interface, can be found by an in-vitro recording of neurons directly cultured on the 3D soft electrode arrays with a comparison to the platinum-based two-dimensional electrode arrays.

6:05 AM S.SM06.07.09
Designing Nanostructured Interfaces—Focus on Shape Changes and Clustering of Nanogels Chandan K. Choudhury, Vaibhav Palkar and Olga Kuksenok; Clemson University, United States

Understanding and controlling dynamics of gels at fluid-fluid interfaces is critical for a plethora of bioinspired and biointerfaces since hydrogels can be biocompatible, compliant, and responsive to a number of orthogonal stimuli. Herein, we use Dissipative Particle Dynamics simulations to focus on the shape changes of a nanogel as it adsorbs from the aqueous phase onto the interface between two immiscible fluids effectively acting as compatibilizer. Upon adsorption at the interface, the hydrogel spreads over the interface adopting various shapes depending on its size and crosslink density. We characterize these shapes by the shape anisotropy and an effective extent of spreading. We highlight the differences between these characteristics for cubic and spherical nanogels and show that the choice of the cubic shape over the spherical one results in a wider range of topographies that could be dynamically prescribed onto the soft interface due to the gels’ adsorption. Further, we focus on the interactions between multiple gels placed at the fluid-fluid interface. We show that controlling the shapes and clustering of the gels at the interfaces via variations in solvent quality results in tailoring dynamics and topography of soft nanostructured interfaces. Hence our findings provide insights into design of nanostructured bioinspired and biointerfaces with topographies controlled externally or by the properties of the surrounding bioenvironment.

6:15 AM S.SM06.07.10
High-Performance Biocompatible MRI Contrast Agents—Exploiting Inter-Particle Interactions with Permanent and Dynamic Nanoparticle Arrays Aaron King1, Caroline Bray2, Stephen C. Hall3, Lara K. Bogart1, Sebastien Perrier1 and Gemma-Louise Davies1; 1University College London, United Kingdom; 2CSIRO, Australia; 3University of Warwick, United Kingdom

Magnetic resonance imaging (MRI) is a powerful non-invasive imaging technique, the effectiveness of which can be improved through the introduction of contrast agents (CAs).1 Magnetic iron oxide nanoparticles have demonstrated excellent potential in biomedicine and have been used as clinical MRI contrast agents (e.g. Feridex, Resovist), though their popularity has plummeted recently due to their low efficacy. There is therefore a real need for new contrast agents with excellent MRI contrast capabilities and good biocompatibility.

The importance of the strong interactions between neighbouring magnetic nanoparticles has been well documented when producing high performance MRI contrast agents. These interactions, and thus the anisotropy, can be increased in a number
of different ways. One such method, is via the utilisation of biopolymers, such as DNA and heparin, as templating
stabilisers.

However, the inherently high polydispersity of such biopolymers, means that a lack of precise control over these vital interparticle interactions. To remedy this we have exploited synthetic analogues of the naturally occurring anticoagulant heparin, to be used as a templating stabiliser in the production of iron oxide-based MRI contrast agents. This new family of negative contrast agents demonstrates excellent MRI contrast capabilities ($r_2$ values reaching 434.2 mM$^{-1}$s$^{-1}$ at 25 °C and 23 MHz, several times higher than similar commercial analogues). Such behaviour results from additional control over the polymers molecular weight and thus number of sulfonate seeding sites. This affords the opportunity to finely tune interactions between neighbouring particles and therefore the MRI properties of said contrast agents. Variable field relaxometry provided unexpected but important insights into the dynamic environment of the hydrated materials, providing reasoning for their exceptional MRI behavior. Thanks to the polymer’s templating backbone and flexible conformation in aqueous suspensions, nanocomposites appear to behave as “multi-core” clustered species, enhancing interparticle interactions whilst retaining necessary water diffusion.

The vital importance of anisotropy and the interactions between superparamagnetic nanoparticles on resulting MR contrast has been further investigated through the production of permanent 1-dimensional magnetic nanostructures. Building on the templating effects of sulfonated polyelectrolytes we discuss a novel magnetically driven one-pot synthetic strategy to produce 1-D contrast agents which boast excellent MRI capabilities.

HDFs was 24 h later than the major release period of encapsulated MC3T3 cells. For the bijels-derived hybrids with large pore size (~60 μm), the release rates of HDFs and MC3T3 cells were similar. A possible explanation for the differences is that the sizes of cells and pores in hybrids could affect cell release. HDFs have a larger cell size (~50 μm) than MC3T3 cells (20-30 μm), which may have caused slower release of HDFs in bijels-derived hybrids with small pore size. This investigation has demonstrated that bijel-derived bicontinuous hybrid structures are a good vehicle for cell delivery in tissue engineering. By controlling the pore size of hybrid structures, the release of different types of cells could be controlled. The released live cells could proliferate well and migrate in and outside the hybrid structures.

S.SM06.08.03
Poplar Reinforced Biocomposites Via Cellulose Nanofibril Modification Xianhui Zhao, Kai Li, Daniel Rasmussen, Halil Tekinalp, Erin Webb and Soydan Ozcan; Oak Ridge National Laboratory, United States

A common material used for large-scale 3D printing is a composite consisting of acrylonitrile butadiene styrene (ABS) polymer compounded with carbon fiber (CF/ABS). However, the high cost of CF/ABS indicates a market for 3D printing with bioderived materials. Natural lignocellulosic fibers have the advantages of biodegradability, abundance, low density, low cost, and easy availability. In the present study, poplar fibers (Populus spp.) were modified using cellulose nanofibril (CNF) slurry (~3 wt% solid). The modified CNF/poplar fibers were used to reinforce ABS. The biocomposites obtained were characterized using techniques including tensile testing, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), rheometer, thermogravimetric analysis (TGA), and scanning electron microscope (SEM). The tensile strength and Young’s modulus of neat ABS were 36 MPa and 1,901 MPa, respectively. After the addition of CNF/poplar fibers into ABS, the tensile strength and Young’s modulus of the biocomposites increased by 19% and 143%, respectively. The physical treatment of doping CNF solution on poplar fibers was found to be an effective technique to improve the thermomechanical properties of biocomposites.

S.SM06.08.06
Blow-Spun Hybrid PEO-PCL Scaffolds with Improved Mechanical and Biological Properties Meichen Liu and David Mills; Louisiana Tech University, United States

Tissue-engineered scaffolds play an important role in the repair or regeneration of tissues and organs. Scaffolds provide strength, stability, and support for cell and tissue development and growth. Common scaffold materials are natural and synthetic polymers, however, each one has its own limitations and different disadvantages. Interestingly, in order to promote the mechanical properties and increase the bioactivity, the composite systems composed of various sources or types of polymers can retain the advantages of each material. Furthermore, composite polymer systems have the ability to allow stem cell adhesion and differentiation and to carry drug molecules and special biological molecules, like growth factor and enzyme. Research on composite scaffolds is focused on identifying composites with enhanced mechanical properties, sustained drug-releasing capabilities and the ability to support tissue development and growth.

In this study, we produced and characterized a novel nanocomposite polymer scaffold composed of poly-ethylene oxide (PEO), polycaprolactone (PCL) and halloysite clay nanotubes (HNTs). PGS, a polymer with repeating -O-CH2-CH2- units, and PCL, a hydrophobic aliphatic polyester with exceptional biodegradable and biocompatible properties, were used in combination with HNTs to form nanocomposite polymer scaffolds. The nanocomposite polymer scaffold thin films were prepared by solution blow spraying, which is an easy and convenient way to make fibers and films. We characterized the structural, morphological, thermal and functional properties of these novel nanocomposite polymer (PEO-PCL-HNT) scaffolds. The nanocomposite polymer scaffolds should be biocompatible and resorbable, maintain long-term cellular viability and functionality, have the ability to induce cellular differentiation leading to complex tissue formation, have the improved mechanical properties to support cell growth and have sustained-release capabilities.

S.SM06.08.08
Polysaccharide-Based Hybrid Hydrogels as Tissue Engineering Scaffolds and/or Drug Delivery System Jinku Kim and Byungduk Kim; Hongik University, Korea (the Republic of)

Introduction: Hydrogels have potential in many biomedical applications such as tissue engineering and drug delivery system. Among those, Polysaccharide-based hydrogels such as hyaluronic acid (HA) have been extensively studied for tissue engineering applications, for example cartilage tissue engineering, partly because they are involved in cellular processes such as proliferation, morphogenesis, and wound repair. A number of polysaccharide-based hydrogels were designed, synthesized by free radical polymerization and their properties were analyzed in vitro and in vivo. In this study, we hypothesized that the properties of polysaccharide-based hydrogels can be controlled and enhanced by combining with small
molecules (e.g., proteins) or large molecules (e.g., PEG-based hydrogels). To test this hypothesis, novel biodegradable polysaccharide-based hydrogels were developed by combining polysaccharides (e.g., hyaluronic acid or HA) with PEG based macromers such as PEG sebacic acid diacrylates (PEGSDA) via free radical polymerization under mild conditions. Their physicochemical properties (e.g., swelling ratios) as well as biological properties were evaluated.

**Materials & Methods:** Polysaccharide-based hydrogels were synthesized by free radical polymerization under mild conditions and their properties were controlled by incorporation of proteins (e.g., collagen or growth factors) or synthetic polymers such as polyethylene glycol (PEG). Physicochemical properties and *in vitro* and *in vivo* biological properties were investigated using mesenchymal stem cells (MSCs) and rat mandibular defect models.

**Results:** The chitosan-based hydrogels conjugated with collagen and/or growth factors were well synthesized under mild conditions. Growth factors were delivered from the hydrogel systems in a controlled manner. The encapsulated MSCs showed their potential of condrogenic differentiation *in vitro*. The physically crosslinked chitosan-based hydrogels revealed their capability of bone regeneration on the critical-sized defects (CSD) in rat mandibular. In addition, the physicochemical properties of hyaluronic acid-based polysaccharide hydrogels can be controlled by combining them with PEG-based hydrogels.

**Conclusion:** Polysaccharide-based hydrogels with well controlled their properties can be synthesized by incorporations of additives such as growth factors or synthetic hydrogels. These hybrid polysaccharide-based hydrogels can be useful as tissue engineering scaffolds and drug delivery systems to repair or regenerate the defects in organs or tissues, caused by injuries or diseases.

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**References**

S.SM06.08.10

**A Screen-Printable Ph Sensor for Smart Textiles** Sooyoung Kim¹, Jongwon Lee¹, Minyoung Choi¹, Ju-Hee So² and Hyung-Jun Koo¹; ¹Seoul National University of Science and Technology, Korea (the Republic of); ²Korea Institute of Industrial Technology, Korea (the Republic of)

Recently, wearable sensors attract tremendous interest as real-time monitoring of physiological activities or environmental conditions becomes more important for many smart devices. Screen printing of sensing materials directly on fabric could not only enhance portability but also improve productivity by enabling a roll-to-roll process. Here, we present a solid-state pH sensor formed by a reliable screen printing technique. The pH sensor consists of two patterned electrodes. One is made of polyaniline(PANI)-carbon nanotube(CNT)-agarose composite. PANI, CNT, and agarose are a pH-sensing material, a conducting filler, and a binder and matrix material, respectively. For preliminary test, the composite in a paste state is deposited by doctor blade method with thickness of 150 um. The film shows negative dependence on pH condition: e.g. higher potential at lower pH. The other electrode is a “reference” electrode, made of Ag/AgCl thin film with ion-selective solid membrane. The resulting electrode shows similar current-voltage curves with commercial Ag/AgCl reference electrode. Finally, the compositions of PANI film as well as the conditions for screen printing such as mesh thickness, printing temperature & speed, etc. are optimized, to establish the continuous, roll-to-roll process of a pH-sensor patterned directly on fabric by the screen printing.

S.SM06.08.11

**Synthesis and Characterization of a New Antibacterial N-halamine Coating Based on Polydopamine.** Nadia Nazi; Sorbonne Université, France

In the presence of moisture, surfaces are an ideal support for the development of biofilms containing bacteria that can be pathogenic. This poses a real public health, economic or even environmental problems in view of the use of biocides to eradicate this phenomenon. Due to the rise of multi-drug resistant microorganism, the investigation of new antibacterial coating is extremely requested.

The goal of this study is the development of a new regenerative antimicrobial coating based on polydopamine, containing haloamine (or *N*-halamine) functions (>N-Cl or/and >N-Br) that have oxidative properties due to the oxidation state +1 of Cl or Br. Thus, the antimicrobial activity of *N*-halamines is attributable to halogen exchange reactions between *N*-halamines and microorganisms, leading to death of the microorganisms. *N*-halamines are broad-spectrum biocidal groups due to their mode of action, i.e. oxidation, bacteria should not develop resistance, unlike...
after repeated use of antibiotics.

The protection of surfaces with N-halamine compounds requires the immobilization of amine, amide or imine functions that will be transformed into haloamine either during synthesis or by post-treatment in the presence of NaOCl or NaOBr. The originality of this antibacterial coating is its regenerative proprieties. In fact, N-halamines, after contact with bacteria, can be regenerated by simple immersion of the coating in a diluted bleach recharge.

The purpose of this study was to investigate the synthesis and the antibacterial properties of a new N-halamine coating based on polydopamine (PDA). First, the formation of the PDA coating by oxidative polymerization of dopamine in aqueous solution was studied and characterized. The thickness of the deposited layer reached a constant value around 50 nm after 24h of functionalization. Then this film was chlorinated by contact with a NaOCl solution in order to form on and into the coating chloramine functions. An amount of 1016 at/cm² of chlorine was successfully grafted into the surface. Finally, the antibacterial properties of the modified PDA coating were evaluated by testing its properties toward Escherichia coli. Bacterial viability in contact with the PDA-Cl film evaluated by epifluorescence microscopy revealed promising results.

References

S.SM06.08.12
Poly(lactic acid) with On-Demand Mechanical Properties Kai Li1, Denver Mcgrady1,2, Darby Ker1, Xianhui Zhao1, Reagan Newman1,2, Matthew Rowe3, Halil Tekinalp1 and Soydan Ozcak1,3; 1Oak Ridge National Laboratory, United States; 2Pellissippi State Community College, United States; 3University of Tennessee, United States

Stimuli-responsive materials, or smart materials, has been intensively studied for decades and numerous interesting materials have been developed. Among them, materials with controllable mechanical properties have found use in a wide variety of applications including aerospace, civil applications, and implantable medical devices. However, synthetic hydrogels are the most heavily investigated. Considering its sustainability, a biodegradable polyactic acid (PLA) based free-stand film with controllable mechanical properties was developed. It was found that through chain end modification with anthracene (AN), PLA experiences a 10-fold increase in toughness with no change in tensile strength. Interestingly, after 365 nm UV light irradiation, AN modified PLA became brittle and tensile strength increased by 20%. π-π* stacking of AN groups was proposed to be the mechanism behind the toughening, and light induced dimerization of two AN group resulted in the brittleness. Based on the light reversible dimerization nature of the AN group, light with different wavelengths (365 nm and 254 nm) can be used to control the mechanical properties of newly developed PLA+AN materials in solid state.

S.SM06.08.13
NIR Triggered Upconversion Nanocomposites for Synergistic Photodynamic and Photothermal Therapy Lei Ma and Xiujun J. Li; The University of Texas at El Paso, United States

Development of near-infrared (NIR) laser triggered photo cancer therapy is highly desirable but still a big challenge. Herein, NaYF₄:Yb/Er Upconversion Nanoparticles (UCNPs) was rationally synthesized through a novel low-temperature hydrothermal method, exhibiting photoluminescence emissions at the wavelength of 538, 653 and 839 nm, under 980 nm laser radiation. The UCNPs were firstly surface-modified with silanization of tetraethyl orthosilicate (TEOS) and aminopropyltrimethoxysilane (APTMS) for water solubility improvement and amine terminals decoration. Subsequently, via a carbodiimide coupling reaction, UCNPs were grafted with benzoyloxy pyrrolidine based C₆₀ derivatives, as photosensitisizers. Finally, gold nanorods (AuNRs) with localized surface plasmon resonance (LSPR) at 980 nm were synthesized, carbosylic polyethylene glycol (PEG) functionalized and covalently conjugated around the UCNPs-C₆₀ nanocomposite to obtain a multifunctional platform for photothermal therapy (PTT) and photodynamic therapy (PDT). Notably, under NIR laser irradiation, singlet oxygen was effectively generated from an upconverting photodynamic combination of UCNPs and C₆₀, while localized hyperthermia was simultaneously induced by LSPR activity of AuNRs. The therapeutic efficacy was validated in vitro on breast cancer cell lines MCF-7 and MDA-MB-231 by various microscopic and biochemical studies under a significantly mild NIR irradiation and low dosage of the nanoplatforms. Furthermore, according to cell viability comparative analysis, such nanocomposite presents a remarkable synergistic therapeutic effect by the combination of PTT and PDT. Overall, this work provides an innovative strategy for the design and understanding of clinical
Synthesis and Surface Modification Effect of BaTiO$_3$ Nanoparticles by Sodium Oleate and Chitosan on Their Piezoresponse Force Microscopy (PFM)  

Luis M. Angelats Silva$^1$, Jose Roldan Lopez$^1$, Nikita A. Emelianov$^2$, Henry León-León$^1$ and Rudy Céspedes-Vásquez$^3$;  
1Universidad Privada Antenor Orrego, Peru; 2Kursk State University, Russian Federation; 3Universidad Nacional de Trujillo, Peru

Spherical titanium barium nanoparticles with an average size about 100 nm in the tetragonal crystal phase were obtained by peroxide synthesis and then with formation of OH groups on its surface by hydrogen peroxide. To prevent their agglomeration and reduce the toxic effect, the surface of nanoparticles was chemically modified with sodium oleate and chitosan. Influence of surface modification by these compounds on piezoresponse force microscopy and their structure were investigated.

Laser-Induced Strong Marangoni Effect in Deformation and Manipulation of Ferrofluid  

Feng Lin$^1$, Talari Talari Vishal$^2$, Junyi Zhao$^3$, John Schaibley$^4$, Dong Liu$^2$, Zhiming M. Wang$^1$ and Jiming Bao$^2$;  
1University of Electronic Science and Technology of China, China; 2University of Houston, United States; 3Washington University in St. Louis, United States; 4University of Arizona, United States

Optical manipulation of fluid or droplet has long been investigated for applications in microfluidics. The light-induced thermocapillary effect is one of the strategies in optical control of liquid. We demonstrate the laser-induced deformation of ferrofluid surfaces with ultra-violet to infra-red lasers. The surface deformation reaches the bottom and breaks the liquid, achieving the highest liquid deformation thickness for over 1000 µm. The deformation process and rupture are related to strong Marangoni effect, high laser absorption and low viscosity of ferrofluid. As applications of the laser-controlled ferrofluid, we show that a ferrofluid droplet in the capillary can be easily moved horizontally and vertically by the illumination of a laser beam. We also demonstrate that letters and patterns can be written on the black surface of ferrofluid thin film with a laser beam even with a common laser pointer. Laser manipulation of ferrofluid also makes it a controlling vehicle for varieties of liquid or droplets.

Preparation and Characterization of Nitroxide-Based Magnetic Nanoemulsions Directed toward MRI-Visible Targeted Delivery System  

Kota Nagura and Naoki Komatsu; Kyoto Univ, Japan

We have prepared various all-organic magnetic soft materials containing a cyclic nitroxide radical moiety as a spin source [1]. In this talk, we report the preparation of all-organic magnetic nanoemulsions composed of the non-ionic surfactant and the hydrophobic nitroxide radical compound [2]. The properties of the nanoemulsions have been investigated by small angle neutron scattering (SANS) and dynamic light scattering (DLS) analyses, EPR spectroscopy, and MRI method. The nanoemulsions showed high colloidal stability, high reduction resistance to ascorbic acid, low cytotoxicity and an enough contrast enhancement in the proton longitudinal relaxation time (T1)-weighted MR images in (-)-PBS in vitro and in vivo. Furthermore, an additional hydrophobic anticancer drug such as Taxol® was simultaneously encapsulated inside the nanoemulsions. We expect that the drug-loaded nanoemulsions can be used as a biocompatible magnetic drug carrier for MRI-visible targeted delivery system.


One-Pot Synthesis of Highly Water-Soluble Iron Oxide Nanoparticles with Functional Groups in Polyols for T1-Weighted MRI  

Pohlee Cheah, Paul Brown and Yongfeng Zhao; Jackson State University, United States

The direct synthesis of water soluble iron oxide nanoparticles with both controlled size and functional groups on the surface has gained intensive interests. In this study, ultrasmall iron oxide nanoparticles (IONPs) with different functional groups were successfully synthesized via one-pot synthesis. The IONPs are prepared by first thermal decomposition of iron acetylacetonate Fe(acac)$_3$, precursor in diethylene glycol (DEG), followed by mixing the surface ligands at the end of the reaction. This facile synthesis method enabled binding of different surface materials such as dopamine hydrochloride (Dopa),
polyethylene glycol with thiol end group (thiol-PEG), and polyacrylic acid (PAA) onto the IONPs. The size growth of IONPs can be well controlled as evidenced by transmission electron microscopy (TEM) studies. The high water stability of nanoparticles was correlated with the change of hydrodynamic size and zeta potential. While TEM results showed no significant change in the nanoparticles core size before and after surface modification, hydrodynamic size slightly increases due to the presence of ligands molecules on the surface. The attachment of surface ligands was studied by FTIR and TGA. FTIR results indicated the corresponding functional group for each surface ligands as a result of surface modification. In addition, we confirmed the introduce of functional groups by bioconjugation of fluorescence dyes on the surface. The magnetic resonance phantom study show that the resulted nanoparticles can be used for T1-weighted MRI imaging. The effect of surface ligands on the relaxivities of IONPs were also studied.

S.SM06.08.26
Activation of Electrocured Bioadhesives Using DC and AC for Electroceutical Therapies Manisha Singh and Terry W. Steele; Nanyang Technological University, Singapore

Stimuli sensitive adhesives can be cured with temperature, UVA, and voltage. However, heat and light cured adhesives are limited to heat-sensitive and transparent substrates. Electrochemically mediated adhesive curing (i.e. electrocuring) can be utilized on a wide range of substrates including heat-sensitive and opaque surfaces. When an applied voltage potential is raised above a certain threshold, voltage activation initiates the diazirine groups to crosslink neighboring surfaces. Under the influence of direct current (1-3 mA), electrocuring progresses from the cathode to the anode but the maximum migration of the electrocuring is limited to 60-70% of the surface area. The application of alternating current (AC) is hypothesized to improve the electrocuring progression resulting in 100% surface activation, with a subsequent improvement in material properties. Structure-activity relationships of DC vs. AC currents are evaluated for the migration rate, shear modulus, gelation time, and adhesion strength of Voltaglue. Complete progression is achieved under AC stimulation and the maximum bioadhesion strength achieved for AC is 33 % higher than that for DC stimulation.

SYMPOSIUM S.SM07

Bioinspired Synthesis and Manufacturing of Materials
November 21 - November 21, 2020

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5:00 AM *S.SM07.01.01
Switchable Protein Interfaces for Controlled Assembly of Biomaterials Dominic J. Glover; University of New South
The fabrication of nanoscale devices requires architectural templates on which to align functional molecules in complex arrangements. Nature has met this challenge of nanofabrication by exploiting the remarkable ability of proteins to self-assemble into ordered and intricate nanostructures. Protein assemblies in nature can also serve as inspiration to build novel material templates with defined size and symmetry. Furthermore, control over assembly and disassembly processes of protein nanostructures will enable dynamic protein devices to be created that can sense and respond to specific input signals. This presentation will highlight recent engineering of modular protein subunits whose assembly and disassembly can be controlled to create novel biomaterials, including electrically conductive protein nanowires.

The central protein building block in our approach is gamma-prefoldin (gPFD), a filamentous protein chaperone from a hyperthermophilic archaeon. The protein-protein interfaces of gPFD were redesigned with helical sequences to create unique subunits that assemble into filaments through orthogonal dimeric coiled coils. Subsequently, these multicomponent filaments could be used to position and align functional enzymes. To gain switch-like control over the assembly process, post-translational modification systems were exploited to regulate the binding kinetics of coiled coils. By placing protein kinase recognition motifs in the interface of synthetic coiled coils of varied sequences, we could in vitro phosphorylate the coiled coils and thereby modulate electrostatic interactions. These engineerable protein interfaces are now being applied to control the assembly and disassembly of protein nanostructures. In one example, we aligned cytochrome c proteins on gPFD filaments to create metalloprotein nanowires. Electrochemical transport measurements indicated the nanowires could conduct current between electrodes at the redox potential of the cytochromes, and subsequently be used to interface with enzymes. The ability to control protein interactions will allow the design of smart protein devices capable of sensing inputs such as enzymatic activity, for applications in the disassembly of nanocages for drug delivery and new types of biosensors.

5:15 AM S.SM07.01.02
Biotemplated Carbon Nanofibers for Chemical and Biological Defense Krystina L. Hess1, Jifa Qi2,3, Michael Kim1, Greg Peterson1, Angela Belcher2,3, and Jared DeCoste1; 1U.S. Army Combat Capabilities Development Command Chemical Biological Center, United States; 2Koch Institute for Integrative Cancer Research, United States; 3Massachusetts Institute of Technology, United States

The nanomaterials field is rapidly evolving as scientists and engineers attempt to solve increasingly complex problems. Researchers are focused on the synthesis of new materials, assembly into higher order structures, improving consistency of materials properties, and synthesis at large scales. One area of increasing interest for creating new materials is biotemplating, an approach that uses a biological molecules, such as DNA or viruses, as scaffolds for deposition of materials of interest. This strategy has several notable advantages, including the exploitation of unique morphologies, the possibility of genetic engineering, and rapid and sustainable production at large scales. The M13 bacteriophage, in particular, is an attractive template for synthesizing nanomaterials and facilitating self-assembly.

Bacteriophages, or phages, are viruses that infect bacteria and replicate by coopting the cellular machinery. The phage genome can be genetically engineered to induce the display of specific surface proteins that may promote binding of a wide variety of molecules. This programmable functionalization makes phages an attractive template for nanotechnology applications ranging from batteries to vaccine carriers. The M13 filamentous phage is of particular interest due to its nanofiber-like shape and the high copy number (~2,700) of the pVIII major coat protein present along the 900 nm length, presenting many locations for material interactions. This particular phage is well studied and characterized, and can be easily manipulated on the genomic level due to its simplicity.

We have designed a novel, biorenewable, bacteriophage-templated, carbon-based material with a very high surface area (up to 2000 m²g⁻¹) and tunable porosity. The M13 filamentous phage was first used to create a resin-like material by adding resorcinol and formaldehyde. The incorporation of benzoazole chemistry into this process results in the formation of uniform resorcinol-formaldehyde (RF) nanofibers and allows for the incorporation of heteroatoms and functional groups that can promote material binding. RF resins can serve as precursors for mesoporous carbon aerogels with controllable porosity and particle size. Carbon materials have been explored for many applications, including filtration of small molecules and gas storage, due to their high surface area and microporous structures. To create a material with these features, resin-coated phage were burned at a high temperature, resulting in “carbonized” nanofibers, termed BioCNFs. The desirable structure and surface area of the BioCNFs were confirmed by transmission electron microscopy and nitrogen isotherms, respectively. The material properties of BioCNFs could be tailored to specific applications by adjusting the precursor composition and carbonization temperature. Micro-breakthrough testing of BioCNFs revealed a high adsorption capacity for and neutralization activity against a range of chemical warfare agents (CWAs) and toxic industrial chemicals (TICs). Remarkably, this
performance either met or exceeded that of current state-of-the-art materials such as activated carbon and metal organic frameworks. This capability can be harnessed for military or industrial applications in part due to the ability of BioCNFs to be integrated into a variety of materials ranging from decontamination wipes to gas masks.

Biosynthesis is on track to revolutionize the way new materials are developed. The biotemplating method is gaining traction because a biological material can be manipulated to promote certain properties and binding capabilities. BioCNFs, created from the biotemplating of phage, can be grown in a biorenewable manner and can be easily engineered to address emerging chemical and biological threats. Future studies with this material will focus on further optimization for chemical filtration and development of gas storage capabilities.

5:25 AM S.SM07.01.03
Bioinspired Synthesis of Hybrid Materials through Peptoid-Based Approaches Chun-Long Chen; Pacific Northwest National Laboratory, United States

In nature, biominerals (e.g. bones and teeth) are outstanding examples of hierarchically-structured hybrid materials whose formation and functions are controlled over multiple length scales by high information content biomacromolecules. Inspired by these feats of nature, many biomimetic approaches have been developed for the preparation of nanostructured hybrid materials. These approaches are attractive because they generate complex, functional nanomaterials under mild aqueous synthetic conditions. Despite the advances in developing bioinspired materials synthesis approaches, the rules of designing sequence-defined molecules that lead to the predictable synthesis of hybrid materials are unknown.

One of the most advanced classes of sequence-defined protein-mimetics are peptoids. They offer unique opportunities for producing complex architectures with tunable functions based solely on sidechain chemistry. In this presentation, two peptoid-based approaches for controlled synthesis of hierarchically-structured hybrid materials will be discussed. The first involves the design and synthesis of surfactant-like amphiphilic peptoids for controlling formation and morphogenesis of inorganic nanomaterials. The second approach exploits self-assembling peptoids for controlled synthesis of hierarchically structured hybrid materials. A combination of in situ imaging and molecular simulations were used to elucidate the principles underlying peptoid-controlled synthesis of hybrid materials with the ultimate goal of enabling predictive materials synthesis across scales.

References
(2) Sun, J.; Zuckermann, R. N. Peptoid polymers: a highly desirable bioinspired material. ACS Nano 2013, 7, 4715-4732.

5:35 AM *S.SM07.01.05
Directed Discovery of Short Peptide Modules for Assembly, Recognition and Reporting Rein Ulijn; CUNY Advanced Science Research Center, United States

We are interested in how functionality emerges from sequence in ensembles of very short peptides, and subsequently how these functions can be incorporated into functional materials. Instead of using sequences known in biological systems, we use unbiased computational and experimental approaches to search and map the peptide sequence space, which has provided new families of functional short peptides. The talk will focus on our latest results in three areas. First, we will demonstrate how to program molecular order and disorder in tripeptides, and how the conformations adopted by these peptides can be exploited to regulate assembly properties, and give rise to tunable emission in the visible range. Second, we will demonstrate how dynamic exchange of peptide sequences can form adaptive libraries that provide insights into peptide sequences that can complex ligands. Finally, we discuss peptide-based melanin mimics with tunable chromophoric properties that are achieved through oxidative incorporation of amino acids.
Bioinspired Humidity Driven Peptide Materials Roxana Piotrowska\textsuperscript{1,1}, Travis Hesketh\textsuperscript{2}, Xi Chen\textsuperscript{1,3} and Rein Ulijn\textsuperscript{1,1}; \textsuperscript{1}City University of New York, United States; \textsuperscript{2}University of Strathclyde, United Kingdom; \textsuperscript{3}The City College of New York, United States

While natural functional materials offer exceptional mechanical properties and reversibly respond to various stimuli, engineering their analogs with tunable properties remains challenging mainly due to complexity. Here we take advantage of bottom-up assembly to develop tunable peptide based materials that reversibly change their structure in response to applied stimulus. To do so we propose the use of simple tripeptide crystals as biocompatible, cheap and tunable materials which have significant responses to changes in relative humidity (RH). We selected tri-peptide sequences that contain hydrophobic - YF dyad, and charged amino acid. Using RH controlled Atomic Force Microscopy (AFM), Fourier-Transform Infrared Spectroscopy (FTIR), Powder X-ray Diffraction (PXRD) and Molecular Dynamics Simulations (MD) we observed that these supramolecular tri-peptide assemblies form three-dimensional, porous crystal networks that undergo reversible shape change in response to applied RH.

We demonstrated sequence-dependent performance allowing for tuning such properties as stiffness (0.5-2GPa), strain (3-25%), energy density (10-100kJ/m$^3$) or pore size. The modulation of peptide-sequence dependent properties help us identify key parameters that contribute to functionality during transition processes, such as dual network domains, the importance of structured water and strengthening of hydrogen bonds, hierarchical order, order/disorder domains and intrinsic porosity. Due to their intrinsic order, short-peptide crystals are an excellent platform to investigate the fundamental understanding of the relationship between function and structure. We believe that these findings open up a magnitude of possibilities for programing simple, bioinspired peptide materials.

Bioinspired Manufacturing of Molecular Composites for Critical Technologies Melik C. Demirel, Sezin Sayin and Oguzhan Colak; The Pennsylvania State University, United States

Recent advances in nanotechnology of two-dimensional (2D) layered materials combined with parallel improvements in biotechnology and synthetic biology demonstrated that more complex composites materials with properties engineered precisely to optimize performance could be achieved. We propose to create functional programmable materials with user defined physical properties from composites of 2D-layered materials and polymeric proteins \cite{1}. Our approach is based on an ultra-fast microscopy technique to screen molecular morphology of polymeric proteins \cite{2}. These proteins have several advantages as programmable materials \cite{3}: (i) their chain length, sequence, and stereochemistry can be easily controlled, (ii) their molecular structure and morphology is well-defined, (iii) they provide a variety of functional chemistries for conjugation to 2D materials, and (iv) they can be designed to exhibit a variety of physical properties. The variability of the amino-acid sequences in the polymeric proteins, which will dictate the degree of crystallinity and alignment of the protein layers, are used to control the interactions at the 2D material/protein interface, ultimately dictating the functional physical properties (e.g., electrical resistivity and thermal conductivity) of novel materials and devices . References: \cite{1} Demirel et al., Advanced Functional Materials 28 (27), 1704990, 2017; \cite{2} Tomko et al., Nature nanotechnology 13 (10), 959, 2018; \cite{3} Jung et al., Proceedings of the National Academy of Sciences 113 (23), 6478-6483, 2016.

Bioengineering and Processing of Spider Silk Proteins for Technical and Biomedical Applications Thomas Scheibel; University of Bayreuth, Germany

Proteins reflect one fascinating class of natural polymers with huge potential for technical as well as biomedical applications. One well-known example is spider silk, a protein fiber with excellent mechanical properties such as strength and toughness. We have developed biotechnological methods using bacteria as production hosts which produce structural proteins mimicking the natural ones. Besides the recombinant protein fabrication, we analyzed the natural assembly processes and we have developed spinning techniques to produce protein threads closely resembling natural silk fibers. In addition to fibers, we employ silk proteins in other application forms such as hydrogels, particles or films with tailored properties, which can be employed especially for biomaterials applications. Our bio-inspired approach serves as a basis for new materials in a variety of technical as well as biomedical applications.

Spider silk fibers show excellent mechanical properties such as a combination of strength and elasticity yielding a so far
unreached fiber toughness. Such fibers can be used e.g. in various textile applications. In biomedical applications the performance of materials largely depend on their surfaces and is further strictly related to the materials biocompatibility. Often the appearance of unwanted side effects hampers the applicability of biomaterials including foreign body responses and inflammation, and interaction of cells with a material’s surface, for example cell adhesion. In case of implants or catheters cell adhesion plays a crucial role for the overall function of the to-be-used material. To change the properties of in-use polymers and to adopt their biocompatibility, we established coatings based on engineered spider silk proteins. All kinds of polymers (polyurethane, polytetrafluoroethylene, silicone) have so far be stably coated with recombinant spider silk proteins, which can themselves be functionalized. Several parameters of the silk proteins can be easily adopted to the intended application, including the surface net charge, hydrophilicity etc. Several cell types, including HaCaT keratinocytes (epidermal cells), B50 neuronal cells, C2C12 myoblasts (muscle cells) and BALB/3T3 fibroblasts (connective tissue), exhibit low or no adhesion on the silk-coated materials. In an vivo study in Sprague-Dawley rats, silk coatings diminished the risk of side effects of silicone breast implants such as fibrosis.

Drug delivery systems allow tissue / cell specific targeting of drugs in order to reduce total drug amounts administered to an organism and potential side effects upon systemic drug delivery. Spider silk proteins represent a new class of (bio)polymers that can be used as drug depots or drug delivery systems. A recombinant polyanionic spider silk protein, which can be processed into different morphologies such as particles, films, or hydrogels, has been shown to fulfil most criteria necessary for its use as biomaterial. Further, such particles have been shown to be well-suited as drug carriers for polycationic or neutral drugs, but cellular uptake of such particles is low.

Spider silk hydrogels can also be employed as new bioinks for biofabrication. Their elastic behavior dominate over the viscous behavior over the whole angular frequency range with a low viscosity flow behavior and good form stability. No structural changes occur during the printing process, and the hydrogels solidify immediately after printing by robotic dispensing. Due to the form stability it was possible to directly print multiple layers on top of each other without structural collapse. Cell-loaded spider silk constructs can be easily printed without the need of additional cross-linkers or thickeners for mechanical stabilization. Encapsulated cells show good viability in such spider silk hydrogels.

6:25 AM S.SM07.01.11
Degradable Hydrogels for Ocean Sensing Jennifer M. Boothby and Zhiyong Xia; Johns Hopkins University Applied Physics Lab, United States

Traditionally, ocean salinity and temperature are measured using Conductivity, Temperature and Depth (CTD) sensors. CTDs are relatively large, rigid devices that are negatively buoyant. These CTDs are expensive and prone to marine biofouling (esp. for the conductivity probes), which greatly reduces the durability of these systems. Velellas are a subclass of jellyfish that live on the ocean surface. Velellas are often also called sailors-by-the-wind since their biological sails mimic conventional boat sails. Inspired by the Velellas, we proposed to develop a unique Vellela Sensor system based on biodegradable hydrogels that can measure ocean surface temperature, salinity and indirectly, the winds at the ocean surface via Global Positioning System (GPS)-tracking.

Here, we report a cost effective approach for making the biodegradable hydrogels for this application. Our approach uses click-chemistry to tailor the molecular structure of polyethylene glycol (PEG) hydrogel networks in order to control the mechanical properties and degradation time. Oligomer chains were built by base catalyzed thiol-Michael addition reactions between acrylates and thiols, where the end groups are controlled by the molar rations between the reactants. The molecular weight of oligomer chains of varying monomer ratios and monomer weights is measured by dynamic light scattering, and the ester group content is measured by Fourier Transform Infrared Spectroscopy. The oligomer chains were crosslinked by radical polymerization, yielding either thiol-ene networks from thiol-capped chains or acrylate-capped chains. Tensile tests were used to determine the effect of varying these chemistries on mechanical properties, and degradation tests were carried out in both deionized water and artificial seawater. The method of crosslinking affects the degradation profile of the networks though the oligomer compositions are nearly identical. Importantly, the size and composition of the degradation products are characterized by dynamic light scattering and nuclear magnetic resonance to confirm sufficient degradation occurs and safe byproducts are released. Effects of molecular weight between crosslinks on the lower critical solution temperature of the hydrogels and the impacts on degradation were also addressed. Further research will include deployment of these hydrogels in ocean environments to determine the susceptibility to biofouling and the actual ocean lifetime.

6:35 AM S.SM07.01.16
Automating Micro-Rheology Using Differential Dynamic Microscopy, Robotic Liquid Handling and Machine
Differential dynamic microscopy (DDM) is a micro-rheology technique that enables parameter-free estimation of the mean-squared displacement of tracer particles embedded in a test medium. The mean-squared displacement of tracer particles is a bridge to important rheological information including the complex shear modulus and thus DDM provides an avenue to truly automated and potentially high-throughput micro-rheology.

In this presentation, we discuss an automated pipeline based on DDM which incorporates robotic liquid handling and machine learning. We present the utility of the pipeline in two case studies. First, we show how a complex, multi-parameter gel point formulation space of silk hydrogels can be objectively navigated and characterized. Second, we present results of high-throughput viscosity measurement of pre-polymers and polymer melts in non-aqueous solvents. We discuss challenges to automation including the mitigation of bulk drift in samples prepared using liquid handling robots, quality control in the face of numerous automation failure modes, and issues encountered in generalizing hardware and analysis over broad time scales and sample chemistries.

Accelerating Antibody Discovery with Cell-Free Systems

The COVID-19 pandemic has highlighted the need for rapid, high-throughput, and robust therapeutic antibody screening platforms. Advances in both synthetic selections and antibody repertoire mining have enabled the rapid identification of hundreds of candidate binders in a single experiment. However, the expression and evaluation of these candidate antibodies still remains a major bottleneck in the discovery pipeline due to labor intensive steps and process throughput mismatches. In this work, we present a newly developed workflow that leverages cell-free protein synthesis (CFPS) and an Echo® 525 acoustic liquid handler to enable the expression and evaluation of hundreds of antibodies in a single experiment. Our workflow consists of a cell-free DNA assembly step to generate antibody expression templates, a modified E. coli CFPS system to express antibodies, and the AlphaLISA protein-protein interaction assay to evaluate binding. Each step of this workflow can be carried out entirely within 384-well plates without ever going into cells, making it highly suitable for automation. The resulting platform is capable of evaluating more than an order of magnitude more antibody candidates in less than half the time when compared to state-of-the-art antibody discovery pipelines. To validate the platform, we expressed 13 different human antibodies, 12 of which neutralize the SARS-CoV-2 virus. We evaluated these antibodies by mapping their target epitopes and evaluating their ability to compete with ACE2, the SARS-CoV-2 target human receptor. Our results are largely consistent with published literature on these antibodies, indicating our workflow is suitable for identifying therapeutic candidates. We expect that these advancements will accelerate antibody discovery and development not only for viral diseases like COVID-19, but for the entire antibody industry.

Cell-Free Synthetic Biology Chassis for Nanocatalytic Photon-to-Hydrogen Conversion

We demonstrated synthetic use of biology cell-free expression chassis for the design and assembly of an entirely man-made energy transformation nano-bio hybrid assembly. Similarly to a natural light-driven proton pump bR from H. salinarium, the pump bRSyn in artificial purple nano-membranes was integrated with TiO2 semiconductor nanoparticles, yielding a catalytic assembly for photon-to-hydrogen conversion. The system produces H2 at a turnover rate of 240μmol of H2 (μmol protein)−1 h−1 under green and 17.74 mmol of H2 (μmol protein)−1 h−1 under white light at ambient conditions, in water at neutral pH with methanol as a sacrificial electron donor. While the cell-free expression technique has been successfully developed as a handy approach for rapid high fidelity production of membrane proteins for fundamental structure–functional studies, cell-free methodology can become a useful flexible platform for on-demand expression of natural and designed light-responsive membrane architectures with precisely controllable structure, nanoscale dimensions, and photochemical properties. Such biological building blocks can be consequently integrated with semiconductor nanoparticles via systemic manipulation at the nanoparticle–bio interface toward directed evolution of energy nanomaterials and nanosystems.

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Living Materials with Programmable Functionalities Grown from Engineered Microbial Co-Cultures

Tzu-Chieh Tang1,1, Charlie Gilbert2,2, Wolfgang Ott1,2, Brandon Dorr1,1, William Shaw2,2, Timothy K. Lu1,1,1 and Tom Ellis2,2; 1Massachusetts Institute of Technology, United States; 2Imperial College London, United Kingdom

Genetic engineering enables new engineered living materials (ELMs) that harness the remarkable properties of nature to sense and respond to their environment. Bacterial cellulose (BC) is a natural biological material with impressive physical properties, high natural yield and low cost of production that is an attractive substrate for ELMs. Here, inspired by the ‘symbiotic culture of bacteria and yeast’ (SCOBY) used to make fermented kombucha tea, we describe a variety of novel BC-based ELMs containing yeast cells programmed to perform chosen functions. This is achieved via a synthetic SCOBY (Syn-SCOBY) approach that uses a stable co-culture of the model yeast *Saccharomyces cerevisiae* with BC-producing bacteria *Komagataeibacter rhaeticus*. We show that co-cultured yeast can be engineered to secrete enzymes into BC, generating autonomously grown catalytic materials and enabling DNA-encoded modification of BC bulk material properties. We further developed a method for incorporating *S. cerevisiae* within the growing cellulose matrix, creating living materials that can sense chemical and optical inputs. This enabled the growth of living sensor materials that can detect and respond to environmental pollutants, as well as living films that grow images based on projected patterns. Starting with only engineered cells and simple culture media, this novel and robust Syn-SCOBY system empowers the sustainable production of BC-based ELMs with genetically programmable properties under mild conditions.

Photosynthetic Bacterial Reaction Center for Electrode Biointerfaces

Gianluca M. Farinola1, Roberta Ragni1, Francesco Milano2, Danilo Vona1, Gabriella Buscemi1,2 and Massimo Trotta2; 1University degli Studi-Bari Aldo Moro, Italy; 2National Research Council, Italy

Photoenzymes are the specialized component in photosynthetic organisms able to perform light transduction into charge separated states. As natural photoconverters that harvest light by photoactive antennas, generating electron-hole pairs and tunnelling electrons in precise biochemical pathways, they can be exploited for biodevices scaffolds [1-2]. In this frame, the engineering of bioelectronic frameworks have the upmarket asset to be considerate as an eco-friendly and scalability technology, using one of the greener energy source available to us, sunlight, to gain other forms of useful energy. Therefore, the possibility of taking advantage of this unmatched photoconversion efficiency to create functional nanomaterials and bio-hybrid devices is very attractive[3].

The implementation of these unique biological systems into nanostructures or anchoring on devices electrode surfaces require the development of suitable chemical manipulation, because an efficient interfacing with electrodes for electronic applications still represents an issue. To overcome this problem, which limits the performance and applicability of photoenzymes-based technology, several attempts have been undertaken, focusing on the deployment of soft organic materials that can boost the bio-electrode interface. With this aim photoenzymes have been embedded in liposomes [4], giant vesicles [5] and polymersomes [6]. Moving forward, soft material with conductive and tunable features have been tested [7-8] to improve the energy extraction by photosynthetic proteins and the communication between the biological and electronic components in hybrid devices, that will be addressed in this presentation.

**Interfacing Photosynthetic Bacteria with Soft Materials**

Danilo Vona¹, Gabriella Buscemi¹², Mariangela Cantore², Marco Lo Presti¹, Roberta Ragni¹, Francesco Milano², Gianluca M. Farinola¹ and Massimo Trotta²; ¹Università degli Studi di Bari Aldo Moro, Italy; ²Consiglio Nazionale delle Ricerche, Italy

Photosynthesis is the most important metabolic process taking place on Earth. It converts solar energy in many other forms of energy that are used to fuel virtually all other forms of life on our planet. Two forms of photosynthesis are known: oxygenic, developed more recently on Earth and widespread on the entire globe, and anoxygenic, very ancient and limited to small ecological niches. Notwithstanding what would resemble a drawback for its exploitation, anoxygenic bacteria are sturdy, very adaptable and thrive in environmental conditions that would not be accessible to other photosynthetic organisms [1,3]. Anoxygenic photosynthetic bacteria have often been used in combination with several soft materials, including biocompatible polymers[4] and conductive hydrogels[5], for various applications in the field of energy conversion [6].

The most recent results relative to the intimate interface between the whole photosynthetic bacteria, in particular the species *Rhodobacter sphaeroides*, its mutant strains, or portion of the bacteria will be addressed in this presentation.


**Engineering Interfaces of Nanomaterials with Living Bacteria**

Hong Dong, Deborah A. Sarkes, Jessica L. Terrell, Justin P. Jahnke, Meagan C. Small, Margaret M. Hurley and Dimitra N. Stratis-Cullum; CCDC Army Research Laboratory, United States

The ability to control the interactions between bacteria and materials is fundamental for creating living hybrid systems as well as pathogen anti-adhesion. Herein we discuss our work in tuning the abio-bio interfaces for binding nanomaterials to living bacteria either through genetic engineering or through material functionalization. In the first study, living bacteria/nanoparticle hybrids were prepared by genetically controlling binding peptide displayed on bacterial surfaces. *Escherichia coli* (*E. coli*) was engineered with inducible gene circuits to control display of peptides on bacteria with desired sequences. Driven by metal-peptide affinity, nanoparticles such as gold or magnetic nanoparticles could self-assemble onto the bacteria with programmed peptides. Peptide-mediated binding of gold nanoparticles to *E. coli* showed enhanced microbial fuel cell power generation. In the second study, cellulose nanofibrils, a biocompatible and easily modified nanomaterial platform, were chemically functionalized with mannose derivative to be used as a new tool in the control of bacterial pathogenesis. The functionalized nanofibrils were able to regulate fimbriated *E. coli* association due to strong affinity between mannose grafted on nanofibrils and FimH receptor on *E. coli*. These bioactive nanofibrils demonstrated the capability of capturing fimbriated *E. coli* as well as significant inhibition of *E. coli* adherence to mannosylated surfaces.

**Chemical Mechanical Nano-Structuring Implementation on Titanium Based Implants to Control Biocompatibility**

G. Bahar Basim, Kimberly Beers and Debashish Sur; University of Florida, United States

Nano-scale modification of macro-scale 3-dimensional implantable devices is gaining more attention as the cell attachment/detachment mechanisms at the bio-interfaces are profoundly affected by the nanoscale interfacial interactions [1]. Titanium-based biomaterials are widely used for dental prostheses, orthopedic devices, and cardiac pacemakers. Titanium and its alloys are most favored for hard tissue replacement due to their excellent mechanical properties and surface characteristics promoting biocompatibility due to the spontaneous formation of a thick oxide layer in the presence of an oxidizer. This study focuses on the development of a three-dimensional chemical mechanical nano-structuring (CMNS)
In an alkaline media (pH = 10), the swelling ratio was ~ 35 independent of (AATris) and the non-glucose-sensitive crosslinker methylenebisacrylamide (BIS) was created. In this primary network, our concept for the glucose sensitive bases on a semi-interpenetrating network (semi-IPN) architecture. A primary stimulation by a porous cryogel structure and by implementing temporary netpoints which are cleavable by glucose. Copolymer network poly(AAm-co-AATris-co-BIS) from acrylamide (AAM) and the triol groups provided by AATris act as the reversible crosslinks to fix the temporary shape. Form the semi-IPN. The boronic ester bonds, which can be reversibly formed between the PBA groups on linear chains and linear copolymer poly(AAm-co-AAPBA) from AAm and diacrylamido phenylboronic acid (AAPBA) was immobilized to form the semi-IPN. The boronic ester bonds, which can be reversibly formed between the PBA groups on linear chains and the triol groups provided by AATris act as the reversible crosslinks to fix the temporary shape.

Physical signals have been used to control the degree of swelling or to induce a shape-change in hydrogels. Taking in view potential future application of soft materials in life sciences more specific responsivities to biological signals are desirable. Chemical and physical sensors for glucose have been explored extensively motivated by device developments for diabetes treatment. Here we aim at integrating glucose sensitive chemical moieties into hydrophilic polymer networks in order to create a bio-induced shape-memory effect. We hypothesized that glucose-sensitive shape-memory hydrogels can be created by minimizing the volume change upon stimulation by a porous cryogel structure and by implementing temporary netpoints which are cleavable by glucose. Our concept for the glucose sensitive bases on a semi-interpenetrating network (semi-IPN) architecture. A primary copolymer network poly(AAm-co-AATris-co-BIS) from acrylamide (AAM) and N-[Tris(hydroxymethyl) methyl]acrylamide (AATris) and the non-glucose-sensitive crosslinker methylenebisacrylamide (BIS) was created. In this primary network linear copolymer poly(AAm-co-AAPBA) from AAM and m-acrylamido phenylboronic acid (AAPBA) was immobilized to form the semi-IPN. The boronic ester bonds, which can be reversibly formed between the PBA groups on linear chains and the triol groups provided by AATris act as the reversible crosslinks to fix the temporary shape.

In an alkaline media (pH = 10), the swelling ratio was ~ 35 independent of $C_{\text{glu}}$ varied between 0 and 300 mg.dL$^{-1}$. In rheological measurements it could be shown that G’ decreases remarkably from approximately 3800 Pa to approximately 2200 Pa when $C_{\text{glu}}$ was raised from 0 to 90 mg.dL$^{-1}$. In bending experiments shape fixity ($R_f$) and shape recovery ($R_r$) was determined. After 5 programming /recovery cycles a $R_f \approx 80\%$ and a $R_r \approx 100\%$ could be measured. $R_f$ was a function of $C_{\text{glu}}$ in the range from 0 to 300 mg.dL$^{-1}$ which accords with the fluctuation range of $C_{\text{glu}}$ in human blood, and in this way, the SMC could be used to determine $C_{\text{glu}}$. The presented hydrogels could play a role in future Diabetes treatment options that are able to determine the blood glucose level and release insulin according to the detected glucose level automatically and in this way provide painless treatment for diabetes without insulin injection.

Air Force requires wearable sensors to enhance performance and protect warfighters in operational environments. Volatile organic compounds (VOCs) found in exhaled breath are key biomarkers for estimating human physical/physiological statuses. Biorecognition elements (BREs) are biological materials specifically binding to the biomarker of interest. Short peptides (normally composed of 5-15 amino acid residuals) are promising BREs for the selective detection of VOCs. They provide chemical stability, straightforward design and engineering capability, and controlled affinity to a target. Carbon nanotube (CNT) field-effect transistors (FETs) have been generally accepted as a suitable platform for sensor miniaturization and wearable applications. Previous CNT FETs for VOC detection have measured explosives or food quality-related molecules. Selective detection of VOCs in breath, meanwhile, still remains a technical challenge since many VOCs share similar chemical characteristics such as polarity and partition coefficient. To facilitate discovery of peptides selective towards target VOCs, it is important to investigate a wide range of molecular properties relating to the peptides and VOCs. Here, we present an in-operando approach to investigate peptides’ affinity towards VOCs of interest (isopropyl alcohol, acetone, isoprene, and toluene) on a CNT FET platform. CNTs were functionalized by a number of peptides, and binding events between peptide and VOC have been directly observed by measuring changes in the electrical properties of the CNT FET. We tested three groups of peptides (14 total) that were obtained from phage display and/or in-silico modeling. The results showed not only decisive discrimination of the four different breath-related VOCs, but also possible binding affinity of amino acids towards target VOCs. The proposed BRE investigations have potential for selective breath monitoring sensors facilitating real-time human performance assessments.
This talk will present a review of bottom-up analysis and design of materials for various purposes - as structural materials such as bone in our body or for lightweight composites. These new materials are designed from the bottom up and through a close coupling of experiment and powerful computation as we assemble structures, atom by atom. We review case studies of joint experimental-computational work of biomimetic materials design, manufacturing and testing for the development of strong, tough and smart mutable materials for applications as protective coatings, cables and structural materials.

Modeling matter as resonating systems, this talk will then discuss the interface of material and sound, and present how we can transcend scales in space and time to make the invisible accessible to our senses and to manipulate matter from different vantage points, using innovative agents such as AI interacting with human creativity. The impact of this work is the design and making of new materials, art and music, and a deep mathematical understanding of the functional underpinnings of disparate manifestations of hierarchical systems. Building on these concepts, using AI, we explore a new interface of human expression with learned behavior to better understand the physiology and disease etiology due to the misfolding of proteins, explore it as the basis to generative algorithms, and present musical compositions based on the natural soundings of amino acids and proteins.

Using sets of harmonic oscillations as a unifying description, model of disparate hierarchical systems are developed, and then used to illustrate competing concepts of order and disorder and how they are the basis to create functional cross-scale relationships. The insights from this theory explain practically relevant issues such as the strength of silk or the emergence of disease, and the creation of new art. The translation from various hierarchical systems into one another presents a paradigm to understand the emergence of properties in materials, language, visual art, music, and similar systems.

8:55 AM S.SM07.01.35
Biopolymer Nanocomposite Materials from Plant Cells Eleftheria Roumeli1,2, Luca Bonanomi2, Rodinde C. Hendrickx2 and Chiara Daraio2; 1University of Washington, United States; 2California Institute of Technology, United States

Over the past years, significant efforts have been made towards manufacturing innovative sustainable materials. One of the most promising avenues is utilizing the remarkable efficiency and diversity of natural synthesis processes. In this direction, we present here a fabrication platform based on plant cells dehydration, which delivers bulk, biopolymer nanocomposite materials. Plant cells naturally synthesize intricate and hierarchical biopolymer composite structures that comprise their cell walls. Here we demonstrate a modified compression molding method that allows the preservation of cell walls upon dehydration. The final product is a bulk, hierarchical, lamellated biopolymer nanocomposite that is entirely biodegradable. We report the mechanical properties of the pure biopolymer composite, which are superior to other biological matrix materials, such as mycelium or yeast-based composites. Additionally, we demonstrate that filler additives can be incorporated in the fabrication process in order to introduce new properties or tune the native properties of the nanocomposite.

9:05 AM *S.SM07.01.38
Programming Nanoscale Architectures and Lattices Oleg Gang1,2; 1Columbia University, United States; 2Brookhaven National Laboratory, United States

The ability to organize nano-components into the desired architectures with targeted properties is one of the major objectives of nanotechnology. Our efforts are focused on establishing a broadly applicable DNA-based platform for programmable assembly of nano-components into desired and structurally defined organizations. We explore the use of DNA-encoded nano-components and designed DNA constructs to guide self-assembly process towards the desired lattices and arbitrary designed architectures. Through the development of effective assembly strategies, revealing the principles governing these DNA-programmable systems and understanding the role of geometry, interactions and pathways, we develop methods for creation of well-defined three-dimensional lattices, two-dimensional arrays and finite-sized cluster architectures from the inorganic and biomolecular nano-components. Our resent advances in ability to form the desired inorganic, organic and hybrid nanoscale architectures and their applications for nano-optics and biomaterials will be discussed.
Biomineralization Strategies for Synthesizing Defective Metal Oxide Based Nano-Catalysts

Junjie Jiang, Nicholas Bedford, Jason Scott and Rahman Daiyan; University of New South Wales, Australia

Biological systems have provided us much inspiration to design and engineering new materials. For example, nature has utilized biomolecules for the synthesis of complex inorganic structure in a process collective termed biomineralization. In-vitro biomineralization methods are capable of synthesizing nanoscale materials, for instance, SiO₂, TiO₂, and etc. with high surface area and disordered structure occurring under mild reaction conditions. Based on these unique material characteristics, in-vitro biomineralization has great potential for a variety of functional applications, particularly in catalysis wherein access to disordered surface structures is beneficial. As such, in-vitro biomineralization can bring an innovative strategy for synthesizing nanoscale metal oxides which can serve as catalysts and catalyst support materials.

In this work, a biomimetic analogue, protamine, is used to enable a cost-effective, larger scale metal oxide catalyst synthesis approach. The protamine based biomineralization technique was adopted to synthesize a range of mixed metal oxide nanoparticles for a series of reactions. This technique brings many advantageous features for catalytic materials such as nanoscale, high specific surface area, low preparation cost, and stable thermal properties. For example, biomineralized SiO₂-TiO₂ composite metal oxides were implemented for the CO₂ hydrogenation reaction. The modularity of the synthetic techniques enabled surface area increase and additional defect engineering strategies, that lead to the inducing of extra defects on the material which served as active sites to further enhance the catalytic performance. In addition, we have created Zn-Sn mixed metal oxides for catalysts in the electrochemical CO₂ reduction reaction. All materials were thoroughly characterized using a suite of synchrotron characterization methods to establish structure/function relationships. Through these techniques, we have discovered that most materials are largely disordered and change in local structure depending on the synthetic conditions applied. Through these efforts, we have demonstrated a new material manufacturing strategy based on in-vitro biomineralization for nanoscale metal oxide catalysts.

Enhanced Cellulose Nanocrystal Composite Films with Tunable Iridescence Driven by Intercalation of Wood-Derived Amorphous Polymers

Katarina Adstedt¹, Kellina Pierce¹, Elizabeth Popenov¹, Rui Xiong¹, Ren Geryak¹, Vladyslav Cherpak², Dhriti Nepal³, Tim Bunning³ and Vladimir Tsukruk¹; ¹Georgia Institute of Technology, United States; ²University of Colorado Boulder, United States; ³Air Force Research Laboratory, United States

The mechanical performance of cellulose nanocrystal (CNC) is typically enhanced through crosslinking, the addition of strong filler materials or mixing with soft matrices. However, these modifications that can lead to higher mechanical strength tend to disrupt the original helical organization of the chiral phases and destroy the corresponding vivid iridescence. Herein, we demonstrate a unique case of enhanced and tunable structural colors combined with much improved strength of CNC composite materials through the addition of amorphous wood-derived polymers of similar chemical composition. Adding these polysaccharides, pullulan, dextran, and xylan, promotes seamless integration into the original helicoidal organization with full chain intercalation, even at very high loading, a unique behavior for composites from components with different structural organization, amorphous and chiral nematic in our case. CNC-polymer composites demonstrate enhanced mechanical performance, nearly a two-fold increase in toughness. A systematic red-shift in selective light reflection is observed for all polymer composites due to the gradual increase in pitch length because of the intercalation of natural polymer backbones into helicoidal organization without disturbing long-range ordering. The utilization of wood-derived amorphous polymers with similar composition, hydrogen bonding capabilities, and mechanical properties, instead of foreign synthetic components provides a sustainable method of significant mechanical enhancement of chiral composite films without disrupting the original helicoidal organization and vivid iridescence with controlled color appearance.

Developing Non-Iridescent Structural Colors on Flexible Substrates with High Bending Resistance

Mario A. Echeverri¹, Anvay Patil¹, Ming Xiao¹,², Weiyao Li¹, Matthew D. Shawkey³ and Ali Dhinojwala¹; ¹University of Akron, United States; ²Harvard University, United States; ³University of Ghent, Belgium

Nanostructured materials producing structural colors have a great potential in replacing toxic metals or organic pigments.
Electrophoretic deposition (EPD) is a promising method for producing these materials quickly on a large scale. However, the colors reported so far lack brightness, saturation, and mechanical stability. Herein we use EPD assembly to co-deposit silica (SiO₂) nanoparticles with precursors of synthetic melanin, polydopamine (PDA), to produce mechanically robust, wide-angle structurally colored coatings. We use spectrophotometry to show that PDA precursors enhance saturation of structural colors and nanoscratch testing to demonstrate that they increase the mechanical stability of the EPD coatings. Stabilization by PDA precursors allows us to coat flexible substrates that can sustain bending stresses, opening an avenue for electro-printing on flexible materials.

S.SM07.02.08
**Synthetic Biology—New Capabilities for Army Materials Applications** Joshua A. Orlicki and Justin P. Jahnke; Army Research Laboratory, United States

The emerging field of synthetic biology provides opportunity and new capabilities for the precision synthesis, assembly, and function of materials. Currently, there are significant challenges for the integration of bio-derived and bio-based technologies in the defense-oriented materials space. Army platforms must reliably operate over wide temperature ranges (e.g., -40 to 75 deg C), extremes in humidity, exhibit durability to be fielded for long periods of time (e.g., 5+ years) and endure strain rate deformations from low strain, high frequency vibration to high strain impact events. We are making initial forays into the synthesis and assembly of materials, and are developing protocols to probe performance metrics, production repeatability, and aging. Materials under evaluation include bio-derived organics and bio-templated inorganics, and integration into materials systems has been undertaken using both traditional processes and bio-synthetic processes. This poster will give an overview of current projects employing the tools of Synthetic Biology and highlight the key performance targets of these materials.

S.SM07.02.14
**Anisotropic Hydrogels Templated by Chromonic Liquid Crystals for Biomedical Applications** Suitu Wang¹, Jennifer M. Boothby², Daniel Maruri¹, Victor D. Varner³ and Taylor H. Ware¹; ¹University of Texas at Dallas, United States; ²Johns Hopkins University Applied Physics Laboratory, United States

Approaches to control the microstructure of hydrogels are critical for the control of cell-material interactions. Herein, we report a versatile approach for the synthesis of anisotropic polyacrylamide hydrogels by lyotropic chromonic liquid crystal (LCLC) templating. Specifically, polyacrylamide hydrogels with aligned porosity can be obtained by polymerizing the network in the presence of an aligned chromonic phase. By varying crosslink density, the resulting hydrogels have tunable pore size and distinct mechanical anisotropy. For example, the elastic moduli measured parallel and perpendicular to the LCLC order are 124.6 kPa ± 7.9 kPa and 17.4 kPa ± 1.1 kPa and the hydrogels have a 4-fold larger swelling normal to the LCLC director than along the LCLC director. This anisotropy can be patterned by using surface anchoring to locally control the nematic director, which in turn patterns the polymer network. The director can be patterned both within the plane and through the thickness of the hydrogels. Fibroblasts cultured on the resulting hydrogels align along the pore walls, which in turn provides a powerful approach to control cell orientation. This new strategy to make anisotropic hydrogels can have potential applications for patternable tissue scaffolds, soft robotics, or microfluidic devices.

Author for Correspondence: taylor.ware@utdallas.edu

S.SM07.02.15
**3D-Printed Shape-Morphing Living Composites** Laura K. Rivera-Tarazona, Tarjani Shukla, Zachary T. Campbell and Taylor H. Ware; The University of Texas at Dallas, United States

Shape-transformation is a prevalent function observed in living systems, from the blooming of flowers to muscle actuation. While current shape changing synthetic materials are capable of sensing non-specific stimuli such as pH, light, temperature or ultrasound, new materials are needed that detect specific biochemical cues and respond mechanically in a programmed manner. Materials that respond to such subtle cues could enable biosensors or drug-delivery devices. Recently, we demonstrated that synthetic materials can be designed to host genetically engineered yeast cells capable of responding to very specific and pre-determined stimuli (e.g. biogenic amines). Specifically, we presented a new method to create programmable shape-morphing composites using polyacrylamide hydrogels embed with *Saccharomyces cerevisiae*. Cellular proliferation within these composites can be spatio-temporally controlled to generate large volume expansions of up to 600% of the composite. Here, we report the design of living composites with shear-thinning properties based on cellulose nanocrystals (CNC) and acrylamide monomers using direct-write printing. CNC concentrations at 11 wt% and 22 wt% enabled active (yeast-embedding) and passive (cell-free) bioinks respectively to be printed. By developing a hydrogel-based printable...
bioink, engineered yeast strains can be patterned into three-dimensional (3D) structures with defined geometry, organization and porosity. Using this control, we spatially pattern cellular proliferation within a monolith to induce complex shape transformations and demonstrate specificity to single amino acids. Finally, we will discuss the 3D printing of a living composite capsule for in vitro biomolecular detection and subsequent drug delivery in a model of the gastrointestinal tract. In this device, genetically-engineered probiotic yeast only proliferate in the presence of a particular biomolecule, such as heme, which leads to expansion of one portion of the capsule. This expansion ruptures the device and releases a hydrophobic compound to the surrounding environment. Our study may enable new opportunities to develop drug-delivery devices for the diagnosis and treatment of gastrointestinal disorders.

S.SM07.02.17
Dynamic Structural Color by Self-Assembling Cellulophaga Lytica
Claretta J. Sullivan¹, Chia-Suei Hung¹, Kennedy Brown¹, Lewis Shabshelowitz²,³, Vincent Chen¹, Pamela Lloyd¹, Maneesh K. Gupta¹, Milana Vasudev¹,², Abby Juhl¹, Wendy Goodson¹ and Patrick Dennis¹; ¹Air Force Research Laboratory, United States; ²University of Massachusetts Dartmouth, United States

Under laboratory conditions, the micron-scale dimensions and gliding motility of some prokaryotes, including Cellulophaga lytica, facilitate the self-assembly of discrete cells into iridescent biofilms. This is in sharp contrast to structural coloration in eukaryotic systems (e.g. lepidoptera, coleoptera), where multiple cell types, complex architectures and fixed structures are frequently involved. We propose using biofilms of C. lytica as a platform for material synthesis since properties derived from their exquisite ordering can be tuned using ‘simpler’ bacterial genetics. Importantly, the sequence of C. lytica strain 7489 is known, making it amenable to future synthetic biology approaches for tailoring. Though facile growth of its biofilms is possible, we report nuances of growth conditions which impact iridescence. Toward a fundamental understanding of the strategies employed in self-assembly, the current study also examines community organization and cellular morphology. Specifically, iridescent and non-iridescent regions of the biofilms are probed using complementary imaging techniques including confocal, electron and atomic force microscopies. These multi-scaled microscopies have provided surprising insights into the biofilm structure. Specifically, we report that differences in morphology and packing correspond to changes in the wavelength of reflected light. To facilitate these studies, sample preparation strategies which allow cells to be imaged in context were developed. In addition to establishing the structure-property relationship derived from the biofilm’s organization, our findings suggest that novel mechanisms may be involved in assembly and that a comprehensive investigation to identify cellular components contributing to assembly is indeed warranted.

S.SM07.02.19
Bioinspired Photonic Crystal Enhancement of Raman Signatures for the Early Detection of Cancer
Milana C. Vasudev, Prathyushkrishna Macha and Matthew Moore; University of Massachusetts Dartmouth, United States

Over the past few decades, cancer and other fatal diseases have become more prevalent affecting large populations around the world. Earlier detection could improve prognosis for the patient. A possible solution includes using photonic crystal-based sensors to detect biomarkers in exosomes shed by cancerous cells. Photonic crystals have become increasingly important for biosensor applications due to the need for a label-free alternative to detect biomarkers. Surface enhanced Raman scattering (SERS) using gold nanoparticles is a sensitive analytical technique, which has been exploited in chemical, molecule and environmental monitoring. In this study, a photonic crystal SERS substrate was designed and synthesized for the early detection of changes which occur in the exosomes shed by the cancerous cells. Optical signal amplification due to gold nanoparticles and photonic components, leads to the enhanced interactions between the analyte and the sensor. Electromagnetic enhancement using photonic crystal substrate can greatly enhance the SERS detection when compared to traditional methods. The two-dimensional photonic structural organization in the comb structures of the ctenophore species, Mnemiopsis Leidyi and Beroe Cucumis was used as the inspiration to design the photonic crystal substrate used in this study. The structural organization of the cilia in the comb rows consists of arrays of hexagonally packed cilia with a central microtubule pair. Transmission electron microscopy was used to study the arrangements of the comb structures. Reverse engineering of these submicron structures aids in designing a novel photonic template. The design of the comb structures was recreated using AutoCAD and Raith software. Photonic nanostructures were synthesized using the direct-write e-beam lithography technique. The structures were characterized with scanning electron microscope (SEM), and reflectance measurements. Gold nanoparticles will be used to in conjugation with the photonic crystal structure and Raman signatures measured, both with and without gold molecules. Finally, these gold nanoparticle coated photonic templates were utilized as a SERS active surface for exosomal detection. Some advantages of utilizing photonic crystals include point of care diagnostics and their response to a multitude of external stimuli including light.

S.SM07.02.22
**Functionalization of Iron Carbide@Iron Oxide Nanoparticles through Conjugated Oleic Acid with L-Asparagine and L-Arginine**

Anya I. Arguelles, Paul Zavala-Rivera, Aaron Rosas Durazo, Armandp Lucero-Acuña, Patricia Guerrero-Germán and Armando Tejeda; Universidad de Sonora, Mexico

The delivery of nanoparticles, as vectors in biological environments, depends on the interaction and stability in the environment where it is delivered. The functional groups are given by surfactants that gives stability to the particles, avoiding the aggregation between themselves aside from chemical associations not only with the environment but also with other molecules depending on the surface charge. Recent studies have shown that the use of carbodiimides has been helpful in achieving changes in the behavior in nanoparticle solution, from organic to aqueous phase [1-3]. There is an extensively research field on surfactants, called "green surfactants", based on the integration of amino acid and proteins, due to the functional groups that compose them, such as carboxyl and amino groups, that can be chemically adhered to the surface through a possible nucleophilic substitution achieving amphiphilic conformations in the form of micelles or enantiomers and dependent on the change of pH for the deliberation of the vehicle in the biological system [4–8].

This research aims iron carbide@iron oxide nanoparticles (ICIONPs) from organic nature[9], coated of amino acids through the conjugation of oleic acid with L-Arginine and L-Asparagine performing by N,N’-dicyclohexylcarbodiimide (DCC) with N-Hydrxysuccinimide (NHS) as a coupling reagents, forming behavioral structures, known as polypeptides, with an organic center and aqueous surface arrangement for encapsulation of nanoparticles as possible interaction with other biological molecules and their application in bioseparation processes.


**Citrus limon as Reducing Agent for the Synthesis of Gold Nanoparticles by Multiwave Ultrasonic Technique**

Juan Carlos Martinez, Julio Cesar Ramos Dominguez, Cesar Fernando Lopez Sanchez and Raul Carrera Cerritos; Instituto Politécnico Nacional, Mexico

Nanotechnology has studied applications in biomedical areas, for which several nanomaterials have been synthesized that present limitations such as toxicity and instability in organisms, so green methodologies have been developed that help reduce this problem. In this work we report the green synthesis of AuNPs using as a reducing agent lemon extract (Citrus limon), and the multiwave ultrasonic technique as an excitation element. As the precursor reagent, trihydrated chlorouric acid (HAuCl4.3H2O, Sigma Aldrich SKU 520918) was used, and as a reducing agent the lemon juice extract. The reaction was carried out in an ultrasonic bath at a frequency of 40kHz, at 55 °C for one hour (Branson 2800 series). The final solution obtained showed a purple coloration, and was characterized by UV-VIS spectrophotometry and transmission electron microscopy (JEOL JEM 1010). Absorbance peak resonant at 530 nm was observed and particle diameters between 12 and 16 nm were obtained. The reported results could be of interest to carry out fusion of nanometric inorganic materials by the ultrasonic technique, and by controlling the temperature and frequency, metal structures with different morphology and properties could be generated.

**SYMPOSIUM S.SM08**
SESSION S.SM08.05: Poster Session: Emerging Strategies and Applications in Drug Delivery
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday
Morning, November 21, 2020
5:00 AM - 8:00 AM
S-SM08

S.SM08.05.01
Imparting Hydrophilicity and Water Absorbability of Polycaprolactone Nanofibrous Membrane by Incorporating Alginate-Chitosan Particles Joshua Kae B. Macugay and Leslie Joy L. Diaz; Department of Mining, Metallurgical and Materials Engineering, University of the Philippines Diliman, Philippines

Polycaprolactone (PCL) have been used in medical applications due to its inertness, biocompatibility, biosorbability and biodegradability. However, its hydrophobic nature and absence of fluid absorption capacity limits its potential in such applications. This can be improved by incorporating particles that will facilitate interaction with water or body fluids. In this study, alginate-chitosan PECs are synthesized and incorporated in PCL nanofibrous membrane. Given this structure, alginate nanoparticles were synthesized to allow incorporation into the membrane. Varying mass ratio of alginate to calcium ions were investigated in the pre-gel formation which was controlled through viscosity measurements. Viscosity decreased significantly from 1.873 to 1.515 cPs indicated the formation of the alginate particles as a consequence to the rearrangement of the long alginate polymer chains into discrete coiled structure. Meanwhile, varying mass ratio of alginate to chitosan was investigated in the polyelectrolyte complexation to facilitate the formation of a stable suspension thereby suggesting formation of alginate-chitosan nanoparticles. A minimum particle size of 1.924 microns is measured for stable solutions. The alginate-chitosan was incorporated into the PCL nanofiber membrane to impart hydrophilicity and water absorbability. Infrared spectroscopy done on the nanofiber membrane confirmed the presence of both PCL and alginate in the final structure. Further, contact angle measurements showed a significant decrease from 82.56 to 73.58° which suggests the improvement of hydrophilicity of the membrane. Water absorption capacity of the membrane increased to 7.82%. Varying the amount of alginate-chitosan particles would allow improvement and control of the nanofiber membrane’s hydrophilicity and water absorption capacity. This material has potential use in wound dressing devices, extracellular membranes, as well as filter membranes in medical devices.

S.SM08.05.03
Antibacterial Activity and Controlled Delivery of Amoxicillin from Polyacrylamide/Starch Hydrogels Ana Valeria Torres Figueroa, Cinthia Jiovanna Pérez Martínez, Teresa Del Castillo, Enrique Bolado Martínez and María Alba Guadalupe Corella Madueño; Universidad de Sonora, Mexico

Hydrogels are water-compatible polymer networks which can increase their volume without losing their shape. The applications for this type of materials depend on their maximum swelling grade and mechanical properties, which are closely related with the cross-linking porosity and the density of the network. Their flexibility degree is very similar to that of natural
tissues, so the hydrogels are considered a very important group in the pharmaceutical industry for biomedical applications, particularly, as controlled drug delivery systems. The advantages of these systems include the possibility of drug delivery at specific sites, the continuity of the treatment during the night, the stability of the drug, its optimal absorption by the tissues, as well as the reduction of side effects. In this study, we report the evaluation of hydrogels of polyacrylamide (PAAm)/starch, synthesized in different molar ratios (100/0, 90/10, 80/20, 70/30, 60/40, 50/50), as a potential platform for the controlled release of amoxicillin. The swelling capacity of the hydrogels and the effect of the molar ratio between both polymers on the antibiotic release kinetics under normal physiological conditions of temperature and pH were evaluated in vitro. Finally, bacterial growth inhibition assays in ATCC strains were carried out to analyze the clinical potential of materials. The results have demonstrated the potential of polymeric hydrogels as controlled release system of amoxicillin.

S.SM08.05.06
Characterization of a Novel Se-bioactive Glass for a Chemotherapeutic Bone Cement Rebecca Potts, Kapil Raghuuraman and Aisling Coughlan; University of Toledo, United States

Selenium (Se) ion release from a bone cement is hypothesized to provide chemotherapeutic effects and to be beneficial in the prevention of recurrence of osteosarcoma in the setting of tumor resection surgery. Se containing compounds have been shown to act as redox modulators with higher selectivity and sensitivity in malignant cells. A four glass series, SiO2-Na2O-CaO-SrO-SeO3, was investigated substituting varying levels of CaO for SeO2. The glass series was synthesized using the air-quench method. This method was repeated twice for each glass in the series in order to ensure homogeneity of the material. This study focuses on the characterization of the bioactive glass and its ability to release beneficial ions in an aqueous environment. Structural and thermal properties were evaluated for the glass series using differential thermal analysis (DTA) along with magic angle spinning nuclear magnetic resonance (MAS-NMR) to confirm network connectivity (NC) calculations. X-ray diffraction (XRD) was used to confirm the presence of an amorphous structure in the series. Inductively coupled plasma mass spectroscopy (ICP-MS) was performed in order to quantify the ion release from the glass in an aqueous environment at physiological temperature for all elements present in the glass. Antibacterial efficacy tests were completed along with cytocompatibility studies via MTT assay of the material plated conditioned media with MC3T3 cells. The glass composition was determined to have bioactive properties, detectable and predictable Se ion release, antibacterial abilities, and also promoted growth of pre-osteoblast cells. Future directions include assessing the ability of the selenium based bioglass to stop or reverse growth of osteosarcoma cells.

S.SM08.05.07
Multifunctional Peptide-Conjugated Non-Viral Gene Vector for Dental Pulp Regeneration Qian Li and Xiaohua Liu; Texas A&M University, United States

Dental pulp, a highly vascularized tissue situated in an inextensible environment surrounded by rigid dentinal walls, receives blood supply solely from a small apical foramen (diameter < 1 mm) of the tooth root canal. Therefore, regeneration of pulp in the full-length tooth root has long been a challenge. In this study, we aimed to develop angiogenic human dental pulp stem cells (hDPSCs) for pulp regeneration in a full-length tooth root. Specifically, we developed a multifunctional peptide-conjugated non-viral gene vector to enhance the expression of vascular endothelial growth factor (VEGF) in hDPSCs, and evaluated the efficiency and bioactivity of the angiogenic transfected hDPSCs in vitro and in a full-length human tooth root model in vivo.

Multifunctional peptide C-R9-G-NLS-W was conjugated to polylisine (PLL) using click chemistry method. The multifunctional peptide-modified PLL encapsulated pVEGF plasmid using electrostatic interaction and formed polymer/gene complexes. Next, hDPSCs were transfected using the gene complexes. Cellular uptake and transfection efficiency were examined using flow cytometry. PCR was used to evaluate VEGF gene expression of the transfected cells at mRNA level. Furthermore, the effects of transfected DPSCs on the cytotoxicity and endothelial vascular-like tube formation were performed by MTT assay and Matrigel assay in vitro. Transfected DPSCs were injected in human tooth roots sectioned into 11 mm segments and implanted in nude mice. The constructs were retrieved after 4 weeks and examined for regeneration of pulp-like tissue and vascularization by histology. The MTT result showed that at higher DNA concentration, the cell viability of peptide-modified complexes group was higher than PLL/pVEGF complexes group. The cellular uptake and transfection efficiency of peptide-modified gene complexes was higher than control group. PCR analysis indicated that the mRNA expression after transfected with peptide-modified gene complexes was enhanced. Furthermore, the gene transfection enhanced endothelial cell migration and vascular-like tube formation. The peptide-conjugated polylisine is an effective non-viral vector for gene delivery and enhanced endothelial cell migration and vascular-like tube formation.
Support: This work was supported by NIH/NIDCR (DE024979)

S.SM08.05.08
Core-Polyethylene-glycol-Lipid Shell Nanoparticles (CPLS NPs) with Tunable Morphology and Surface Charge for Potential Therapeutic Delivery
David T. Loe1, Zhiqiang Shen1, Martin Kröger2, Ying Li1 and Jessica Rouge1; 1University of Connecticut, United States; 2ETH Zürich, Switzerland

Due to their biocompatibility and large payload capacity, liposomes are the premier delivery vehicle for hydrophilic therapeutics. However, traditional procedures produce liposomes without size uniformity and stable nanoscale structures, both of which determine efficacy of delivery. We have found that templating the growth of liposomes promotes uniform size and increases the structural stability, as predicted by simulations in Dissipative Particle Dynamics (DPD). We refer to our construct as a Core–Polyethylene-glycol–Lipid Shell nanoparticle (CPLS NP), synthesized through a bottom up approach utilizing an inorganic nanoparticle as a platform from which to scaffold the liposome. Using colloidal Au NPs as the core of the CPLS, a PEG molecule, functionalized with a thiol functional group, self-assembles into a layer on the surface of the Au NP. The PEG molecule is also functionalized with a lipid moiety. Through a second self-assembly, free lipids adsorb on to the templated lipid at the NP surface. The morphology of the lipid shell is determined by the morphology of the core, a phenomenon caused by the template-scaffold. The surface charge can be tuned by incorporating various ionic lipids, a property of traditional liposomes that is retained in the CPLS. The surface charge of the lipid shell can direct cellular uptake of the CPLS NPs. The CPLS NP retains the attractive features of the liposome, an aqueous lumen and direct fusion to a membrane, while also having a predictable volume and morphology with increased stability, important features for drug delivery applications.

S.SM08.05.09
Metal-organic Framework Preserves Biorecognition of Antibodies on Nanoscale Surfaces Validated by Single Molecule Force Spectroscopy
Lin Kang1,2, Steve Smith1,2 and Congzhou Wang1,2; 1South Dakota School of Mines and Technology, United States; 2South Dakota School of Mines & Technology, United States

Antibody biorecognition forms the basis for numerous biomedical applications such as diagnostic assays, targeted drug delivery and targeted cancer imaging. However, antibodies, especially after being conjugated to surfaces or nanostructures, suffer from stability issues when stored under non-refrigerated conditions. Therefore, enhancing the stability of antibodies on surfaces and nanostructures under ambient and elevated temperatures is of paramount importance for many nanobiotechnology applications. In this study, we introduce a simple and facile approach based on a metal-organic framework (MOF) coating to preserve the biorecognition capability of antibodies immobilized to nanoscale surfaces after exposure to elevated temperatures for a prolonged period. By using atomic force microscopy (AFM)-based force spectroscopy, we demonstrate that the MOF coating is able to preserve the binding force and binding frequency of the anti-CD-146 antibody attached to an AFM tip to CD-146 antigen on the surface of melanoma cells at the single molecule level. We also demonstrate that the MOF coating outperforms another commonly used sucrose coating in terms of maintaining binding force and binding frequency of the antibody to antigen. Herein, the AFM tip functionalized with antibodies provides a nanoscale testbed (analogous to an antibody-conjugated nanostructure) to assess antibody biorecognition at the single molecule level and preservation efficacy under antibody denaturing conditions. This MOF coating approach should be applicable to the preservation of antibody-conjugated nanostructures aiming for targeted drug delivery, targeted cancer imaging, nanobiosensors, and a wide range of applications relying on surface-bound antibodies. The improved stability and elimination of refrigeration requirements will facilitate wide applications of antibody-enabled nanobiotechnology in resource-limited environments and populations.

S.SM08.05.13
Porous Silicon Nanoneedles—An Emerging Nanofabricated Tool for Enhanced Transdermal Drug Delivery
Nazia Tabassum1,2, Maria Alba1,3, Tony Yan1,3 and Nico Voelcker1,3,4; 1Monash University, Melbourne, Australia; 2University of central Punjab, Pakistan; 3Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia; 4Melbourne Centre for Nanofabrication, Australia

The transdermal route is attractive for minimal invasive administration of small and large molecular bioactives. Among the transdermal techniques (e.g. iontophoresis, electroporation, jet injectors, ultrasound, ablation, powder injection), micro/nanoneedles are particularly promising because of their straightforward, cost-effective and safe administration. However, precise control the over degradation rate of micro/nanoneedles within the skin remains a great challenge. Here, we introduce porous silicon nanoneedles (pSiNNs) for pain free transdermal drug delivery of biomolecules with controlled degradation rate.
In this work, 40-50 µm pSiNNs were fabricated via deep reactive ion etching with a tip diameter below 1 µm and a diameter of about 8-10 µm. Then, a porous surface was obtained by electrochemical anodisation. It was found that nanoneedle biodegradability and mechanical strength could be tuned by changing the thickness of the porous layer. pSiNNs with a 4.0 µm porous layer can degrade much quicker than 1.6 µm porous layer. In addition, small as well as macromolecular drug molecules could be uniformly loaded into the porous layer of the pSiNN arrays with high drug loading capacity. *Ex vivo* pig and mouse skin penetration experiment demonstrated that pSiNN can significant increase the transdermal delivery efficacy compared to topical application.

In summary, we have fabricated 40-50 µm pSiNNs with tunable porosity, biodegradability and mechanical strength for transdermal delivery. This platform is able to deliver various biotherapeutics (small molecules to large molecules) through the skin and thereby contributes to innovations in pharmaceutical sciences.

**S.SM08.05.14**

**Nanoparticles to Cancer Cells Through Peptide Ligand-Mediated Endocytosis—Cancer Cell Receptor-Targeting-Versus Cancer Cell Penetrating Peptides**

Eunji Jo and Jeewon Lee; Korea University, Korea (the Republic of)

The performances of endocytosis mediated cell uptake of two different types of functional peptides, cell receptor-targeting peptide (CRTP) and cell penetrating peptide (CPP), were analyzed and compared with a common carrier of functional peptides-heavy chain of human ferritin (huHF) nanoparticle. 24 copies of a CPP(TAT peptide from transduction domain of human immunodeficiency virus) and/or a CRTP (functional peptide with specific and strong affinity with either human integrin(αvβ3) or epidermal growth factor receptor I(EGFR)) were genetically presented and exposed on the surface of each huHF nanoparticle. We confirmed both *in vitro* and *in vivo* tumor-targeting and endocytosis performance of CRTP-presenting huHF nanoparticles and systematically analyzed the cell targeting, endocytosis, and intracellular localization of recombinant huHF nanoparticles labeled with the in the fluorescent dye (Cy5.5) *in vitro* cultures of cancer and normal cells. In particular, it is notable that CRTPs led to a uniformly diffused localization of the huHF nanoparticles in cancer cell cytosol, while CPP-mediated endocytosis made the huHF nanoparticles remain in a narrow confined cell endosomal region. These novel and remarkable findings provide highly useful informations to many researchers both in industry and in academia are interested in developing delivery systems/carriers of anticancer drugs.

**S.SM08.05.20**

**Rescuing Cells from Oxidative Stress Using Surface Functionalized Carbon Quantum Dots**

Jyoti Ahlawat, Sreeprasad T. Sreenivasan and Mahesh Narayan; University of Texas at El Paso, United States

Carbon Quantum Dots (CQDs) has demonstrated high potency to mitigate neuronal oxidative stress and related pathologies, including Alzheimer's disease (AD). However, the application of CQDs is limited due to their inability to cross the Blood Brain Barrier (BBB) without disrupting the structural integrity of tight junctions. Here, we introduce surface modified CQD nanoencased in β-lactoglobulin for easy passage across the BBB and displaying both prophylactic and therapeutic efficacy. The diverse ligand binding ability of β-lactoglobulin was leveraged to encapsulate and transport the surface functionalized CQDs, β-lactoglobulin owing to its biocompatibility was chosen to improve bioavailability of the encapsulated core. Due to the evidences of the role played by Amyloid-β to initiate AD, the study employs Amyloid-β as the model causative species and SH-SY5Y neuroblastoma cell line as the model cell line. Our study illustrates neuroprotective efficacy of the surface functionalized CQDs.

**S.SM08.05.25**

**Light Triggered Switchable Nanosystems for Remotely Targeted Drug Delivery**

Jun Chen; Institute of High Energy Physics, Chinese Academy of Sciences, China

Light triggered switchable nanosystems have recently gained increasing attention as a promising approach of remotely controlled drug delivery. We used the strategy of remotely controlled delivery technology that may overcome the pathophysiological barriers existing in targeted drug delivery. Unlike pathophysiology actived drug targeting strategies, light triggered switchable nanosystems are minimally influenced by the heterogeneity of cells, tissue types, and/or microenvironments. Instead, they are triggered by light (i.e., near-infrared) stimuli, which are absorbed by photoresponsive molecules or nanotransducer. The sequential conversion of light to heat or reactive oxygen species can activate the property change of nanoparticles in a spatio-temporally controlled manner. This talk will present several recent studies of light triggered switchable systems to overcome the pathophysiology barriers and future directions in the application of light-switchable systems for remotely targeted drug delivery.
Service textiles are high-touch surfaces in the healthcare environment and they play an important role in the acquisition and transmission of pathogenic microorganisms, including multi-drug resistant organisms that can survive for weeks on fabrics. Contaminated service textiles have caused infections, which not only affects the safety and health of healthcare personnel and/or patient, but also is incompatible with good hygiene and cross-infection control practices and inconsistent with the expectations of modern healthcare. Here, we use a versatile dip-pad-cure approach to graft/coat polymethacrylamide (PMAA) onto the surfaces of representative service textiles including polyester, cotton, and polyester/cotton blend. Upon treatment with commercial bleach, the amide groups on PMAA were transformed into stable acyclic N-halamines, providing the resultant fabrics with potent, durable (against wash/wear), and rechargeable biocidal activities against *E. coli* (gram-negative bacteria), *S. aureus* (gram-positive bacteria), and *C. albicans* (fungi). The antimicrobial potency of the fabrics could be readily controlled by adjusting the treatment conditions, and the N-halamine contents could be easily determined via a simple chlorine strip test. Further, the comfort performances and the mechanical properties of the antimicrobial fabrics were not adversely affected by the grafting and chlorination treatments. These functions make the N-halamine based antimicrobial fabrics as attractive candidates of service textiles for various healthcare applications.

**S.SM08.05.28**

**Charge Transformable Polymer-Coated Boron Carbon Oxy-Nitride as Novel Theranostic Agent**

Chen-Wei Chiang, Yun Chen Chien, Chih Yi Wang, Wei-Hui Yu, Liang Cheng Chien, Chou Chio Lao, Chi-Shiun Chiang and Pei Yuin Keng; National Tsing Hua University, Taiwan

Herein, we will present the first charge transformable theranostic boron-based nanoparticles for Boron Neutron Capture Therapy (BNCT) and optical imaging. BNCT is an emerging targeted cancer therapy modality that can deliver an immense dose gradient within cellular spatial specificity between tumor and healthy cells. Individually, boron-10 isotope and epithermal neutron flux is not harmful to the body. When combined, boron-10 undergoes a nuclear fission reaction, producing two highly energetic particles in MeV. The alpha-4 and lithium-7 particles deposit all its energy within 5-9 µm in diameter, which corresponds to the size of a single cell. These particles, produced during BNCT treatment, have characteristic of high linear energy transfer (LET) radiation, which induced complex DNA double-strand breaks (DSB). BNCT has showed promising results in clinical trials of patient with recurrent head and neck cancers and enjoyed a good quality of life after receiving two sessions of BNCT treatment. To advance BNCT as one of the cancer treatment modalities, a new and more specific boron drug is needed with superior efficacy compared to currently available boron drug. Specifically, our group is developing the preparation of boron carbon oxynitride (BCNO) nanostructures as a novel theranostic agent, which relies on the inherent luminescence properties of BCNO and the high loading of \(^{10}\text{B}\) within a single nanoparticle for maximizing the efficacy of BNCT treatment. A successful BNCT treatment relies on the delivering a high payload of boron-10 isotopes with high specificity. According to a recent review article on nanoparticle drug delivery, less than 1% of the injected dose of nanoparticle drug reached to the tumor site in small animal studies. This is due to our biological complexity, which demands nanoparticles of different sizes and charges during drug delivery. For examples, for tumor accumulation via EPR effect, the optimal size of the nanoparticles should be between 30-150 nm and possessed a neutral surface charge. Upon accumulation within the tumor microenvironment, a nanoparticle with positive surface charge is known to be effective for cell internalization. Herein, we aim to tackle the latter problem related to the particle surface charge. Positively charge nanoparticles and macromolecules is known to be toxic to cells by forming holes on the cell membrane during internalization and thus resulted in diffusion of cytosolic proteins out of the cells. While this effect is desirable at the cancer cells, the toxic nature of the nanoparticles needs to be first protected with a stealthy polymer ligand until the nanoparticles is delivered to the cancer site. As the first proof of concept, we have successfully synthesized and functionalized BNCO nanostructures with a positively charge polymer followed by a stealthy layer of polyethylene glycol for enhanced tumor accumulation. At the tumor microenvironment, the chemically engineered polymer coating with an acid sensitive bond will break, thus releasing the toxic, and positive charge nanoparticles for effective cell penetration. Previously, our group has successfully showed the functionalization of 5 nm BCNO nanoparticles with polyethyleneimine (PEI) and confirmed the functionality via FTIR and zeta potential measurement. The bare BCNO nanoparticles in water possessed neutral charge while the BCNO@PEI possessed a positive charge in water. Herein, we will present the preparation of the block copolymers with an acid reactive linker, nanoparticle functionalization and finally shows the particle charge transformation. In vitro cell toxicity and cell membrane penetration of a series of polymer-coated BCNO nanostructures will also be presented at this meeting.

**S.SM08.05.32**
Healing Chitosan-Lactic Acid Films as Low-Cost Bovine Milk Whey Protein Carriers for Enhanced Skin Wound Regeneration

In chronic and burn wounds, novel low-cost therapeutic devices and agents are still sought after in order to actively stimulate skin regeneration at the structural, vascular, and immune levels. Recently, bovine milk extracts have been described to have regenerative capabilities comparable to phenytoin in skin-wound in vivo models [1], thus drawing interest in exploiting this potential. Chitosan films are useful in skin regeneration due to their highly adhesive and antimicrobial properties [2], though their use as protein delivery agents needs to be further explored. Additionally, when supplied cutaneously, lactic acid has been found to promote angiogenesis, collagen deposition, and growth factor production, resulting in accelerated skin regeneration for in vivo models [3]. Here we report the isolation and loading of bovine milk whey proteins onto chitosan-lactic acid films, as well as the evaluation of their chemical, thermal, and mechanical properties and release profiles. The incorporation of chitosan (CS), lactic acid (LA), and milk whey proteins (MWP) is expected to yield low-cost, scalable cutaneous delivery biomaterials with antimicrobial, angiogenic, and immunomodulating capabilities as a result of their respective individual properties.

Milk whey was isolated from commercial pasteurized bovine milk by pH adjustments, centrifugation, and salting out. The protein precipitates were quantified with a Bradford colorimetric assay and analyzed via SDS-PAGE. This analysis revealed that the isolated proteins did not degrade as a result of the process, thus validating the whey isolation protocol as reliable. Gel permeation and cationic exchange chromatographies were performed to confirm the identities of the protein components in the isolated milk whey. The deacetylation degree of the chitosan samples was determined by nuclear magnetic resonance. Dialyzed, freeze-dried milk whey protein isolate was loaded onto chitosan films prepared from chitosan-lactic acid solutions. The resulting CS-LA-MWP films were analyzed using texturometry, FTIR, TGA, and DSC to evaluate film adhesion strength on human skin, elastic modulus, and elongation to break; the incorporation of all components; and the degradation and glass transition temperatures. Protein release kinetics were determined by UV-vis spectroscopy. Antibacterial activity in vitro and water vapor permeability were also determined for CS-LA-MWP films. Overall, the protein isolation and film preparation processes reported in this work yielded CS-LA-MWP films that were found to be highly elastic and adhesive, while inhibiting bacterial proliferation and releasing their protein load with an appropriate release profile for skin delivery applications. The regenerative potential of these films will be evaluated shortly in murine skin-wound models.

References:
Acknowledgments:
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**S.SM08.05.36**

*In Vitro Antitumoral Activity of the Black-Tailed Rattlesnake (Crotalus molossus molossus) Venom Encapsulated in Chitosan-Alginate Nanoparticles*

Jorge Jimenez-Canale, Jose A. Sarabia-Sainz, Daniel Fernández-Quiroz, Alexel J. Burgara-Estrella, Hector M. Sarabia-Sainz and Erika Silva-Campa; Univ de Sonora, Mexico

Nanomedicine has led to the development of new materials able to improve the pharmaceutical effect of bioactive components, broadening the options of treatment for several diseases like cancer. Chitosan (Cs) and Alginate (ALG) have been firmly established in recent years as biocompatible, biodegradable, mucoadhesive and low-toxic polymers able to form complexes with bioactive agents, making them promising drug delivery vehicles. Some snake venom toxins such as A2 phospholipases (PLA2s), serine proteinases (SVSPs) and metalloproteinases (SVMPs) have been reported to present antitumoral activity in different tumor cell-lines, making them a promising option to be used as cancer pharmaceuticals. We identified the major proteins of a black-tailed rattlesnake (*Crotalus molossus molossus*) venom through MALDI-QTOF analysis. Additionally, the venom against red blood cells and T-47D breast carcinoma cells was evaluated. Afterwards, the snake's venom was loaded into Cs-ALG nanoparticles through the ionotropic gelation process with tripolyphosphate (TPP), obtaining particles of 504.7 ± 22 nm and a Zeta potential of +41 ± 1.6 mV. The Cs-Venom-ALG complex was able to deliver the venom into the breast carcinoma cells through endocytosis, inhibiting their viability and inducing morphological changes in the T-47D cells. Thus, we suggest the potential use of *C. m. molossus* venom toxins entrapped within polymer nanoparticles for the future development and research of cancer pharmaceuticals.

**S.SM08.05.39**

*Nature-Inspired Nanocomposites Endow Epigenetic Mediated Neurotherapeutic Potential of Neuroprotective Agents in PD Prevention*

Mohammed N. Sardoiwala, Subhasree R. Choudhury and Surajit Karmakar; Institute of Nanoscience and Technology, India

Posttranslational modification and agglomeration of α-Synuclein (α-Syn), mitochondrial dysfunction, oxidative stress and loss of dopaminergic neurons are hallmark of Parkinson’s disease (PD). The α-synucleinopathy is attributed to phosphorylation and aggregation of α-Syn. A strategy to degrade or reduce phosphorylated protein paves the way to develop PD therapy. Hence, nanoformulations of emerging neuroprotective agents, metformin and FTY720 have been evaluated in *in vitro* and *ex vivo* experimental PD models. Nature inspired bio-compatible polydopamine nanocarrier for metformin delivery and chitosan nanocarrier for FTY720 has been employed to enhance delivery, brain targeting and bio-availability of drugs. Nanomaterials have shown effective neuroprotection with controlled drug release to improve absorption and bio-availability of drugs. The neuroprotective potential was arbitrated by downregulation of phospho-serine 129 (pSer129) α-Syn, with reduction in oxidative stress, prevention of apoptosis and anti-inflammatory activities. The neuroprotective mechanism uncovered novel physical interaction of protein phosphatase PP2A-polycoromb protein EzH2 and EzH2-pSer129 α-Syn to mediate ubiquitination and degradation of agglomerated pSer129 α-Syn. In summary, this study divulges the enhanced neuroprotective role of Met loaded PDANPs and FTY720 nanocomposites by reversing the neurochemical deficits by confirming an epigenetic mediated nanotherapeutic approach for the PD prevention.

SESSION S.SM08.01: Bioinspired Materials for Drug Delivery

On Demand Abstracts Available for Viewing On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020

S-SM08

5:00 AM *S.SM08.01.02*

*High Density Lipoprotein Biomimetic Nanoparticles for Drug and Vaccine Delivery*

Anna Schwendeman; University of Michigan, United States

High density lipoprotein (HDL) is a nanoparticle (~8-10 nm) composed of a lipid membrane bilayer wrapped around by a
“belt” of amphipathic helices of Apolipoprotein A-I (ApoA-I). HDL travels in directly interacts with macrophages in arterial plaques to efflux excess cholesterol and subsequently deliver it to the liver by a process of reverse cholesterol transport (RCT). Our research focus is on design of synthetic high density lipoprotein (HDL) nanoparticles for treatment of cardiovascular disease. We discover novel ApoA-I mimetic peptides, explore biophysics of peptide-lipid interactions and optimize HDL compositions for interaction with specific cellular receptors, transporters and enzymes involved in RCT. We examine sHDL biodistribution, pharmacokinetics and pharmacodynamic properties. We take advantage of small size and clinical safety of sHDL to use it platform for drugs and vaccines delivery. This talk will cover the use of sHDL nanoparticles to deliver liver X receptor agonist to atheroma to reduce inflammation and atherosclerosis. This strategy utilizes pharmacological ability of sHDL to serve as an acceptor of cholesterol effluxed from atheroma. The use of sHDL nanoparticles for personalized vaccine and chemo-immuno therapy delivery results in development lasting protective immunity against tumor reoccurrence in animal models of colon cancer, glioblastoma and melanoma.

SESSION S.SM08.02: Novel Biomaterials for Drug Delivery

5:00 AM *S.SM08.02.01
Reactive Oxygen Species Delivery by Nanoformulation Xiaoyuan (Shawn) Chen; National Institutes of Health, United States

The reactive oxygen species (ROS)-mediated mechanism is the major cause underlying the efficacy of photodynamic therapy (PDT). The PDT procedure is based on the cascade of synergistic effects between light, a photosensitizer (PS) and oxygen, which greatly favors the spatiotemporal control of the treatment. This procedure has also evoked several unresolved challenges at different levels including (i) the limited penetration depth of light, which restricts traditional PDT to superficial tumors; (ii) oxygen reliance does not allow PDT treatment of hypoxic tumors; (iii) light can complicate the phototherapeutic outcomes because of the concurrent heat generation; (iv) specific delivery of PSs to sub-cellular organelles for exerting effective toxicity remains an issue; and (v) side effects from undesirable white-light activation and self-catalyzation of traditional PSs. In this talk, the current status and the possible opportunities of nanomedicine for ROS generation for cancer therapy will be discussed in detail.

5:15 AM S.SM08.02.11
Efficient Delivery of Nerve Growth Factors to the Central Nervous System for Neural Regeneration Duo Xu and Yunfeng Lu; University of California, Los Angeles, United States

The central nervous system (CNS) plays a central role in the control of sensory and motor functions, and the disruption of its barriers can result in severe and debilitating neurological disorders. Neurotrophins are promising therapeutic agents for neural regeneration in the damaged CNS. However, their penetration across the blood-brain barrier remains a formidable challenge, representing a bottleneck for brain and spinal cord therapy. We have developed a nanocapsule-based delivery system that enables intravenously injected nerve growth factor (NGF) to enter the CNS in healthy mice and nonhuman primate. In pathological conditions, the delivery of NGF enables neural regeneration, tissue remodeling, and functional recovery in mice with spinal cord injury. This technology can be utilized to deliver other neurotrophins and growth factors to the CNS, opening a new avenue for tissue engineering and the treatment of CNS disorders and neurodegenerative diseases.

5:25 AM S.SM08.02.12
Fabrication of Non-Spherical and Multiphasic Particles with Independent Control of Particle Size, Shape and Chemistry Catherine Snyder, Sai P. Kobaku, Geeta Mehta and Anish Tuteja; University of Michigan, United States

Introduction: Cancer is the second leading cause of death in the world and current treatment methods have low 5-year survival rates. One potential solution to improving treatment methods is targeted nanoparticle drug delivery. Nanoparticles can be engineered to increase the efficacy of chemotherapeutic drugs through increased targeting and dose delivery. Despite proven benefits of nanoparticle drug delivery, it comes with its own challenges, the largest of which is overcoming the physiological barriers between the nanoparticle injection site and the tumor in the body. In order to better understand the pharmacokinetics of nanoparticles in vivo, nanoparticle characteristics need to be varied in a systematic study to identify ideal
formulations. This systematic study would need to test nanoparticles of different sizes, shapes, and chemistries with multiple phases, and these properties would need to be independently varied. Current fabrication methods are unable to make monodisperse, multiphasic or non-spherical particles and spherical particles, and to independently alter each parameter.

**Objective:** To address the need of a nanoparticle fabrication method which can modulate particle properties in a systematic and independent manner, we have developed a novel polymeric particle synthesis technique, called Wettability Engendered Templated Self-assembly (WETS) and have demonstrated the ability to control size, shape and composition independently.

**Methods and Results:** The WETS methodology uses surfaces with patterned wettability to self-assemble discrete, monodisperse polymer particles in an array after dip-coating in a polymer solution. These particles can have dimensions ranging from 25 nm to 150 µm, and can have a variety of non-spherical, planar geometries such as disks, squares, triangles and hexagons. Size and shape are independently controlled through the patterned wettability surface and the dip-coating parameters. Additional dip-coating layers of other polymers on top of previously deposited polymer layers allows for the fabrication of multiphase particles with each phase able to independently encapsulate a different therapeutic or diagnostic agent. As each phase is added to the particle individually, the size and composition of the phases can be independently altered. Single and multiphasic spherical particles are formed from the reconfiguration of non-spherical particles in a predictable manner. Multiphasic spherical particles can be tuned to create Janus or core-shell morphologies based on reconfiguration parameters. These results show the ability to synthesize varied particles with a single method which is required to make direct comparisons between particle characteristics in order to develop improvements in cancer therapies.

**Conclusion:** With the novel WETS fabrication method, we have demonstrated the ability to have systematic and independent control over the size, shape and composition of polymeric particles in a predictable manner. This method will allow for a systematic study of nanoparticle pharmacokinetics in vivo in order to identify ideal nanoparticle formulations for cancer therapies. Continued work is focused on the scale up of WETS in order to undertake in vitro and in vivo studies in the future.

5:45 AM S.SM08.02.18

**All-Atom Simulation Method for Dipolar Assembly and Alignment of Single Domain Magnetic Nanoparticles** Akhlak-Ul Mahmood and Yaroslava G. Yingling; North Carolina State University, United States

Magnetic nanoparticles under the influence of the external magnetic field have been widely studied for the past few decades due to their potential applications in bio and nanotechnology. However, the interplay of dipolar and Zeeman interactions during the assembly process is a major question that remained to be answered. Current modeling and simulation techniques are primarily limited to coarse-grained methods, which lack proper resolution for understanding these processes at the atomic level. In this work, we developed a novel method to study the dipolar and Zeeman interactions within stable single domain (SSD) magnetic nanoparticles using atomistic molecular dynamics simulation. The primary advantage of this technique is the atomistic resolution that permits the study of magnetic nanoparticles' alignment and their explicit interactions with the surrounding environment. Our methodology permits the investigation of the formation of chain and ring shapes of 3.2 nm and 8.2 nm cubic and spherical Magnetite (Fe3O4) nanoparticles functionalized with Oleic Acid under the influence of an external magnetic field and detailed investigation of the role of solvent properties on shape formation. This developed method can be used as a plugin with the LAMMPS molecular dynamics software to study the behavior of small magnetic nanoparticles to gain insights into the physics and chemistry of different magnetic assembly processes.

5:45 AM S.SM08.02.18

**Gold-Implanted Plasmonic Quartz Plate as a Launch Pad for Laser-Driven Photoacoustic Microfluidic Pumps** Feng Lin¹, Talari Talari Vishal², Junyi Zhao³, John Schaibley⁴, Dong Liu⁵, Zhiming M. Wang¹ and Jiming Bao²; ¹University of Electronic Science and Technology of China, China; ²University of Houston, United States; ³Washington University in St. Louis, United States; ⁴University of Arizona, United States

Enabled initially by the development of microelectromechanical systems, current microfluidic pumps still require advanced microfabrication techniques to create a variety of fluid-driving mechanisms. Here we report a generation of micropumps that involve no moving parts and microstructures. This micropump is based on a principle of photoacoustic laser streaming and is simply made of an Au-implanted plasmonic quartz plate. Under a pulsed laser excitation, any point on the plate can generate a directional long-lasting ultrasound wave which drives the fluid via acoustic streaming. Manipulating and programming laser beams can easily create a single pump, a moving pump, and multiple pumps. The underlying pumping mechanism of photoacoustic streaming is verified by high-speed imaging of the fluid motion after a single laser pulse. As many light-absorbing materials have been identified for efficient photoacoustic generation, photoacoustic micropumps can have diversity in their implementation. These laser-driven fabrication-free micropumps open up a generation of pumping technology and
opportunities for easy integration and versatile microfluidic applications

5:55 AM S.SMO8.02.19
Supramolecular Hydrogels for Drug Delivery and Thermal Stabilization of Biologics  Mark W. Tibbitt; ETH Zürich, Switzerland

In this talk, we will present our recent work on the synthesis and engineering of supramolecular hydrogels for controlled drug delivery and thermal stabilization of encapsulated biologics. Polymer–nanoparticle (PNP) hydrogels have been produced from drug-loaded nanoparticles (NPs) and cross-linking polymers. These transient physical assemblies are formed through supramolecular interactions between the NPs and the polymers and exhibit shear-thinning and self-healing behavior suitable for injection or extrusion. In our lab, we are applying PNP hydrogels for local injection of therapeutics and as immune-modulatory biomaterials. In addition, we have developed the platform as a universal rheological carrier for biomaterials additive manufacturing. Uniquely, the nano-carrier can accommodate a range of secondary polymers for post-print stabilization and functionality. We are exploiting these printable PNP gels to assemble additively manufactured drug delivery systems for dual release of both hydrophobic and hydrophobic molecules. We also employ dynamic covalent chemistry to design moldable polymeric hydrogels. Here, we have fabricated ideal reversible networks and investigated how the molecular characteristics of the dynamic covalent cross-links impact the emergent material properties. We have leveraged this understanding to design biomaterials that can encapsulate, thermally stabilize, and release temperature-sensitive biologics. We are exploiting these materials to mitigate the global reliance on the cold chain in the distribution of value-added biologics and biotherapeutics, including vaccines. In total, this talk will illustrate how molecular design of hydrogels can enable emerging applications in drug delivery from injectable biomaterials, additively manufacturing controlled release systems, and materials for the thermal stabilization of biologics.

6:10 AM S.SMO8.02.20
Polyglycerol-Grafted Nanoparticles Improve Stealth Effect by Resisting Protein Corona Formation—A Comparison Study to PEG  Yajuan Zou and Naoki Komatsu; Kyoto University, Japan

In biological fluids, proteins are adsorbed onto the surface of nanoparticles (NPs) to form a coating known as protein corona. Most of the corona proteins act as opsonin which activates the macrophage from immune system to uptake NPs, leading to the rapid removal of NPs [1]. This restricts the development of nanomedicine. Although conjugation with linear polyethylene glycol (PEG) is the standard approach to reduce protein attachment and to avoid non-specific uptake, it cannot fully prevent the opsonization. On the other hand, we have demonstrated polyglycerol (PG) as a promising alternative to PEG, because PG enhanced the aqueous dispersibility and gave stealth effect to NPs [2]. In order to understand the role of PG, we compare protein affinity and stealth effect of PG and PEG grafted nanodiamond (ND-PG and ND-PEG, respectively) with different density in this paper. Protein analyses by sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE) indicated that PG was much more resistant than PEG to adsorption of the opsonin proteins such as IgG and complement protein. In particular, there was almost no protein on the dense PG layer. In vitro stealth effect was revealed by TEM; almost no ND-PG was observed in the TEM images of U937 macrophage, while there was ND-PEG in the macrophage. This indicates that PG has much better stealth effect than PEG. In vivo stealth effects including blood circulation and biodistribution will be reported in due course.


SESSION S.SMO8.03: Micro/Nano Devices for Drug Delivery
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-SM08

5:00 AM S.SMO8.03.02
Theranostic Microcapsules for Image-Guided and Ultrasound-Enabled Drug Delivery  Eugenia Kharlampieva; University of Alabama, United States

The ability to track drug carriers in their administered environment in real time and to release the drug in a controlled, minimally invasive manner are hallmarks of an advanced drug delivery system. This presentation focuses on ultrasound-sensitive multilayer capsules as efficient contrast-enhanced imaging agents utilizing ultrasound, magnetic resonance imaging...
Owing to the active contrast, long circulation, customizable size, shape, composition, and precise delivery of high payload that can influence immune responses for prolong circulation in the blood. The ability of this material to conjugate concentrations, these materials present a powerful and safe platform for imaging-guided precision drug delivery.

Metallic nanomaterials in polymers have been used in a variety of biomedical applications including drug delivery, enhanced antibacterial activity, and tumor ablation. The plasmonic response of metallic nanomaterials involves electrons that oscillate at resonance with incident light. The plasmon resonance frequency at the particles’ surface is dependent on factors such as nanoparticle (NP) size, shape, composition, state of aggregation, and environment. In the case of polymers impregnated with metallic nanomaterials, non-propagating surface plasmon modes within the electromagnetic spectrum enable the conversion of optical energy to thermal energy with a coincident temperature change within the polymer. In previous work, investigators have used polymer capsules containing metallic nanomaterials in the shell to melt the shell and release encapsulated drugs in the presence of light. Such capsules are functionalized to target cancer tissues and, once at the correct locale, are activated by light to treat tumors or other cancerous matter. For this work, we will focus on topical, electrospun fiber drug delivery systems that can be stored and activated in the presence of light to release treatments such as antibiotics or coagulants when needed.

In our previous work, colloidal gold NPs (GNPs, max. absorption $\lambda = 522$ nm) were incorporated into polymer films and electrospun into fibers to utilize the NP plasmonic response for localized heating of the polymer. Mathematical modeling was used to describe the GNP distribution and heat/melt profile surrounding each GNP under illumination in the polymer, demonstrating that a bulk temperature change of only 0.2 °C results in a 20-nm-diameter melted polymer sphere around the GNP. Such results provided us with a mathematical guide to predict the GNP size that would result in a desired melt thickness. In our previous work, it was shown that by reducing the radius of polymer material around the GNP though the use of nanoscale-diameter electrospun fibers in place of an infinite thin film (centimeter scale) heating of the bulk material increased by 72 %. This result is attributed to the reduction of polymer material surrounding each GNP. Bulk heating of polymer blend films containing GNPs were mapped using a forward-looking infrared (FLIR) camera system with light-emitting diodes (LEDs). Change in temperature observed in the thin films was related to photothermal energy conversion efficiency of the thin films through heat transfer calculations. Significantly, the GNP-doped film photothermal conversion efficiency increased by 1.8 times (75.7 % increase) under 530-nm LED illumination. Based on the mathematical model developed, the enhanced heating observed, and the enhanced efficiencies of the materials explored thus far, future objectives include developing these materials further for light activated drug delivery systems. Future work will include developing the mathematical model for silver nanoplates (SNPs), which demonstrated a stronger...
absorption response and are more economical than gold. SNPs used will be doped into polymer thin films and electrospun into fibers, and bulk heating will be monitored on the FLIR system. Heating in the thin films versus nanoscale-diameter fibers will be compared, and efficiencies of the materials will be calculated. In addition, ideal photothermal heating will be studied through altered nanomaterial concentrations in the polymers. The relationship between photothermal heating and SNP concentration will elucidate any plasmonic coupling and guide material optimization schemes.

5:35 AM S.SM08.03.07
Polymer Nanosheets: Multi-Scale Drug Controlled Release Systems and Production Rigoberto C. Advincula; Case Western Reserve University, United States

Layered polymer systems than can be fabricated using roll-to-roll methods have been demonstrated using film extrusion methods. Together with lithography, they enable the fabrication of capsules and colloidal particles that have controlled kinetics for release of agents both pre-loaded and post-loaded. In this talk, we demonstrate the scalability of drug release using a hierarchical configuration of layers that can be fabricate layer-by-layer as applied to patches, capsules, and nanosheets. The methods make use of solution methods as well as polymer multilayer extrusion methods more popularly known as the CLIPS process. The solution methods take advantage of the physisorption of polyelectrolytes to form suspendable ultrathin nanosheets. It is possible to achieve a production scale of roll-to-roll films using the CLIPS process. The controlled release of model drugs is demonstrated under buffer conditions including the demonstration on the preparation of patches and nanosheets.

5:45 AM *S.SM08.03.08
Minimally Invasive In Vivo Brain Modulation with Neuron-Type Specificity Guosong Hong; Stanford University, United States

Understanding the complex neural circuity and its correlation to specific behaviors requires spatially and temporally precise modulation of neuron subtypes in certain brain regions. One major challenge of existing neural modulation techniques is the tradeoff between invasiveness and depth: invasive implants of electrodes and optical fibers are usually required for electrical and optogenetic modulation of neural activity in deep brain, while non-invasive brain stimulation methods lack penetration depth and neuron-type specificity of brain modulation. The invasive brain implant and head tethering result in acute tissue damage and chronic gliosis at the neural interface, leading to degradation of recording and stimulation capabilities over time. In this talk, I will present the latest advances of minimally invasive approaches for in vivo neuron-type specific brain modulation from my lab at Stanford University. First, I will describe a new approach termed ‘sono-optogenetics’, which uses a circulation delivered rechargeable light source for non-invasive optogenetics in deep brain regions through the intact scalp and skull. In this approach, we address the challenge of limited tissue penetration of visible photons via the intravenous delivery of mechanoluminescent nanoparticles, which can act as local light sources in the brain when triggered by brain-penetrant focused ultrasound (FUS). After delivery, these particles can be recharged by 400-nm photoexcitation light in superficial blood vessels during circulation, and turned on by FUS to emit 470-nm light repetitively in the intact brain for optogenetic stimulation. Second, I will describe a type of new deep-brain stimulating devices termed ‘injectable photovoltaics’ for a wireless, gliosis-free neural stimulation interface. Micron-sized, ultraflexible and wirelessly powered microdevices can be delivered into the brain via syringe injection so as to disturb the brain as little as possible when deployed. These injectable devices are fabricated with photovoltaic polymers, turning brain-penetrating near-infrared light into electrical impulses for deep-brain neural stimulation. These two brain-modulation approaches have the potential of generating transformative results for both neuroscience research and neurological applications, not only expanding the toolbox of neuromodulation techniques, but also offering strategies for clinical translation of therapeutic neural implants.

SESSION S.SM08.04: Drug Delivery for Immunotherapy and Gene Editing
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-SM08

5:00 AM *S.SM08.04.01
New Delivery Vehicles for Gene Editing Enzymes Niren Murthy1,2; 1University of California, Berkeley, United States; 2Innovative Genomics Institute, United States
Cas9 based therapeutics have the potential to revolutionize the treatment of genetic diseases. However, safe and effective methods for delivering the Cas9-guide RNA complex (Cas9 RNP) need to be developed before the clinical potential of Cas9 based therapeutics can be fully realized. In this presentation, I will describe non-viral delivery strategies developed in our laboratory for delivering the Cas9 RNP. The first delivery strategy is termed CRISPR-Gold. CRISPR-Gold is composed of gold nanoparticles assembled with the Cas9/gRNA ribonucleoprotein (RNP) complex, donor DNA, and an endosomal disruptive polymer. CRISPR-Gold was able to correct the DNA mutation that causes Duchenne muscular dystrophy (DMD) in mdx mice via homology directed DNA repair (HDR), with an efficiency of 5.4% after an intramuscular injection. In addition, CRISPR-Gold was able to edit the brains of adult mice and rescued mice from the repetitive behaviors caused by autism. In this presentation, I will also describe other strategies for delivering the Cas9 RNP based on encapsulation in block copolymers and conjugation with peptides. Collectively, our experience suggests that non-viral strategies for delivering the Cas9 RNP have great potential for treating DMD and other genetic diseases.

5:15 AM *S.SM08.04.04
Harnessing Biomaterials to Study and Control Immune Function Christopher M. Jewell; University of Maryland, College Park, United States

Our research combines immunology and biomaterials to understand the interactions between synthetic materials and immune tissues, and to design more selective therapeutic vaccines for cancer and autoimmunity. This presentation will highlight our recent efforts toward these goals combining materials science and bioengineering tools, cell culture, animal models, and samples from human patients. In one example I will discuss new degradable polymer depots that could improve the selectivity of therapies for autoimmune diseases such as multiple sclerosis and diabetes by locally reprogramming the function of lymph nodes – tissues that coordinate immune function. A second area will present the lab's efforts to self-assemble immune signals into modular nanostructures. This rational design approach allows activation of programmable combinations and levels of immune pathways triggered. Modular control over these aspects of immune signaling could help improve the efficacy of vaccines for cancer and infectious disease, and enhance the efficiency of vaccine translation.

SYMPOSIUM S.SM09

Advances in 3D Printing for Medical Applications
November 21 - November 30, 2020

Symposium Organizers
Susmita Bose, Washington State University
Richard Hague, University of Nottingham
Jayme Keist, The Pennsylvania State University
Roger Narayan, North Carolina State University

* Invited Paper

SESSION S.SM09.03: Live Lightning/Flash I: Advances in 3D Printing for Medical Applications
Session Chair: Roger Narayan
Saturday Afternoon, November 28, 2020
S.SM09

5:00 PM INTRODUCTION AND WELCOME

5:01 PM *S.SM09.01.01
Tip-Based Nanoscale 3D Printing Wonho Jhe and Sangmin An; Seoul National University, Korea (the Republic of)
Viscoelastic complex fluids exhibit rheological nonlinearity at a high shear rate. Although typical nonlinear effects, shear thinning and shear thickening, have been usually understood by variation of intrinsic quantities such as viscosity, one still requires a better understanding of the microscopic origins, currently under debate, especially on the shear-thickening mechanism. We present accurate measurements of shear stress in the bound hydration water layer using noncontact dynamic force microscopy. We find shear thickening occurs above $10^6$ 1/s shear rate beyond 0.3-nm layer thickness, which is attributed to the nonviscous, elasticity associated fluidic instability via fluctuation correlation. Such a nonlinear fluidic transition is observed due to the long relaxation time (1 us) of water available in the nanoconfined hydration layer, which indicates the onset of elastic turbulence at nanoscale, elucidating the interplay between relaxation and shear motion, which also indicates the onset of elastic turbulence at nanoscale above a universal shear velocity of 1 mm/s. This extensive layer-by-layer control paves the way for fundamental studies of nonlinear nanorheology and nanoscale hydrodynamics, as well as provides novel insights on viscoelastic dynamics of interfacial water. We will also discuss the tip-based microfluidic characterization and manipulation of liquids.

Material Horizons for Volumetric Additive Manufacturing

As additive manufacturing (AM, also known as 3D printing) technologies have proliferated, approaches based on solidification of photosensitive liquid resins have showed great promise due to their superior resolution and precision. However, these techniques have been largely limited to prototyping applications due to the constraints on available materials and their mechanical properties, as well as slow builds and poor surface quality resulting from layer-wise fabrication. With the advent of volumetric AM (VAM), complete 3D structures with complex geometries can now be produced in a single step, leaping over the traditional limitations of layer-by-layer approaches to 3D printing. Volumetric 3D printing generates a 3D distribution of absorbed optical energy within a volume of photosensitive material, concurrently curing all points within a target geometry, on a timescale of 10s to 100s of seconds. No substrate is required as the part forms unsupported in the resin container. The most versatile implementation of VAM is known as computed axial lithography (CAL) which adapts the principles of computed tomography (CT) to generate a sequence of intensity-modulated projections, which are then beamed sequentially into a rotating resin container via a DLP projector to create the required energy dose. Because there is no fluid motion, and no hydrodynamic forces during a build, this approach is particularly compelling for very soft materials such as the hydrogels widely used in tissue engineering and regenerative medicine applications. The absence of support structure also enables complex geometries such as vasculature to be built. Successful volumetric 3D printing requires spatio-temporal control over the polymerization reaction at all points within the fabrication volume. This demands a more detailed understanding of a host of process parameters, compared with traditional layered approaches. Perhaps the most important such parameters are the absorbed volumetric energy dose $E_{\text{vol}}$, as well as the rate at which this dose is delivered. The progress of the photochemical reaction may then be characterized in terms of a variety of metrics, such as double-bond conversion, or the evolution of mechanical and optical properties of the material. We investigate the inter-relationship of these properties, obtained from ex-situ measurements such as real-time FTIR spectroscopy, photo-rheology, and mechanical testing, developing a quantitative framework for predicting volumetric structure formation. An additional resin characteristic critical for CAL printing is nonlinear threshold behavior. This allows resin that receives a sub-threshold dose to remain liquid, and derives from the interaction of the generated radicals and inhibitory species present in the resin. For some chemistries the inhibitory effect is provided by dissolved molecular oxygen, but for other formulations, deliberately including another inhibitor is necessary. We discuss the implications of these interacting factors for photo-resin design within the volumetric AM paradigm, as well as more broadly in photopolymer-based AM methods. We also discuss several material classes for VAM, including high-performance engineering materials, as well as cell-culture compatible hydrogels.

References

Vivo
Dynamically Adjustable Real-Time Tuning of Catheter-Injectable Delivery of Functional Hydrogels towards

intensity (0~150 µW output from a 105µm core multimode fibre), we can extrude hydrogels with stiffnesses dynamically tuning the stiffness at the catheter tip. We show that by modulating the absolute and relative flow rates as well as the UV catheter with extended length and small diameter, intensity modulation of UV to cross-link the precursor aids greatly in being deployed using this technique. To demonstrate the initial utility of this system, we successfully performed embolization of a saccular aneurysm model (diameter ~ 12 mm) and a capillary vasculature model (diameter <1 mm) using a pulsatile manner to avoid iatrogenic damages has yet to be fully explored. In the present work, we demonstrate a method of in-situ extrusion of hydrogels with compositions and chemomechanical properties that can be dynamically adjusted “on-the-fly” using a custom catheter that is utilized intravascularly. A custom UV-integrated, multi-lumen microcatheter (inner/outer lumen diameters: 0.6/1.28 mm) was assembled and a suite of low viscosity, shear thinning gelatin-based precursors were formulated for delivery. While the shear thinning property makes this precursor a suitable choice for injection through a catheter with extended length and small diameter, intensity modulation of UV to cross-link the precursor aids greatly in tuning the stiffness at the catheter tip. We show that by modulating the absolute and relative flow rates as well as the UV intensity (0~150 µW output from a 105µm core multimode fibre), we can extrude hydrogels with stiffnesses dynamically varying from <10 to 80 kPa. In addition, through the dual luminal architecture, it is also possible to sequentially switch or coaxially coextrude two types of precursor compositions. The concentrations and diffusivities of additives (as preliminarily demonstrated using food dyes) within the extruded scaffold can also be dynamically altered by 10^3 and 10^2 orders respectively, in a single piece of extruded hydrogel fibre, therefore allowing applications a highly customizable drug depot to be deployed using this technique. To demonstrate the initial utility of this system, we successfully performed embolization of a saccular aneurysm model (diameter ~ 12 mm) and a capillary vasculature model (diameter <1 mm) using a pulsatile...
vascular flow phantom. The former required the extruded hydrogels to be relatively stiffer via increased photo-cross linking to fill the aneurysm while avoiding leakage into the parent vessel. In capillary embolization, the precursor was injected with lower crosslinking leading to increased viscosity to penetrate further into the vessels to fully embolize the structure. These findings yield direct application ideas in therapeutics such as vascular embolization in a variety of disease states, including cerebral aneurysms, arterio-venous malformations, vascularized tumors, and hemorrhagic vessels. The system can also be utilized for intravascular drug delivery and targeted cell therapies, which may require the physician to constantly adapt to the state of the patient. Further, such a dynamically tunable hydrogel delivery method may be able to serve as a supporting host matrix for functional sensing devices such as microelectrode arrays and quantum dot based chemical sensors.

6:01 PM S.SM09.01.10
Fiber Devices for Tissue Engineering Louis A. van der Elst, Merve Gokce Kurtoglu and Alexander Gumennik; Intelligent Systems Engineering, Indiana University, United States

Bioink extrusion-printing, while capable of creating macroscopically accurate anatomic models, fails to replicate the microstructure of the natural tissue due to resolution limitation of this bottom-up fabrication approach. We re-engineer the extrusion process to co-extrude a fiber device in line with the hydrogel bioink. This allows deviation from a pure bottom-up towards a combined approach, where a bottom-up extrusion process creates the macrostructure, while the fiber device in a top-down fashion subsequently promotes the growth of natural microstructure from within the volume of the print.

Fibers can embed a range of bio-functional and biosensing devices and systems. We aim to incorporate microfluidic, ultrasonic, and shape-memory-alloy (SMA) structures mimicking the functionalities of microvasculature, innervation, and musculature, respectively, into a single fiber-device. Those functional structures are created by a thermal draw of fibers from multimaterial preforms – a process familiar from an optical communication fiber fabrication. In this process, the macroscopic preform – a thick and short rod, cross-sectionally structured to meet the desired fiber functionality – is heated to become a viscous liquid and scaled by a thermal draw into a thin and long fiber, preserving the cross-sectional geometry of the preform. Then the fiber cores are patterned axially by a spatially coherent material selective capillary instability to form arrays of ultrasonic transducers contacted in parallel and microchannels with periodic outlets spanning the entire fiber length\(^1\).

In the extrusion process, the fiber is coated with hydrogel, contains tissue cells, extracellular matrix material, nutrients and growth-factors, forming a scaffolded print-line that is raster-layered into a printed model cross section additively constructing the final model in a layer-by-layer manner. Subsequently, the fiber-embedded microchannel structure is used as artificial vasculature supplying building material and nutrients into surrounding bioink to ignite the creation of natural vasculature and promote the proliferation of the bioink-contained tissue cells with their subsequent maturation into a natural-tissue-like structure. The ultrasonic transducers embedded in the fiber are used to sense the changes in the surrounding material density, monitoring cell-proliferation process, thus serving as artificial tactile nerves. SMA cores, contracting upon transduction of electric current, mimic the function of muscle yarns.

The proposed bioprinting approach will likely deliver a biosynthetic tissue with natural-like microstructure opening new routes in regenerative medicine, such as wound infilling and organ replacement. Moreover, it would allow creating lab-bench anatomical models of realistic tissue, in which bio-material delivery and biosensing is performed volumetrically with a microscale resolution, thus forming a novel stand-alone platform for investigation of micrometabolic processes. Such a platform would be a valuable asset to drug toxicity investigation, and real-time survivability monitoring of such artificial tissues and organs both in-vitro and in animal subjects.


6:21 PM S.SM09.01.12
Genomic-DNA Coated 3D Printed Materials for Drug Capture Daryl Yee, Robert H. Grubbs and Julia R. Greer; California Institute of Technology, United States

Since the discovery of chemotherapy in the beginning of the 20\textsuperscript{th} century, researchers around the world have been actively developing new and more effective chemotherapeutic agents to better treat cancer. Traditionally, chemotherapeutic agents work by interfering with cell division. However, by virtue of their mechanism of action, healthy normal cells can also be
targeted and destroyed. As a result, while chemotherapy is an effective way of managing cancer, the resulting side effects limits its use. One approach currently taken to reduce these side effects is to deliver the chemotherapy drugs directly to the tumor via transarterial chemoembolization, or other similar procedures. While this has been effective in reducing systemic toxicity, more can be done to improve this. Ideally, a device that could sequester any unreacted chemotherapy agents could be installed "downstream" of the tumor prior to them entering systemic circulation. Such drug-capture materials have yet to be realized due to the difficulty in achieving materials that have the right surface chemistry and geometry for blood flow.

Working together with medical doctors, computational fluid dynamics experts, chemists, and materials scientists, we report the fabrication of DNA functionalized 3D printed porous materials that can be used to capture doxorubicin and cisplatin, two commonly used DNA-targeting chemotherapy agents. We discuss the concept behind the device, the use of 3D printed materials as an ideal substrate, and the chemistries considered in drug binding. To achieve scalability of these devices, we developed a method of attaching cheaply available genomic DNA to these materials, a departure from commonly used synthetic DNA. We characterize the surface of the structure and verify the binding of DNA to the surface via XPS, EDS and the use of chemical assays. The efficacy of these functionalized materials were demonstrated in PBS, where we observed a >70% reduction in doxorubicin concentration over a period of 20 minutes, highlighting the viability of this as a method of drug capture.

SESSION S.SM09.04: Live Lightning/Flash II: Advances in 3D Printing for Medical Applications
Session Chair: Roger Narayan
Sunday Morning, November 29, 2020
S.SM09

10:15 AM INTRODUCTION AND WELCOME

10:16 AM *S.SM09.01.13
4D Printing of Advanced Scaffolds with Controlled Growth Factor Delivery for Tissue Engineering
Min Wang; The University of Hong Kong, Hong Kong

Additive manufacturing, popularly known as “3D printing”, includes an array of technologies such as fused deposition modelling (FDM), selective laser sintering (SLS) and inkjet printing. Compared with conventional manufacturing technologies, 3D printing has many distinctive advantages, including the construction of 3D structures with complex shapes and functionalities. Therefore, 3D printing technologies have seen increasing popularity in many areas, such as product design and development, industrial production, consumer goods, aerospace, and education. 3D printing has already made a tremendous impact in our society. The exciting TED Talk in 2013 by Tibbitts of MIT ushered in a new era in additive manufacturing: 4D printing. With 4D printing, 3D printed static objects will change their shapes over time, i.e., 4D printing uses 3D printing technologies to produce shape-morphing objects. Such objects can meet the demanding requirements in particularly applications. The concept of 4D printing has been evolving and one popular definition of 4D printing is that the shape, property and functionality of a 3D printed object can evolve with time in predefined and programmable designs. There have been numerous investigations into the application of 3D printing in biomedical engineering. So far, the greatest biomedical applications of 3D printing are in the tissue engineering field. Tissue engineering offers a new approach to treat difficult problems in human tissue repair. It involves using live cells to form implantable devices for body tissue regeneration. In scaffold-based tissue engineering, a scaffold provides a microenvironment for cells to adhere, proliferate and differentiate and a structural framework for new tissue formation. 3D printing has many advantages in scaffold fabrication, such as control of pore size, porosity, etc. Furthermore, 3D printing can make multilayered scaffolds with different layer characteristics. Most human body tissues are complex and hierarchical and their regeneration requires structurally complex scaffolds that resemble tissue structures and can provide biochemical cues such as growth factors (GFs). Incorporating GFs and even live cells in scaffolds can greatly facilitate tissue regeneration. Since 2004, we have been investigating 3D biomedical printing and have used different 3D printing techniques for developing bone tissue engineering scaffolds (e.g., S.H.Lee, W.Y.Zhou, W.L.Cheung, M.Wang, “Producing Polymeric Scaffolds for Bone Tissue Engineering Using the Selective Laser Sintering Technique”, Transactions of the Society For Biomaterials 30th Annual Meeting, Memphis, TN, USA, 2005, 348). We have also been exploring 4D printing in tissue engineering (e.g., C.Wang, Y.Zhou, M.Wang, “In situ Delivery of rhBMP-2 in Surface Porous Shape Memory Scaffolds Developed through Cryogenic 3D Plotting”, Materials Letters, Vol.189 (2017), 140-143). This talk will give an overview of our work in 3D/4D printing of scaffolds for
regenerating tissues such as bone and blood vessels. It will focus on the design and 4D printing of shape-morphing and GF-delivering scaffolds for tissue engineering.

10:36 AM S.SM09.01.15
3D Printed Diamond Technology—A New Material for Biomedical Applications Kate Fox, Aaqil Rifai, Nour Mani and Nhiem Tran; RMIT University, Australia

Diamond is quickly becoming an interesting material for medical implants with evidence that it provides not only a good biointerface but also an antimicrobial surface. Previously ultrananocrystalline diamond was shown to be a good bionic implant material [1] and our group have shown that a polycrystalline diamond coating can be produced on a 3D printed titanium substrate [2]. However up until now, all diamond implants have been as a coating material, with limitations as to its capacity to be used as a three dimensional surface. Here we present our recent results fabricating diamond implants using additive manufacturing including presenting for the first time a hybrid 3D diamond-titanium printed material which was recently published [3]. Diamond implants fabricated via using three different techniques (i) nanodiamond seeding, (ii) polycrystalline diamond coating and (iii) composite diamond-titanium biomaterial all showed superior cellular proliferation compared to the as-printed SLM titanium.as well as a decrease in microbial activity. The possibility of 3D diamond opens up large possibilities for new diamond technologies


10:46 AM S.SM09.01.16
Ultra-High Resolution Inkjet Printing of Vascular Structures Brian Derby; University of Manchester, United Kingdom

It is now more than 30 years since the principles of Additive Manufacturing or 3D Printing moved from a concept to practical implementation and over 20 years since the first publications on its use to fabricate implantable medical devices. In this period it has rapidly progressed from being seen as a topic for Science Fiction to now a method for the production of prototype and in vitro model tissues for tissue-on-a-chip applications and laboratory animal studies. Indeed there are several commercial organizations that have developed and market commercial Bioprinters. However, despite these not inconsiderable advances, the original target of printed cell-laden implants or tissue patches have still not been realized.

A key obstacle to the use of 3D printing for the fabrication of cell-laden constructs is the need to provide a functional vasculature for the maintenance of cell viability through the provision of oxygen and nutrients, as well as a pathway for waste removal. It is well known that the diffusion limit in the 3D culture of cells limits spheroid size to a few hundred μm and that the capillaries in healthy tissue have a diameter of 5 – 10 μm and are typically spaced around 50 μm. However, current additive manufacturing routes that are in widespread use in biofabrication have a spatial resolution > 100 μm. Hence, new approaches to producing high resolution vascular structures and models for angiogenesis are required.

Here we describe the use of ultra-high resolution inkjet printing (UHIJP) as a route to fabricate vascular structures in gelatine methacrylate (GelMA) hydrogels. This technique is related to electrospaying and electrospinning in that a local electric field is used to form a "Taylor Cone" with the meniscus of a fluid at a fine nozzle. Through using a controlled electrical pulse, individual mono-sized droplets are ejected with volume down to a single femtolitre (10-18 m³) with droplet diameters in the range 1 - 3 μm. UHIJP has been used to print structures from a thermoreversible hydrogel based on triblock polymers of polyethylene oxide and polypropylene oxide (Pluronic F127). These are subsequently encapsulated in GelMA and photopolymerised before removal of the Pluronic and replacement with an aqueous fluid. The exposed internal surface of the vascular structure can be modified with proteins such as laminin or fibrinogen to promote cell adhesion and this has been demonstrated through seeding with human umbilical vein endothelial cells (HUVECs) to allow fully endothelized structures with vascular diameter as small as 20 μm.

In order to ensure continuous tubular structures without obstruction, more complex vascular designs have been fabricated with minimum diameters of approximately 60 μm and seeded with HUVECs. Confocal microscopy shows that these structures are fully endothelized and act as an effective barrier to labelled dextran probes. As a further demonstration of the
utility of the structures, the GelMA matrix has been seeded with human dermal fibroblasts and this has been co-cultured with
the HUVEC lined vasculature demonstrating cell viability is maintained after several days in culture.

11:06 AM S.SM09.01.18
3D Printing PEEK Materials as Potential Bone Replacement and Dental Applications Rigoberto C. Advincula; Case Western Reserve University, United States

3D Printing has been a highly successful method to bring new materials and complexities in design through digital manufacturing. It has enabled advancement from rapid prototyping through actual production. Because of its mechanical, chemical and biological properties, 3D-printed polyether ether ketone (PEEK) has great potential as a customized bone replacement. Its density and mechanical properties are closer to bone compared to most Ti-based alloys. In this study, PEEK samples were printed using fused deposition modeling (FDM) and evaluated in terms of their dimensional accuracy, crystallinity, and mechanical properties. The dimensional integrity and surface quality of the printed materials are important. Crystallinity and mechanical properties increased with elevated chamber temperature and post-printing annealing. In this study, we also utilized three available commercial printers. Variations of material properties from three printers are evident. Many factors affect the quality of 3D-printed PEEK. Future FDA regulations for 3D-printed products are needed for this highly customizable manufacturing process to ensure safety and effectiveness for biomedical applications. Future work will report on nanocomposite fabrication and testing.

11:16 AM S.SM09.01.19
Light-Directed 3D Printing of Ionically Crosslinked Hydrogels for Smart Biomaterials and Microfluidics Ian Yan Wong; Brown University, United States

3D printing is a promising approach for designer biomaterial architectures with information-rich structure and dynamic functionality. In particular, stimuli-responsive hydrogels consisting of crosslinked, hydrophilic polymers could be used for tissue engineering, drug delivery and other biomedical applications. One design consideration is that these biomaterials must be responsive to at least two physicochemical stimuli – the first to pattern desired structures and additional orthogonal stimuli to trigger dynamic behaviors such as degradation, actuation, or self-adhesion. Here, we show that light-directed 3D printing based on ionic crosslinking enables smart materials with biologically-inspired functionalities. First, we demonstrate reversible 3D printing of alginate hydrogel microstructures to template hydrogel microfluidics and pattern collective cell migration. Second, we add graphene oxide into these alginate hydrogels to enhance mechanical properties and oil repulsion in seawater-like conditions. Finally, we prepare double network hydrogels that stimuli-responsive and self-adhesive as a simple “do-it-yourself” construction set for soft machines and microfluidic devices. This modular approach enables “plug-and-play” hydrogel parts for iono soft machines that emulate actuation, sensing, and fluid transport in living systems.

11:26 AM S.SM09.01.20
Cellular Self-Assembly for Faster Maturation of Bioprinted Tissues in Autologous Tissue Engineering Ashkan Shafiee; Wake Forest Institute for Regenerative Medicine, United States

Bioprinting of autologous tissues encompasses many different steps, and accelerating the process can be very critical for patients with an urgent need of organs. The first step for the transition from “trial and error” to “predict and control” phase of the bioprinting is to understand the underlying science of this unique technology. The physical aspects of self-assembly and the dynamics of multicellular systems used with printing technologies for tissue fabrication are therefore very important. We have developed a microscopic and mathematical method to study tissue fusion, an essential element of self-assembly phenomena during tissue maturation in the post-bioprinting procedure. The model is generalized for different bioink geometries. A mathematical method is introduced, and microscopic interactions at the cellular level in the maturation of bioprinted tissues have been studied. The fusion of tissue-like cell aggregates (cellular bioinks) is elaborated with the help of bonds among their adhesion molecules. The statistical mechanics is used to describe the fusion procedure. Consequently, the partition function for the model and the system total energy are calculated and compared to understand the effect of bioink geometries on the acceleration of the maturation of bioprinted tissues. We identified the driving force and energy of the self-assembly in the maturation of bioprinted tissues. The force and energy are not only critical to control bioprinted final product but also significant for other multicellular interactions such as cancer metastasis and migrations, in which decelerating the procedure is important. Based on our microscopic and mathematical method, we introduce some topological criteria for bioinks for faster maturation of bioprinted tissues.
Modulating the Reaction of Primary Human Immune Cells to 3D Printed Scaffolds

Jürgen Groll, Tina Tylek, Carina Blum and Katrin Schlegelmilch; University of Würzburg, Germany

Influencing or ideally directing the innate immune response after implantation remains one of the major challenges in the development of biomaterials and the design of three dimensional (3D) scaffolds [1]. Macrophages are key players of the innate immune system that can roughly be divided into the pro-inflammatory M1 type and the anti-inflammatory, pro-healing M2 type. While a transient initial pro-inflammatory state is helpful in early phases, a prolonged inflammation deteriorates a proper healing and subsequent regeneration. One promising strategy to drive macrophage polarization is precise control over biomaterial geometry. For example, a concave-structured poly(2-hydroxyethyl methacrylate) hydrogel with a highly ordered architecture and exactly equally-sized pores of up to 40 μm, showed a pronounced infiltration of murine macrophages being mainly directed towards the healing phenotype in vivo [2].

For regenerative approaches, it is of particular interest to identify geometrical parameters that direct human macrophage polarization. The additive manufacturing technique of melt electrowriting (MEW) is an especially suitable and advantageous approach in this context as it enables the production of highly defined scaffold geometries built of fibers with diameters in the lower micrometer range [3]. Our group has demonstrated the ability of cells to attach, infiltrate, and proliferate upon seeding onto MEW scaffolds [4], and that the surface modification of MEW scaffolds results in specific interaction with cells [5, 6]. This talk will present our findings in applying MEW for the fabrication of fibrous 3D scaffolds made from poly(ε-caprolactone) (PCL) with precisely defined inter-fiber spacing from 100 μm down to 40 μm in a variety of pore geometries (rectangular, triangular and round). These scaffolds facilitate primary human macrophage elongation accompanied by differentiation towards the M2 type, which was most pronounced for box-shaped pores with 40 μm inter-fiber spacing [7]. Moreover, a novel way of producing double-hierarchical scaffolds by MEW will be presented that induce an even stronger M2-type differentiation stimulus for human macrophages.

Literature

3D Printing Self-Supporting and Aligned Microfluidics

Michael C. McAlpine1, Ruitao Su1, Joshua R. Uzarski2, Michael Wiederoder2 and Steven Koester1; 1University of Minnesota, United States; 2U.S. Army Combat Capabilities Development Command (CCDC) Soldier Center, Natick, United States

Elastomer based microfluidic devices microfabricated via conventional methodologies, such as soft lithography and stereolithography, have been used for applications such as chemical species mixing, fast bio-chemical assays, controlled cell culturing etc. However, several challenges exist for these methods, including long fabrication times, limited throughput, complex manual alignment steps, and difficulty integrating functional elements such as electrodes, valves, sensing elements, and/or 3-D structures for mixing or sorting. A more freeform fabrication methodology is demanded to enable new applications in microfluidics. Here, we demonstrate a novel 3D printing strategy that can effectively overcome the above issues via precisely controlling the extrusion of polymeric inks into self-supporting microfluidic structures. Specifically, extruded silicone filaments are stacked in an orientation such that adhesion and gravity are balanced during printing, eliminating the need for sacrificial materials. This creates interconnected hollow structures, such as micro chambers and channels, with a minimum inner diameter of 100 micron. The advantage of 3D printed self-supporting microfluidic structures are further demonstrated via several types of devices. First, chemical species mixers are printed with silicone channels, embedded with micro herringbone ridge arrays that are printed with the biocompatible material, polycaprolactone (PCL).
Optimization of the mixing effect is conducted via facile adjustment of the geometric profile of the herringbone ridges. Next, a multi-channel salinity sensor is created via directly printing silicone channels and chambers aligned onto prefabricated electronic circuits. A seamless and robust bonding is formed between the microfluidic structures and the substrate as the material cures. We also demonstrate that, with this printing strategy, functional microfluidic valves and pumps can be readily printed with overlapping silicone channels and UV-curable encapsulating polymers. Finally, going beyond the planar morphology, branching microfluidic channels are printed onto a spherical surface, demonstrating the potential application of 3D printed microfluidics onto curved surfaces. In the future, this may even be the human body as directly printed physiological sensors. The demonstrated methods overcome current limitations by enabling rapid, high-throughput, high-resolution fabrication of elastomeric microfluidic devices on planar and non-planar geometries with integrated multi-material functional elements for diverse applications.

SESSION S.SM09.01: 3D Printed Medical Devices
On Demand Abstracts Available for Viewing Starting On Demand Abstracts Available for Viewing Starting Saturday Morning, November 21, 2020
S-SM09

5:00 AM *S.SM09.01.01
Tip-Based Nanoscale 3D Printing Wonho Jhe and Sangmin An; Seoul National University, Korea (the Republic of)

Viscoelastic complex fluids exhibit rheological nonlinearity at a high shear rate. Although typical nonlinear effects, shear thinning and shear thickening, have been usually understood by variation of intrinsic quantities such as viscosity, one still requires a better understanding of the microscopic origins, currently under debate, especially on the shear-thickening mechanism. We present accurate measurements of shear stress in the bound hydration water layer using noncontact dynamic force microscopy. We find shear thickening occurs above 10^6 1/s shear rate beyond 0.3-nm layer thickness, which is attributed to the nonviscous, elasticity associated fluidic instability via fluctuation correlation. Such a nonlinear fluidic transition is observed due to the long relaxation time (1 us) of water available in the nanoconfined hydration layer, which indicates the onset of elastic turbulence at nanoscale, elucidating the interplay between relaxation and shear motion, which also indicates the onset of elastic turbulence at nanoscale above a universal shear velocity of 1 mm/s. This extensive layer-by-layer control paves the way for fundamental studies of nonlinear nanorheology and nanoscale hydrodynamics, as well as provides novel insights on viscoelastic dynamics of interfacial water. We will also discuss the tip-based microfluidic characterization and manipulation of liquids.

5:15 AM *S.SM09.01.03
Material Horizons for Volumetric Additive Manufacturing Maxim Shusteff1, Caitlyn Cook1, Johanna Schwartz1, Erika Fong1, James Oakdale1, Bryan Moran1, Allison Kaczmarek1,2, Hossein Heidari3, S.M. Luk1, Charles Rackson4, Robert McLeod1 and Hayden Taylor2; 1Lawrence Livermore National Laboratory, United States; 2Clemson University, United States; 3University of California, Berkeley, United States; 4University of Colorado Boulder, United States

As additive manufacturing (AM, also known as 3D printing) technologies have proliferated, approaches based on solidification of photosensitive liquid resins have showed great promise due to their superior resolution and precision. However, these techniques have been largely limited to prototyping applications due to the constraints on available materials and their mechanical properties, as well as slow builds and poor surface quality resulting from layer-wise fabrication. With the advent of volumetric AM (VAM), complete 3D structures with complex geometries can now be produced in a single step, leaping over the traditional limitations of layer-by-layer approaches to 3D printing. Volumetric 3D printing generates a 3D distribution of absorbed optical energy within a volume of photosensitive material, concurrently curing all points within a target geometry, on a timescale of 10s to 100s of seconds. No substrate is required as the part forms unsupported in the resin container. The most versatile implementation of VAM is known as computed axial lithography (CAL) which adapts the principles of computed tomography (CT) to generate a sequence of intensity-modulated projections, which are then beamed sequentially into a rotating resin container via a DLP projector to create the required energy dose. Because there is no fluid motion, and no hydrodynamic forces during a build, this approach is particularly compelling for very soft materials such as the hydrogels widely used in tissue engineering and regenerative medicine applications. The absence of support structure also enables complex geometries such as vasculature to be built. Successful volumetric 3D printing requires spatio-temporal control over the polymerization reaction at all points within the
fabrication volume. This demands a more detailed understanding of a host of process parameters, compared with traditional layered approaches. Perhaps the most important such parameters are the absorbed volumetric energy dose $E_{VOL}$, as well as the rate at which this dose is delivered. The progress of the photochemical reaction may then be characterized in terms of a variety of metrics, such as double-bond conversion, or the evolution of mechanical and optical properties of the material. We investigate the inter-relationship of these properties, obtained from ex-situ measurements such as real-time FTIR spectroscopy, photo-rheology, and mechanical testing, developing a quantitative framework for predicting volumetric structure formation. An additional resin characteristic critical for CAL printing is nonlinear threshold behavior. This allows resin that receives a sub-threshold dose to remain liquid, and derives from the interaction of the generated radicals and inhibitory species present in the resin. For some chemistries the inhibitory effect is provided by dissolved molecular oxygen, but for other formulations, deliberately including another inhibitor is necessary. We discuss the implications of these interacting factors for photo-resin design within the volumetric AM paradigm, as well as more broadly in photopolymer-based AM methods. We also discuss several material classes for VAM, including high-performance engineering materials, as well as cell-culture compatible hydrogels.

References


5:30 AM S.SM09.01.05
Additive Manufacturing of Borosilicate Glass via Stereolithography Omena Okpowe1, Andriy Durygin2, Vadym Drozd2, Nezih Pala2 and Chunlei Wang1,2, 1Florida International University, United States; 2Florida International University, United States

Borosilicate glass is a type of glass material consisting SiO$_2$ and B$_2$O$_3$ as network formers and alkali oxide modifiers. Their excellent optical transparency, chemical resistance, low thermal expansivity and tunable chemical composition make them useful for a wide range of applications such as lab ware, medical implants, microelectromechanical systems (MEMS), sensing and detection etc. Conventional glass fabrication techniques involve melting, casting and use of undesirable chemicals and these imply that there is little room for flexibility in shape and resolution. Recent surge in additive manufacturing efforts now show that ceramic glasses can now be fabricated via stereolithography. However this has not been shown possible for borosilicates due to their low softening temperatures. Herein, we report a simple additive manufacturing protocol for fabricating 3D low softening temperature borosilicate glass. It entails first fabricating a liquid glass composite, printing on a layer by layer basis to form a 'green ensemble'. This 'green ensemble' must then be debound to yield a 'brown ensemble' and sintered to yield transparent and amorphous glass ensembles. The properties of the printed glass depend on thermal processing parameters (temperature, time and environment) and these can be readily tuned and optimized to yield 3D glass for a wide range of applications. The printed glass show good optical properties, show no devitrification and exhibit minimal surface roughness requiring no further polishing and finishing typically associated with other glass fabrication techniques.

5:40 AM S.SM09.01.07
Additive Manufacturing for Transdermal Biosensor Applications Roger Narayan; North Carolina State University, United States

Two photon polymerization is an additive manufacturing method that offers many advantages over conventional processes for scalable mass production of medical devices, including microneedles and other medical devices with small-scale features. First, the raw materials (e.g., inorganic-organic hybrid materials and acrylate-based polymers) used in two photon polymerization can be purchased at low cost. Second, two photon polymerization can be established in a conventional environment; no cleanroom facilities or other types of specialized facilities are required. Third, two photon polymerization is a straightforward approach for creating medical devices with complex and small-scale features. Two photon polymerization has been used to create hollow microneedles with a larger range of shapes and dimensions than conventional microneedle fabrication methods. We have prepared several types of hollow microneedle-based biosensors using microneedles that were fabricated using either two photon polymerization or digital micromirror device-based stereolithography. In these biosensors, the sensors (either colorimetric or electrochemical) are located within the bores of the microneedles or underneath the microneedles. Application-specific testing and functional testing of the microneedle-based biosensors will be considered.

5:50 AM S.SM09.01.09
Dynamically Adjustable Real-Time Tuning of Catheter-Injectable Delivery of Functional Hydrogels towards In...
Hydrogels have long been considered a significantly promising class of biomaterials. While the chemomechanical tunability of a multitude of hydrogels have been demonstrated in vitro, the ability to deliver these materials in a minimally invasive manner to avoid iatrogenic damages has yet to be fully explored. In the present work, we demonstrate a method of in-situ extrusion of hydrogels with compositions and chemomechanical properties that can be dynamically adjusted “on-the-fly” using a custom catheter that is utilized intravascularly. A custom UV-integrated, multi-lumen microcatheter (inner/outer lumen diameters: 0.6/1.28 mm) was assembled and a suite of low viscosity, shear thinning gelatin-based precursors were formulated for delivery. While the shear thinning property makes this precursor a suitable choice for injection through a catheter with extended length and small diameter, intensity modulation of UV to cross-link the precursor aids greatly in tuning the stiffness at the catheter tip. We show that by modulating the absolute and relative flow rates as well as the UV intensity (0~150 µW output from a 105µm core multimode fibre), we can extrude hydrogels with stiffnesses dynamically varying from <10 to 80 kPa. In addition, through the dual luminal architecture, it is also possible to sequentially switch or coaxially coextrude two types of precursor compositions. The concentrations and diffusivities of additives (as preliminarily demonstrated using food dyes) within the extruded scaffold can also be dynamically altered by 10^3 and 10^2 orders respectively, in a single piece of extruded hydrogel fibre, therefore allowing applications a highly customizable drug depot to be deployed using this technique. To demonstrate the initial utility of this system, we successfully performed embolization of a saccular aneurysm model (diameter ~ 12 mm) and a capillary vasculature model (diameter <1 mm) using a pulsatile vascular flow phantom. The former required the extruded hydrogels to be relatively stiffer via increased photo-cross linking to fill the aneurysm while avoiding leakage into the parent vessel. In capillary embolization, the precursor was injected with lower crosslinking leading to increased viscosity to penetrate further into the vessels to fully embolize the structure. These findings yield direct application ideas in therapeutics such as vascular embolization in a variety of disease states, including cerebral aneurysms, arterio-venous malformations, vascularized tumors, and hemorrhagic vessels. The system can also be utilized for intravascular drug delivery and targeted cell therapies, which may require the physician to constantly adapt to the state of the patient. Further, such a dynamically tunable hydrogel delivery method may be able to serve as a supporting host matrix for functional sensing devices such as microelectrode arrays and quantum dot based chemical sensors.

Bioink extrusion-printing, while capable of creating macroscopically accurate anatomic models, fails to replicate the microstructure of the natural tissue due to resolution limitation of this bottom-up fabrication approach. We re-engineer the extrusion process to co-extrude a fiber device in line with the hydrogel bioink. This allows deviation from a pure bottom-up towards a combined approach, where a bottom-up extrusion process creates the macrostructure, while the fiber device in a top-down fashion subsequently promotes the growth of natural microstructure from within the volume of the print.

Fibers can embed a range of bio-functional and biosensing devices and systems. We aim to incorporate microfluidic, ultrasonic, and shape-memory-alloy (SMA) structures mimicking the functionalities of microvasculature, innervation, and musculature, respectively, into a single fiber-device. Those functional structures are created by a thermal draw of fibers from multimaterial preforms – a process familiar from an optical communication fiber fabrication. In this process, the macroscopic preform – a thick and short rod, cross-sectionally structured to meet the desired fiber functionality – is heated to become a viscous liquid and scaled by a thermal draw into a thin and long fiber, preserving the cross-sectional geometry of the preform. Then the fiber cores are patterned axially by a spatially coherent material selective capillary instability to form arrays of ultrasonic transducers contacted in parallel and microchannels with periodic outlets spanning the entire fiber length \[1\].

In the extrusion process, the fiber is coated with hydrogel, contains tissue cells, extracellular matrix material, nutrients and growth-factors, forming a scaffolded print-line that is raster-layered into a printed model cross section additively constructing the final model in a layer-by-layer manner. Subsequently, the fiber-embedded microchannel structure is used as artificial vasculature supplying building material and nutrients into surrounding bioink to ignite the creation of natural vasculature and promote the proliferation of the bioink-contained tissue cells with their subsequent maturation into a natural-tissue-like structure. The ultrasonic transducers embedded in the fiber are used to sense the changes in the surrounding material density, monitoring cell-proliferation process, thus serving as artificial tactile nerves. SMA cores, contracting upon transduction of electric current, mimic the function of muscle yarns.

The proposed bioprinting approach will likely deliver a biosynthetic tissue with natural-like microstructure opening new
routes in regenerative medicine, such as wound infilling and organ replacement. Moreover, it would allow creating lab-bench anatomical models of realistic tissue, in which bio-material delivery and biosensing is performed volumetrically with a microscale resolution, thus forming a novel stand-alone platform for investigation of micrometabolic processes. Such a platform would be a valuable asset to drug toxicity investigation, and real-time survivability monitoring of such artificial tissues and organs both in-vitro and in animal subjects.


6:10 AM *S.SM09.01.11*

**The Investigation of Nano-Liter Droplets for Bioprinting Applications**

Wai Yee Yeong1,2, Wei Long Ng1,2, Christie Dudenhofer3 and Keith Moore3; 1Nanyang Technological University, Singapore; 2HP-NTU Digital Manufacturing Corporate Lab, Singapore; 3HP Inc., United States

The use of drop-on-demand (DOD) bioprinting has attracted numerous attention for numerous biological applications due to its precise control over material volume and deposition pattern in a contactless printing approach to facilitate important cell-cell and cell-matrix interactions. In this work, a HP d300e Digital Dispenser will be used for precise deposition of nano-liter droplets. Here, we propose the use of a general purpose polyvinylpyrrolidone (PVP)-based bio-inks for printing of nano-liter cell droplets. Different PVP-based bio-inks (0 – 3% w/v) are prepared and evaluated for their printability in term of droplet formation and droplet impact on substrate surface; the short-term and long-term viability of printed cells (primary human skin fibroblasts) are also evaluated. We will discuss the range of printable cell concentration and its corresponding droplet resolution, cell viability and proliferation over time post-printing. Furthermore, we also will demonstrate different DOD printing strategies to initiate the hydrogel cross-linking mechanism and achieve tunable material properties within the hydrogel constructs.

6:20 AM *S.SM09.01.12*

**Genomic-DNA Coated 3D Printed Materials for Drug Capture**

Daryl Yee, Robert H. Grubbs and Julia R. Greer; California Institute of Technology, United States

Since the discovery of chemotherapy in the beginning of the 20th century, researchers around the world have been actively developing new and more effective chemotherapeutic agents to better treat cancer. Traditionally, chemotherapeutic agents work by interfering with cell division. However, by virtue of their mechanism of action, healthy normal cells can also be targeted and destroyed. As a result, while chemotherapy is an effective way of managing cancer, the resulting side effects limits its use. One approach currently taken to reduce these side effects is to deliver the chemotherapy drugs directly to the tumor via transarterial chemoembolization, or other similar procedures. While this has been effective in reducing systemic toxicity, more can be done to improve this. Ideally, a device that could sequester any unreacted chemotherapy agents could be installed "downstream" of the tumor prior to them entering systemic circulation. Such drug-capture materials have yet to be realized due to the difficulty in achieving materials that have the right surface chemistry and geometry for blood flow.

Working together with medical doctors, computational fluid dynamics experts, chemists, and materials scientists, we report the fabrication of DNA functionalized 3D printed porous materials that can be used to capture doxorubicin and cisplatin, two commonly used DNA-targeting chemotherapeutic agents. We discuss the concept behind the device, the use of 3D printed materials as an ideal substrate, and the chemistries considered in drug binding. To achieve scalability of these devices, we developed a method of attaching cheaply available genomic DNA to these materials, a departure from commonly used synthetic DNA. We characterize the surface of the structure and verify the binding of DNA to the surface via XPS, EDS and the use of chemical assays. The efficacy of these functionalized materials were demonstrated in PBS, where we observed a >70% reduction in doxorubicin concentration over a period of 20 minutes, highlighting the viability of this as a method of drug capture.

6:30 AM *S.SM09.01.13*

**4D Printing of Advanced Scaffolds with Controlled Growth Factor Delivery for Tissue Engineering**

Min Wang; The University of Hong Kong, Hong Kong

Additive manufacturing, popularly known as “3D printing”, includes an array of technologies such as fused deposition modelling (FDM), selective laser sintering (SLS) and inkjet printing. Compared with conventional manufacturing technologies, 3D printing has many distinctive advantages, including the construction of 3D structures with complex shapes...
and functionalities. Therefore, 3D printing technologies have seen increasing popularity in many areas, such as product design and development, industrial production, consumer goods, aerospace, and education. 3D printing has already made a tremendous impact in our society. The exciting TED Talk in 2013 by Tibbits of MIT ushered in a new era in additive manufacturing: 4D printing. With 4D printing, 3D printed static objects will change their shapes over time, i.e., 4D printing uses 3D printing technologies to produce shape-morphing objects. Such objects can meet the demanding requirements in particularly applications. The concept of 4D printing has been evolving and one popular definition of 4D printing is that the shape, property and functionality of a 3D printed object can evolve with time in predefined and programmable designs. There have been numerous investigations into the application of 3D printing in biomedical engineering. So far, the greatest biomedical applications of 3D printing are in the tissue engineering field. Tissue engineering offers a new approach to treat difficult problems in human tissue repair. It involves using live cells to form implantable devices for body tissue regeneration. In scaffold-based tissue engineering, a scaffold provides a microenvironment for cells to adhere, proliferate and differentiate and a structural framework for new tissue formation. 3D printing has many advantages in scaffold fabrication, such as control of pore size, porosity, etc. Furthermore, 3D printing can make multilayered scaffolds with different layer characteristics. Most human body tissues are complex and hierarchical and their regeneration requires structurally complex scaffolds that resemble tissue structures and can provide biochemical cues such as growth factors (GFs). Incorporating GFs and even live cells in scaffolds can greatly facilitate tissue regeneration. Since 2004, we have been investigating 3D biomedical printing and have used different 3D printing techniques for developing bone tissue engineering scaffolds (e.g., S.H.Lee, W.Y.Zhou, W.L.Cheung, M.Wang, “Producing Polymeric Scaffolds for Bone Tissue Engineering Using the Selective Laser Sintering Technique”, Transactions of the Society For Biomaterials 30th Annual Meeting, Memphis, TN, USA, 2005, 348). We have also been exploring 4D printing in tissue engineering (e.g., C.Wang, Y.Zhou, M.Wang, “In situ Delivery of rhBMP-2 in Surface Porous Shape Memory Scaffolds Developed through Cryogenic 3D Plotting”, Materials Letters, Vol.189 (2017), 140-143). This talk will give an overview of our work in 3D/4D printing of scaffolds for regenerating tissues such as bone and blood vessels. It will focus on the design and 4D printing of shape-morphing and GF-delivering scaffolds for tissue engineering.

6:45 AM S.SM09.01.15
3D Printed Diamond Technology—A New Material for Biomedical Applications Kate Fox, Aaqil Rifai, Nour Mani and Nhiem Tran; RMIT University, Australia

Diamond is quickly becoming an interesting material for medical implants with evidence that it provides not only a good biointerface but also an antimicrobial surface. Previously ultrananocrystalline diamond was shown to be a good bionic implant material [1] and our group have shown that a polycrystalline diamond coating can be produced on a 3D printed titanium substrate [2]. However up until now, all diamond implants have been as a coating material, with limitations as to its capacity to be used as a three dimensional surface. Here we present our recent results fabricating diamond implants using additive manufacturing including presenting for the first time a hybrid 3D diamond-titanium printed material which was recently published [3]. Diamond implants fabricated via using three different techniques (i) nanodiamond seeding, (ii) polycrystalline diamond coating and (iii) composite diamond-titanium biomaterial all showed superior cellular proliferation compared to the as-printed SLM titanium as well as a decrease in microbial activity. The possibility of 3D diamond opens up large possibilities for new diamond technologies.


6:55 AM S.SM09.01.16
Ultra-High Resolution Inkjet Printing of Vascular Structures Brian Derby; University of Manchester, United Kingdom

It is now more than 30 years since the priciples of Additive Manufacturing or 3D Printing moved from a concept to practical implementation and over 20 years since the first publications on its use to fabricate implantable medical devices. In this period it has rapidly progressed from being seen as a topic for Science Fiction to now a method for the production of prototype or in vitro model tissues for tissue-on-a-chip applications and laboratory animal studies. Indeed there are several commercial organizations that have developed and market commercial Bioprinters. However, despite these not inconsiderable advances,
the original target of printed cell-laden implants or tissue patches have still not been realized.
A key obstacle to the use of 3D printing for the fabrication of cell-laden constructs is the need to provide a functional
vasculature for the maintenance of cell viability through the provision of oxygen and nutrients, as well as a pathway for waste
removal. It is well known that the diffusion limit in the 3D culture of cells limits spheroid size to a few hundred μm and that
the capillaries in healthy tissue have a diameter of 5 – 10 μm and are typically spaced around 50 μm. However, current
additive manufacturing routes that are in widespread use in biofabrication have a spatial resolution > 100 μm. Hence, new
approaches to producing high resolution vascular structures and models for angiogenesis are required.
Here we describe the use of ultra-high resolution inkjet printing (UHJP) as a route to fabricate vascular structures in gelatine
methacrylate (GelMA) hydrogels. This technique is related to electrospaying and electrospinning in that a local electric field
is used to form a "Taylor Cone" with the meniscus of a fluid at a fine nozzle. Through using a controlled electrical pulse,
individual mono-sized droplets are ejected with volume down to a single femtolitre (10^-18 m^3) with droplet diameters in the
range 1 - 3 μm. UHJP has been used to print structures from a thermoreversible hydrogel based on triblock polymers of
polyethylene oxide and polypropylene oxide (Pluronic F127). These are subsequently encapsulated in GelMA and
photopolymerised before removal of the Pluronic and replacement with an aqueous fluid. The exposed internal surface of the
vascular structure can be modified with proteins such as laminin or fibrinogen to promote cell adhesion and this has been
demonstrated through seeding with human umbilical vein endothelial cells (HUVECs) to allow fully endothelized structures
with vascular diameter as small as 20 μm.
In order to ensure continuous tubular structures without obstruction, more complex vascular designs have been fabricated
with minimum diameters of approximately 60 μm and seeded with HUVECs. Confocal microscopy shows that these
structures are fully endothelized and act as an effective barrier to labelled dextran probes. As a further demonstration of the
utility of the structures, the GelMA matrix has been seeded with human dermal fibroblasts and this has been co-cultured with
the HUVEC lined vasculature demonstrating cell viability is maintained after several days in culture.

7:05 AM S.SM09.01.18
3D Printing PEEK Materials as Potential Bone Replacement and Dental Applications Rigoberto C. Advincula; Case
Western Reserve University, United States

3D Printing has been a highly successful method to bring new materials and complexities in design through digital
manufacturing. It has enabled advancement from rapid prototyping through actual production. Because of its mechanical,
chemical and biological properties, 3D-printed polyether ether ketone (PEEK) has great potential as a customized bone
replacement. Its density and mechanical properties are closer to bone compared to most Ti-based alloys. In this study, PEEK
samples were printed using fused deposition modeling (FDM) and evaluated in terms of their dimensional accuracy,
crystallinity, and mechanical properties. The dimensional integrity and surface quality of the printed materials are important.
Crystallinity and mechanical properties increased with elevated chamber temperature and post-printing annealing. In
this study, we also utilized three available commercial printers. Variations of material properties from three printers are evident.
Many factors affect the quality of 3D-printed PEEK. Future FDA regulations for 3D-printed products are needed for this
highly customizable manufacturing process to ensure safety and effectiveness for biomedical applications. Future work will
report on nanocomposite fabrication and testing.

7:15 AM *S.SM09.01.19
Light-Directed 3D Printing of Ionomically Crosslinked Hydrogels for Smart Biomaterials and Microfluidics Ian Yan
Wong; Brown University, United States

3D printing is a promising approach for designer biomaterial architectures with information-rich structure and dynamic
functionality. In particular, stimuli-responsive hydrogels consisting of crosslinked, hydrophilic polymers could be used for
tissue engineering, drug delivery and other biomedical applications. One design consideration is that these biomaterials must
be responsive to at least two physicochemical stimuli – the first to pattern desired structures and additional orthogonal stimuli
to trigger dynamic behaviors such as degradation, actuation, or self-adhesion. Here, we show that light-directed 3D printing
based on ionic crosslinking enables smart materials with biologically-inspired functionalities. First, we demonstrate
reversible 3D printing of alginate hydrogel microstructures to template hydrogel microfluidics and pattern collective cell
migration. Second, we add graphene oxide into these alginate hydrogels to enhance mechanical properties and oil repulsion
in seawater-like conditions. Finally, we prepare double network hydrogels that stimuli-responsive and self-adhesive as a
simple “do-it-yourself” construction set for soft machines and microfluidic devices. This modular approach enables “plug-
and-play” hydrogel parts for ionic soft machines that emulate actuation, sensing, and fluid transport in living systems.
Bioprinting of autologous tissues encompasses many different steps, and accelerating the process can be very critical for patients with an urgent need of organs. The first step for the transition from “trial and error” to “predict and control” phase of the bioprinting is to understand the underlying science of this unique technology. The physical aspects of self-assembly and the dynamics of multicellular systems used with printing technologies for tissue fabrication are therefore very important. We have developed a microscopic and mathematical method to study tissue fusion, an essential element of self-assembly phenomena during tissue maturation in the post-bioprinting procedure. The model is generalized for different bioink geometries. A mathematical method is introduced, and microscopic interactions at the cellular level in the maturation of bioprinted tissues have been studied. The fusion of tissue-like cell aggregates (cellular bioinks) is elaborated with the help of bonds among their adhesion molecules. The statistical mechanics is used to describe the fusion procedure. Consequently, the partition function for the model and the system total energy are calculated and compared to understand the effect of bioink geometries on the acceleration of the maturation of bioprinted tissues. We identified the driving force and energy of the self-assembly in the maturation of bioprinted tissues. The force and energy are not only critical to control bioprinted final product but also significant for other multicellular interactions such as cancer metastasis and migrations, in which decelerating the procedure is important. Based on our microscopic and mathematical method, we introduce some topological criteria for bioinks for faster maturation of bioprinted tissues.

7:40 AM *S.SM09.01.22

**Modulating the Reaction of Primary Human Immune Cells to 3D Printed Scaffolds**  
Jürgen Groll, Tina Tylek, Carina Blum and Katrin Schlegelmilch; University of Würzburg, Germany

Influencing or ideally directing the innate immune response after implantation remains one of the major challenges in the development of biomaterials and the design of three dimensional (3D) scaffolds [1]. Macrophages are key players of the innate immune system that can roughly be divided into the pro-inflammatory M1 type and the anti-inflammatory, pro-healing M2 type. While a transient initial pro-inflammatory state is helpful in early phases, a prolonged inflammation deteriorates a proper healing and subsequent regeneration. One promising strategy to drive macrophage polarization is precise control over biomaterial geometry. For example, a concave-structured poly(2-hydroxyethyl methacrylate) hydrogel with a highly ordered architecture and exactly equally-sized pores of up to 40 μm, showed a pronounced infiltration of murine macrophages being mainly directed towards the healing phenotype in vivo [2].

For regenerative approaches, it is of particular interest to identify geometrical parameters that direct human macrophage polarization. The additive manufacturing technique of melt electrowriting (MEW) is an especially suitable and advantageous approach in this context as it enables the production of highly defined scaffold geometries built of fibers with diameters in the lower micrometer range [3]. Our group has demonstrated the ability of cells to attach, infiltrate, and proliferate upon seeding onto MEW scaffolds [4], and that the surface modification of MEW scaffolds results in specific interaction with cells [5, 6]. This talk will present our findings in applying MEW for the fabrication of fibrous 3D scaffolds made from poly(ε-caprolactone) (PCL) with precisely defined inter-fiber spacing from 100 μm down to 40 μm in a variety of pore geometries (rectangular, triangular and round). These scaffolds facilitate primary human macrophage elongation accompanied by differentiation towards the M2 type, which was most pronounced for box-shaped pores with 40 μm inter-fiber spacing [7]. Moreover, a novel way of producing double-hierarchical scaffolds by MEW will be presented that induce an even stronger M2-type differentiation stimulus for human macrophages.

**Literature**

3D Printing Self-Supporting and Aligned Microfluidics Michael C. McAlpine1, Ruitao Su1, Joshua R. Uzarski2, Michael Wiederoder2 and Steven Koester1; 1University of Minnesota, United States; 2U.S. Army Combat Capabilities Development Command (CCDC) Soldier Center, Natick, United States

Elastomer based microfluidic devices microfabricated via conventional methodologies, such as soft lithography and stereolithography, have been used for applications such as chemical species mixing, fast bio-chemical assays, controlled cell culturing etc. However, several challenges exist for these methods, including long fabrication times, limited throughput, complex manual alignment steps, and difficulty integrating functional elements such as electrodes, valves, sensing elements, and/or 3-D structures for mixing or sorting. A more freeform fabrication methodology is demanded to enable new applications in microfluidics. Here, we demonstrate a novel 3D printing strategy that can effectively overcome the above issues via precisely controlling the extrusion of polymeric inks into self-supporting microfluidic structures. Specifically, extruded silicone filaments are stacked in an orientation such that adhesion and gravity are balanced during printing, eliminating the need for sacrificial materials. This creates interconnected hollow structures, such as micro chambers and channels, with a minimum inner diameter of 100 micron. The advantage of 3D printed self-supporting microfluidic structures are further demonstrated via several types of devices. First, chemical species mixers are printed with silicone channels, embedded with micro herringbone ridge arrays that are printed with the biocompatible material, polycaprolactone (PCL). Optimization of the mixing effect is conducted via facile adjustment of the geometric profile of the herringbone ridges. Next, a multi-channel salinity sensor is created via directly printing silicone channels and chambers aligned onto prefabricated electronic circuits. A seamless and robust bonding is formed between the microfluidic structures and the substrate as the material cures. We also demonstrate that, with this printing strategy, functional microfluidic valves and pumps can be readily printed with overlapping silicone channels and UV-curable encapsulating polymers. Finally, going beyond the planar morphology, branching microfluidic channels are printed onto a spherical surface, demonstrating the potential application of 3D printed microfluidics onto curved surfaces. In the future, this may even be the human body as directly printed physiological sensors. The demonstrated methods overcome current limitations by enabling rapid, high-throughput, high-resolution fabrication of elastomeric microfluidic devices on planar and non-planar geometries with integrated multi-material functional elements for diverse applications.
the matrix or onto the surface of 3D scaffolds for enhancing tissue regeneration. Scaffolds mimicking the natural extracellular matrix of human tissues can serve very well as a substrate for cell attachment, proliferation, and differentiation and thus facilitate new tissue formation in vivo. The architectures (pore size, shape, interconnectivity, porosity, etc.) and properties (biological and mechanical) of scaffolds should be carefully controlled to match the defect shape and size and features of the target tissue. 3D printing technologies enable us to fabricate porous scaffolds with accurate control over their architectures and properties. On the other hand, 3D printing of shape morphing polymers has attracted great attentions in tissue engineering as scaffolds with shape morphing ability can reshape themselves after implantation to match the defect and anatomy of host tissues. Biomolecules such as growth factors have been often used in tissue engineering to accelerate tissue regeneration; and vascular endothelial growth factors (VEGF) is used in the regeneration of gastrointestinal tract and vasculature. In this study, an extrusion-based 3D printing system was used to construct porous scaffolds which have abilities of self-folding upon heating to the body temperature and controlled release of VEGF. For 3D printed scaffolds, the self-folding ability was achieved by using a shape memory polymer poly(D, L-lactide-co-trimethylene carbonate) (PDLLA-TMC) which could change shape at a temperature greater than 37°C, while the controlled release of growth factor was achieved by using gelatin methacrylate (GelMA) as the functional layer to load VEGF. In scaffold fabrication, a planar porous structure was firstly fabricated by accurate deposition of viscous PDLLA-TMC solution. The permanent tubular shape of PDLLA-TMC was made by folding printed planar porous structure into a tube on a glass stick at 80°C. Then PDLLA-TMC tubular porous structure was flattened at 25°C. Finally, GelMA loaded with VEGF was printed onto the PDLLA-TMC planar porous scaffold layer and crosslinked by UV. Shape morphing of PDLLA-TMC/GelMA-VEGF scaffolds was studied by immersing scaffolds in water at 37°C. Planar porous scaffolds could fold automatically into tubes within 60s. SEM examinations showed that interconnected macropores were regularly arranged on the scaffolds. In vitro release tests revealed a sustained and steady release of VEGF in the 21 day tests. For rat mesenchymal stem cells (rMSCs) seeded on scaffolds, LIVE/DEAD assay results indicated very good cell viability. MTT assay results showed good cell proliferation after 1, 4, 7-day culture. This study has demonstrated a good strategy to develop unique scaffolds for tubular tissues or organs such as vasculature and gastrointestinal tract.

S.SM09.02.08
A Versatile 3D Printed Layer Sandwiching Approach with Integrated Sensing for POC Diagnostics Ankit Kumar, Indian Institute of Technology Roorkee, India

Despite the recent advances in high-sensitivity lab-on-chip assays, adapting them for point-of-care settings remains a challenge due to the complexities in fabrication, and the need for an external measurement system. In this paper, I present a novel layer-sandwiching approach with an integrated Surface-Mount-Device (SMD) based on-chip absorbance measurement system, which allows for rapid prototyping of Point-of-Care (POC) assays.

In this approach, the layers are 3D printed using a 3DS Projet MJP Multijet printer which allows for the fabrication of 100 μm thickness flexible layers and sub-100 micron width channels. While the optical transparency of the material allows for on-chip signal acquisition, the use of SMD LEDs enables low power operation and the availability of a wide range of narrow emission spectrums. The sandwiched device has the middle layer as the flow layer and is sandwiched between two layers of parafilm. These three layers are then further sandwiched between an optical readout system. The hydrophilic nature of the 3D printed flow layer allows for a capillary-driven flow of reagents and the two parafilm layers prevent leakage. Because of the stacked nature of the layers, the device could also be disassembled, cleaned and reused.

The system was tested by performing MTT assay on-chip. For this test, human prostate cancer cells were treated with 20 μM Camptothecin in a standard 96 well plate. The cells were incubated for 24 hrs at 5% CO2 and 37°C. Then MTT dye was added and after 4 hrs of incubation, DMSO was added for dissolving the formazan crystals. Absorbance measurement for each well was performed separately on a spectrophotometer, and on the 3D printed device with 595 nm emission SMD-LEDs, and a strong correlation was found.

The proposed fabrication approach is far simpler than conventional methods. The high sensitivity, capillary-driven flow and the low cost of manufacturing make this system ideal for performing POC diagnostics assays, and other field assays where it’s not possible to carry the bulky and expensive measurement systems.

S.SM09.02.13
Effect of Heat Treatment on Grainscale Stress Relaxation and Microstructure of Additively Manufactured Ti-6Al-4V Caleb Andrews, Mitra Taheri, Cemile Basgül, Steven Kurtz, Tae Wook Heo, Ibo Matthews and Rongpei Shi; Johns Hopkins University, United States; Drexel University, United States; Lawrence Livermore National Laboratory, United States

2020 MRS Virtual Spring/Fall Meeting, November 27-December 4, 2020, Spring Abstracts Final Program 2/3/21
While additive manufacturing (AM) is capable of providing a method of producing geometrically complex and highly detailed structures that conventional manufacturing methods cannot, the generation of residual stress in many AM processes can negatively impact properties and performance. This research aims to address knowledge gaps in understanding how residual stresses are distributed at the grain and subgrain scale, the dislocation structures that accommodate these stresses, and how post-processing stress relief strategies effect this. Utilizing the selective laser melting (SLM) process, spinal cage implants were manufactured from ELI Ti64 powder which were then subjected to stress relieving heat treatment cycles above and below the Ti64 β transus as a function of time and cooling rate. Residual stress was than quantitatively measured via HR-EBSD and bulk properties informed via compression testing. It was found that grain scale stress decreased at an inversely proportional rate with heat treatment time, while the retention of β phase significantly changed the stress and dislocation distribution.

S.SM09.02.14
Thiol-ene Clickable Gelatin as Bioink for Biofabrication—Expanding the Fabrication Window through Macromolecular Cross-Linkers Sarah Bertlein1, Alessandro Cianciosi1, Bram G. Soliman2, Gabriella Brown2, Khoon S. Lim2, Tomasz Jungst1, Joerg Tessmar1, Gary J. Hooper2, Tim B. Woodfield2, Krystyna Albrecht1 and Jürgen Groll1; ¹University of Würzburg, Germany; ²University of Otago Christchurch, New Zealand

Biofabrication is a young field of research that aims at the automated generation of hierarchical tissue-like structures from cells and materials through Bioprinting or Bioassembly [1]. However, the lack of variety in printable hydrogel systems, which are the mainly used materials for the formulation of bioinks [2], is one major drawback for the advancement of the complete field [3]. Gelatin is often adopted for this purpose, usually modified with (meth-)acyryloyl functionalities for post-fabrication curing by free radical photo-polymerization, resulting in a hydrogel that is cross-linked via non-degradable polymer chains of uncontrolled length.

We have introduced GelAGE as a new thiol-ene clickable and broadly applicable alternative for gelatin-based bioinks [4]. The advantage of this system is the absence of non-degradable polymeric components after cross-linking compared to the free radical polymerization, as well as a better control over cross-linking density, and compatibility with Vis-light addressable initiator systems such as (Ru/SPS). Here we present the evolution of this system by stepwise altering the cross-linker from DTT to PEG-dithiol and star shaped 8-armed PEG-octathiol to multi-thiolated hyaluronic acid and finally a Hyaluronan-AGE / thiolated-Hyaluronan bioink as comparison. This led to a continuous improvement of the printability in terms of shape fidelity with decreasing overall polymer concentrations at constant cytocompatibility. We also present biological evaluation of this system for cartilage engineering.

References

SESSION S.SM09.04.04
Obtaining of a Pla-Ceramic Composite Filament Appropriate in Additive Manufacturing for Use in Tissue Engineering Glenda Glenda Biasotto1, Alex Lopera2,3, Marlon R. Fulla3, Maria A. Zaghetto1, Claudia Patricia Garcia3, Carlos Guillermo Paucar Alvarez7, Juan Luis Palacio Bedoya3, Hugo Armando Estupinan Duran1, Andres Montoya2, Juan Guillermo River2 and Sara Maria Robledo2; 1UNESP, Brazil; 2Universidad Nacional de Colombia, Colombia; 3Universitaria Pascual Bravo, Colombia

Calcium phosphates is the main material found in the bone; for this reason, they are used in the fabrication of scaffolds in tissue engineering applications. However, the application of these materials depends not only the formulation but also on the geometry of the bone to be replaced. 3D printing is positioned as a powerful tool for obtaining specific pieces for high-
Scaffold-based tissue engineering is a major approach in tissue engineering and cells and/or biomolecules can be loaded into the matrix or onto the surface of 3D scaffolds for enhancing tissue regeneration. Scaffolds mimicking the natural extracellular matrix of human tissues can serve very well as a substrate for cell attachment, proliferation, and differentiation and thus facilitate new tissue formation in vivo. The architectures (pore size, shape, interconnectivity, porosity, etc.) and properties (biological and mechanical) of scaffolds should be carefully controlled to match the defect shape and size and features of the target tissue. 3D printing technologies enable us to fabricate porous scaffolds with accurate control over their architectures and properties. On the other hand, 3D printing of shape morphing polymers has attracted great attentions in tissue engineering as scaffolds with shape morphing ability can reshape themselves after implantation to match the defect and anatomy of host tissues. Biomolecules such as growth factors have been often used in tissue engineering to accelerate tissue regeneration; and vascular endothelial growth factors (VEGF) is used in the regeneration of gastrointestinal tract and vasculature. In this study, an extrusion-based 3D printing system was used to construct porous scaffolds which have abilities of self-folding upon heating to the body temperature and controlled release of VEGF. For 3D printed scaffolds, the self-folding ability was achieved by using a shape memory polymer poly(D,L-lactide-co-trimethylene carbonate) (PDLLA-TMC) which could change shape at a temperature greater than 37°C, while the controlled release of growth factor was achieved by using gelatin methacrylate (GelMA) as the functional layer to load VEGF. In scaffold fabrication, a planar porous structure was firstly fabricated by accurate deposition of viscous PDLLA-TMC solution. The permanent tubular shape of PDLLA-TMC was made by folding printed planar porous structure into a tube on a glass stick at 80°C. Then PDLLA-TMC tubular porous structure was flattened at 25°C. Finally, GelMA loaded with VEGF was printed onto the PDLLA-TMC planar porous scaffold layer and crosslinked by UV. Shape morphing of PDLLA-TMC/GelMA-VEGF scaffolds was studied by immersing scaffolds in water at 37°C. Planar porous scaffolds could fold automatically into tubes within 60s. SEM examinations showed that interconnected macropores were regularly arranged on the scaffolds. In vitro release tests revealed a sustained and steady release of VEGF in the 21 day tests. For rat mesenchymal stem cells (rMSCs) seeded on scaffolds, LIVE/DEAD assay results indicated very good cell viability. MTT assay results showed good cell proliferation after 1, 4, 7-day culture. This study has demonstrated a good strategy to develop unique scaffolds for tubular tissues or organs such as vasculature and gastrointestinal tract.

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S.SM09.04.13
Effect of Heat Treatment on Grainscale Stress Relaxation and Microstructure of Additively Manufactured Ti-6Al-4V
Caleb Andrews1, Mitra Taheri1, Cemile Basgül2, Steven Kurtz2, Tae Wook Heo3, Ibo Matthews1 and Rongpei Shi3; 1Johns Hopkins University, United States; 2Drexel University, United States; 3Lawrence Livermore National Laboratory, United States

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S.SM09.04.14
Thiol-ene Clickable Gelatin as Bioink for Biofabrication—Expanding the Fabrication Window through Macromolecular Cross-Linkers
Sarah Bertlein1, Alessandro Cianciosi1, Bram G. Soliman2, Gabriella Brown2, Khoon S. Lim2, Tomasz Jungst1, Joerg Tessmar1, Gary J. Hooper2, Tim B. Woodfield2, Krystyna Albrecht1 and Jürgen Groll1; 1University of Würzburg, Germany; 2University of Otago Christchurch, New Zealand

Biofabrication is a young field of research that aims at the automated generation of hierarchical tissue-like structures from cells and materials through Bioprinting or Bioassembly [1]. However, the lack of variety in printable hydrogel systems, which are the mainly used materials for the formulation of bioinks [2], is one major drawback for the advancement of the complete field [3]. Gelatin is often adopted for this purpose, usually modified with (meth-)acryloyl functionalities for post-fabrication curing by free radical photo-polymerization, resulting in a hydrogel that is cross-linked via non-degradable polymer chains of uncontrolled length. We have introduced GelAGE as a new thiol-ene clickable and broadly applicable alternative for gelatin-based bioinks [4]. The advantage of this system is the absence of non-degradable polymeric components after cross-linking compared to the free radical polymerization, as well as a better control over cross-linking density, and compatibility with Vis-light addressable initiator systems such as (Ru/SPS). Here we present the evolution of this system by stepwise altering the cross-linker from DTT to PEG-dithiol and star shaped 8-armed PEG-octathiol to multi-thiolated hyaluronic acid and finally a Hyaluronan-AGE / thiolated-Hyaluronan bioink as comparison. This led to a continuous improvement of the printability in terms of shape fidelity with decreasing overall polymer concentrations at constant cytocompatibility. We also present biological evaluation of this system for cartilage engineering.

References

SYMPOSIUM S.X
* Invited Paper

SESSION S.X.01
Monday Morning, November 30, 2020
Symposium X

10:15 AM *S.X.01.01
The Golden Age of Materials Innovations—From High-k/Metal Gate to AI Hardware Vijay Narayanan; IBM T.J. Watson Research Center, United States

High-k/Metal Gates are ubiquitous in CMOS chips and are a product of intense collaborative research across academia and corporate labs. These new materials re-enabled a roadmap for CMOS scaling from FinFET (current) to Nanosheet (future) device architectures. However, CMOS scaling is slowing down with performance benefits diminishing with each node. At the same time, the need for consuming data has gone up exponentially with deep learning-based AI algorithms being deployed for this purpose and run on specialized AI hardware such as graphical processing units (GPU). However, GPUs consume significant power since data transfer occurs from memory to processor. Resistive Processing Units (RPU) envision artificial neural networks mapped to arrays of non-volatile memory (NVM) elements that execute operations in-memory and constant time, thereby enabling significant power performance benefits. Many NVM elements are being evaluated as RPU but suffer from significant non-idealities and are therefore ripe once again for innovation and collaboration across academia and industry.

Biography:
Vijay Narayanan received his BTech degree in metallurgical engineering from the Indian Institute of Technology, Madras (1995), and his MS degree (1996) and PhD degree (1999) in materials science and engineering from Carnegie Mellon University. After completing post-doctoral research at Arizona State University, Narayanan joined the IBM T. J. Watson Research Center in 2001 where he pioneered high-k/metal gate research and development from the early stages of materials discovery to development and implementation in manufacturing. These high-k/metal gate materials form the basis of all recent IBM systems processors and of most low-power chips for mobile devices. Currently, Narayanan is an IBM Fellow and senior manager at IBM Research where he is the strategist for Physics of AI and leads the team developing analog accelerators for AI applications. Narayanan is an IEEE Senior Member and was elected a Fellow of the American Physical Society in 2011. He is an author of over 100 journal and conference papers, holds more than 200 patents, and edited one book: *Thin Films On Silicon: Electronic And Photonic Applications.*

SESSION S.X.02
Tuesday Afternoon, December 1, 2020
Symposium X

4:00 PM *S.X.02.01
Socially-Directed Science and Technology—Opportunities and Challenges for the Field of Materials Science and Engineering Christine Ortiz; Massachusetts Institute of Technology, United States

We live in an era rife with social inequities and planetary perils, as the collective impact of humans threatens life on earth as we know it, radically transforming our societies and ecosystems. While science and technology and, in particular, the field of materials science and engineering has contributed enormous benefits to humanity, simultaneously it has also been entangled with and contributed to these formidable challenges. In re-imagining a more equitable and sustainable future, let alone bringing it into reality, we must acknowledge, interrogate and understand the historical context, root causes and systemic
structures that underpin the scientific and technological enterprise and our discipline, as well as the institutions of higher learning which serve as its foundation.

Science and technology, rooted in social inquiry, inclusion and equity, is more important than ever to our survival, let alone progress. This presentation will discuss a socially-directed approach to science and technology with a focus on the field of materials science and engineering and integration with humanistic fields such as history, the social sciences, including science, technology and society studies; social justice; and civic design and community-based participatory research, in order to interrogate, understand and shape technologically-driven societal impact towards more equitable, ethical and sustainable outcomes. Emerging areas will be considered such as circular materials design for socioreilient infrastructure, the Anthropocene, materials and environmental in/justice, fire safety materials, social inequity and disparate risks to fire, social life cycle assessment and the case of shipbreaking, ethics and socially-directed computational materials.

Biography:
Christine Ortiz is a scientist, engineer, professor, scholar, former dean and academic entrepreneur. Ortiz is the Morris Cohen Professor of Materials Science and Engineering at the Massachusetts Institute of Technology. Ortiz has over 180 scholarly publications, has supervised the research projects of more than 100 students from 10 different academic disciplines, and received 30 national and international honors, including the Presidential Early Career Award in Science and Engineering which was awarded to her at the White House by President George W. Bush. Ortiz served as the Dean for Graduate Education at MIT between 2010 and 2016, supporting approximately 7,000 graduate students from 100+ countries. With over 25 years of experience in higher education, Ortiz has led cross-institutional initiatives in global education, cross-disciplinary curriculum development, technology-enabled learning, and diversity, equity and inclusion. Ortiz was the founding principal investigator of the MIT University Center of Exemplary Mentoring sponsored by the Alfred P. Sloan Foundation. Ortiz has served on or chaired over 50 task forces, working groups, and committees in higher education. Ortiz served as a regional accreditation commissioner for the Commission on Institutions of Higher Education, New England Association of Schools and Colleges. Ortiz is the founder of a new nonprofit higher education institution, Station1, that is paving a pathway of opportunity through a new model of frontier learning and research — socially-directed science and technology.

SESSION S.X.03
Wednesday Morning, December 2, 2020
Symposium X

10:15 AM *S.X.03.01
Designing Biology Reshma Shetty: Ginkgo Bioworks, Inc., United States

Biology is the most powerful technology on the planet. It’s ability to self-repair, self-replicate and make atomically precise structures is unparalleled among manufacturing technologies. At Ginkgo, we are passionate about harnessing the power of biology by designing it. Unfortunately, despite significant advancements in recent years, the tools and technology for biological design remain woefully inadequate relative to the potential of biological technology. Our limited understanding of how biology works means that, for now, biological design is essentially a search problem. At Ginkgo, we are leveraging automation and software to build a genetic engineering foundry that allows us to more cheaply and scalably search potential biological design space for functional organism designs. In particular, I will highlight the value of combining computer-aided engineering software tools, cheap gene synthesis and high resolution-accurate mass LCMS to develop engineered microbes. Then, I'll discuss how we applied these technologies for improving a "living medicine" for the treatment of a metabolic disorder.

Biography:
Reshma Shetty co-founded synthetic biology Ginkgo Bioworks, Inc. in 2008. Spun out of MIT, Ginkgo’s mission is to make biology easier to engineer. Started in a Cambridge, Massachusetts, apartment, Shetty has helped to grow the company to 200 people and raised $450M in financing. In October 2018, Ginkgo launched Bioworks4, its fourth generation facility for design, fabrication and testing of custom designed microbes. Ginkgo is concurrently engineering more than 50 organisms to spec for customers including Ajinomoto, Cargill and ADM.

Shetty has been active in the field of synthetic biology for 10+ years and co-organized SB1.0, the first international conference in synthetic biology in 2004. In 2005, Shetty and colleagues founded OpenWetWare.org, a wiki for the free sharing of information among biological and biological engineering researchers. In 2006, she was an advisor to the
international Genetically Engineered Machines (iGEM) competition where she was best known for engineering bacteria to smell like bananas and mint. In 2008, *Forbes* magazine named Shetty one of Eight People Inventing the Future and in 2011, *Fast Company* named her one of 100 Most Creative People in Business. In 2014, Ginkgo became the first biotech company to participate in YCombinator. In 2018, *Business Insider* named her one of the most powerful female engineers. Shetty has a BS degree in computer science from the University of Utah and a PhD degree in biological engineering from MIT.