

SYMPOSIUM ET12

TUTORIAL: Advances in Synchrotron X-Ray and Quantum Monte Carlo Techniques with Applications to Functional Materials
November 25 - November 25, 2018

* Invited Paper

TUTORIAL Advances in Synchrotron X-Ray and Quantum Monte Carlo Techniques with Applications to Functional Materials

Sunday Afternoon, November 25, 2018
Hynes, Level 2, Room 203

This tutorial will be divided into two parts. In the first part, the instructor will introduce advanced synchrotron X-ray techniques, focusing on latest developments in coherent X-ray scattering to image defects in solids. In the second part, the instructor will introduce electronic-structure methods, focusing primarily on the latest advances in Quantum Monte-Carlo techniques, with concrete examples on computing different types of properties in solids, relevant for energy materials.

1:30 PM

Advances in Coherent X-Ray Scattering Techniques Dillon D. Fong; Argonne National Laboratory

Synchrotron X-ray methods allow observation of the structure and behavior of materials in their native environment or while undergoing transitions. The continuing advances in X-ray sources are leading to considerable improvements in the coherence of the beam and will eventually enable direct imaging of a material in a non-destructive fashion with atomic-scale resolution. In this tutorial, we will discuss the application of different synchrotron X-ray techniques to the study of materials, with a focus on imaging defects and investigating real-time defect behavior. Examples of current and future experiments exploiting coherence will be provided.

3:00 PM BREAK

3:30 PM

Advances in Quantum Monte Carlo Methods for Solids Luke Shulenburger; Sandia National Laboratory

Predicting properties of materials for energy applications, such as batteries, fuel-cells and photovoltaics, often stresses the capabilities of current electronic structure techniques, such as Density Functional Theory. This tutorial will initially give a broad overview of electronic-structure methods that are used to compute such properties, focusing on their strengths and weaknesses. It will then give a deep dive into the state-of-the-art of Quantum Monte-Carlo techniques as applied to the condensed phase. Concrete examples will be shown from recent calculations pertaining to the properties of functional materials.

SYMPOSIUM ET12

Harvesting Functional Defects in Energy Materials
November 26 - November 29, 2018

Symposium Organizers

Panchapakesan Ganesh, Oak Ridge National Laboratory
Marina Leite, University of Maryland
Annamaria Petrozza, Istituto Italiano di Tecnologia
Hua Zhou, Argonne National Laboratory

Symposium Support

Advanced Photon Source at Argonne National Laboratory

* Invited Paper

SESSION ET12.01: Revealing Roles of Functional Defects in Semiconductor Solar Cells
Session Chairs: Filippo De Angelis and Marina Leite
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room 313

1:30 PM *ET12.01.01

The Versatility of Mesoscopic Solar Cells Anders Hagfeldt; ISIC, EPFL, Lausanne, Switzerland.

In our work on solid-state dye-sensitized solar cells (ssDSSC) we have recently shown that copper phenanthroline complexes can act as an efficient hole transporting material. We prepared ssDSCs with a novel organic dye WS-72 and $[\text{Cu}(\text{tmby})_2]^{2+/+}$ as redox system and achieved record power conversion efficiencies for ssDSCs of 11.7%. Our best DSC efficiency of 13.1% for a liquid Cu-complex electrolyte is achieved by the discovery that the PEDOT based counter electrode can be directly contacted with the dye/ TiO_2 photoelectrode. Thus, there is no space between the two electrodes minimizing diffusion limitations and fill factors up to 0.8 is achieved.

In our work on perovskite solar cells (PSC) we have achieved efficiencies above 22% with a mixed composition of iodide/bromide and organic and inorganic cations. With the use of SnO_2 compact underlayers as electron acceptor contacts we have constructed planar perovskite solar cells with a hysteresis free efficiency above 20%. Through the compositional engineering larger perovskite grains grown in a monolithic manner are observed and reproducibility and device stability are improved. With regards to lifetime testing, we have shown a promising stability at 85 °C for 500 h under full solar illumination and maximum power point tracking (95% of the initial performance was retained). Recently, we have also commented on the standardization of PSC aging tests.

2:00 PM ET12.01.02

Active Materials and Interfaces for Stable Perovskite Solar Cells Antonio Abate; Helmholtz Berlin, Berlin, Germany.

Halide perovskites are quickly overrunning research activities in new materials for cost-effective and high-efficiency photovoltaic technologies. Since the first demonstration from Kojima and co-workers in 2009, several perovskite-based solar cells have been reported and certified with rapidly improving power conversion efficiency. Recent reports demonstrate that perovskites can compete with the most efficient inorganic materials, while they still allow processing from solution as a potential advantage to deliver a cost-effective solar technology.

Compare to the impressive progress in power conversion efficiency; stability studies are rather weak and often controversial. An intrinsic complication comes from the fact that the stability of perovskite solar cells is strongly affected by any small difference in the device architecture, preparation procedure, materials composition and testing procedure.

In the present talk, we will focus on the stability of perovskite solar cells in working condition. We will discuss a measuring protocol to extract reliable and reproducible ageing data. We will present new materials and preparation procedures, which improve the device lifetime without giving up on high power conversion efficiency.

2:15 PM *ET12.01.03

Role of Functional Defects in $\text{Cu}_2\text{ZnSnS}_4$ Solar Cells Sai Gautam Gopalakrishnan, Kuang Yu and Emily A. Carter; Princeton University, Princeton, New Jersey, United States.

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS)-based solar cells, which are based on the kesterite structure of CZTS, constitute an inexpensive, beyond-Si photovoltaic (PV) technology. However, practical CZTS cells often suffer from low open-circuit voltage and poor efficiency. In the first part of the talk, we explain the fundamental origins of poor performance in CZTS, namely disorder in the Cu and Zn sub-lattices caused by anti-site defects. Based on a cluster expansion model built on density functional theory (DFT) calculations, we find that a significant amount of lattice disorder can accumulate within the kesterite structure under typical synthesis conditions. Additionally, we find that Cu-vacancies can beneficially improve performance by reducing band gap fluctuations within bulk CZTS.

One pathway to reduce anti-site defect formation in CZTS is to employ isovalent dopants, such as Cd^{2+} and Ag^+ for Zn^{2+} and Cu^+ , respectively, as suggested by previous experimental studies. Hence, in the second part of the talk, we focus on the effects of Cd- and Ag-doping within CZTS cells, based on our evaluation of the bulk stability, defect (and surface) energetics, and the electronic structure of doped CZTS using DFT-based simulations. Importantly, we find that Cd and Ag can increase efficiencies via contrasting mechanisms, depending on the dopant concentration and Cu-content available during synthesis. For example, we predict that Cd (Ag) stabilizes the lower (higher) band gap stannite (kesterite) structure at high concentrations. Similarly, we find that Cd does not influence the surface energetics of kesterite-CZTS, while Ag decreases the surface energies significantly, which would favor smaller particle sizes. Finally, we suggest the exploration of alternate abundant, non-toxic, isovalent dopants to improve the performance of CZTS.

2:45 PM ET12.01.04

Assessing the Role of Hydrogen in Fermi-Level Pinning in Chalcopyrite and Kesterite Solar Absorbers from First-Principles Calculations Joel B. Varley¹, Tadashi Ogitsu¹, Vincenzo Lordi¹, Kimberly Horsley², Alex DeAngelis² and Nicolas Gaillard²; ¹Lawrence Livermore National Laboratory, Livermore, California, United States; ²University of Hawaii, Honolulu, Hawaii, United States.

Understanding the impact of impurities in solar absorbers is critical to engineering high-performance in devices, particularly over extended periods of time. Here, we use hybrid functional calculations to explore the role of hydrogen interstitial (H_i) defects in the electronic properties of a number of attractive solar absorbers within the chalcopyrite and kesterite families to identify how this common impurity may influence device performance. Our results identify that H_i can inhibit the highly *p*-type conditions desirable for several higher-band gap absorbers and that H incorporation could detrimentally affect the open-circuit voltage (V_{oc}) and limit device efficiencies. Additionally, we find that H_i can drive the Fermi level away from the valence band edge enough to lead to *n*-type conductivity in a number of chalcopyrite and kesterite absorbers, particularly those containing Ag rather than Cu. We find that these effects can lead to interfacial Fermi-level pinning that can qualitatively explain the observed performance in high-Ga content CIGSe solar cells that exhibit saturation in the V_{oc} with increasing band gap. Our results suggest that compositional grading rather than bulk alloying, such as by creating In-rich surfaces, may be a better strategy to favorably engineering improved thin-film photovoltaics with larger-band gap absorbers.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and supported by the HydroGEN Advanced Water Splitting Materials Consortium, established as part of the Energy Materials Network under the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office.

3:00 PM BREAK

3:30 PM *ET12.01.05

Defects in Polycrystalline Solar Cell Absorbers—Addressing the Materials Science Paradigm at the Nanoscale Mariana I. Bertoni; School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, Arizona, United States.

The behavior of solar cells is very often limited by inhomogeneously distributed nanoscale defects. This is the case throughout the entire lifecycle of the solar cell, from the distribution of elements and defects during solar cell growth as well as the charge-collection and recombination during operation, to degradation and failure mechanisms due to impurity diffusion, crack formation, and irradiation- and heat-induced cell damage. This has been known for a while in the field of crystalline silicon, but inhomogeneities are far more abundant in polycrystalline materials, and are the limiting factor in thin-film solar cells where grain sizes are often on the order of the diffusion length.

We will show that the high penetration of hard X-rays combined with the high sensitivity to elemental distribution, structure, and spatial resolution offers a unique avenue for highly correlative studies at the nanoscale. We will present results on CdTe and Cu(In,Ga)Se₂ where carrier collection is directly correlated to the compositional and structural properties of the material under a large variety of synthesis and operating conditions. The segregation of copper at the grain boundaries of both solar absorbers will be discussed in detail as well as the impact to carrier collection efficiency. Furthermore, the kinetics of copper segregation during growth and processing will be presented.

4:00 PM ET12.01.06

Probing Defects in Solar Cell Materials Through Microscale-Resolved Tomography John M. Howard^{1,2}, Elizabeth Tennyson^{1,2}, Bernardo Neves^{2,3} and Marina S. Leite^{1,2}; ¹Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, United States; ²Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, Maryland, United States; ³Department of Physics, Federal University of Minas Gerais, Belo Horizonte, Brazil.

Our society's pressing need for low-cost photovoltaics has triggered an incessant search for materials that can provide high-performance devices, with stable power conversion efficiency. From this class of materials, CIGS is a promising option, with world record efficiency > 22%. Yet, its open-circuit voltage is currently the limiting factor for higher performance. Here, we build a 3D tomography of the voltage response of CIGS solar cells by means of wavelength-dependent photovoltage measurements using confocal optical microscopy. Using only three wavelength-dependent photovoltage scans, we elucidate the spatial variation in the electrical behavior of CIGS devices and assign the voltage response to the top (10 nm thick), the middle (100 nm thick), and the bottom (1000 nm thick) of the thin film. We investigate four devices to compare the influence of their chemical composition and processing method on performance: CIS, Ag-CIS, CIGS with one-step deposition, and CIGS with 3-step deposition processes. We find that, in all cases, the middle section of the tomography map corresponds to the highest yield in voltage (~80% of the overall signal). The Ag-CIS device presents the highest voltage response (192 μV), in agreement with macroscopic measurements. These materials present photovoltage values that negatively contribute to the overall device performance, which is related to the non-radiative recombination centers caused by the boundaries composing the absorbing layers. Our paradigm paves the way for reconstructing the 3D electrical response (voltage and current) of a variety of energy harvesting systems, ranging from photoelectrochemical devices to nanostructured catalysts and perovskite solar cells.

4:15 PM ET12.01.07

The Role of Hydrogenation on Defect Passivation and Enhanced Performance of GaInNAs Solar Cells Amrit Kaphle¹, Ganga R. Neupane¹, Vincent R. Whiteside², Collin R. Brown², Khalid Hossain³, Mohamed A. Khalfioui⁴, Mathieu Leroux⁴, Ian Sellers² and Parameswar Hari¹; ¹Physics and Engineering Physics, Univ of Tulsa, Tulsa, Oklahoma, United States; ²Homer L. Dodge Department of Physics and Astronomy, The University of Oklahoma, Norman, Oklahoma, United States; ³Amethyst Research Inc, Ardmore, Oklahoma, United States; ⁴CRHEA-CNRS, Valbonne, France.

In this study, we present recent results that show the enhanced performance of GaInNAs solar cells by passivating the defects using a UV-activated hydrogenation process. We have studied four cells, a reference cell with no hydrogenation and three cells with low (0.10×10^{15} atoms/cm²), medium (0.50×10^{15} atoms/cm²), and high (1.1×10^{15} atoms/cm²) level of hydrogen incorporation. Previous work has indicated this process improves the performance of a GaInNAs solar cell by a factor of three through passivation of larger nitrogen-nitrogen related complexes and defects [1]. Here, the capacitance-voltage analysis is used to further understand the nature of this passivation in improving solar cell performance. It will be shown that hydrogenation is very effective in enhancing the depletion width and lowering the background doping concentration via the passivation of non-radiative centers in the absorber region. For the reference cell, a narrow depletion width of 206 nm and background doping concentration of 1.7×10^{16} cm⁻³ was measured. As the hydrogen passivation level is increased to high, the depletion width increased to 768 nm, and this resulted in a decrease in background doping concentration to 2.0×10^{15} cm⁻³. We also analyzed the density of trap states using admittance spectroscopy for different levels of hydrogenation. It was observed that hydrogenation is effective for passivating the trap concentration from 7.4×10^{15} cm⁻³ to 8.7×10^{14} cm⁻³. However, the trap energy is almost constant at 0.30 eV for all the level of hydrogenation. Impedance measurements at different applied biases were also performed to investigate minority carrier lifetimes. The minority carrier lifetime increased from ~ 2 μs to ~ 6 μs as hydrogen passivation level increased from low to high. [1] M. Fukuda, V.R. Whiteside, J.C. Keay, A. Meleco, I.R. Sellers, K. Hossain, T.D. Golding, M. Leroux, and M. Al Khalfioui, Appl. Phys. Lett. **106**, 141904 (2015).

4:30 PM ET12.01.08

Ab Initio Defect Characterisation of Candidate Solar Absorber Sb₂Se₃ Christopher Savory^{1,4}, Laurie Phillips², Jon Major² and David O. Scanlon^{1,3,4}; ¹University College London, London, United Kingdom; ²University of Liverpool, Liverpool, United Kingdom; ³Diamond Light Source Ltd., Didcot, United Kingdom; ⁴Thomas Young Centre, London, United Kingdom.

As the world's demand for energy increases, the need for technologies that can efficiently and sustainably generate energy are crucial to our society's development. Photovoltaics are a rapidly developing renewable market, with capacity growing by a multiple of 57 from 2000 to 2015, to a total of 227GW, a higher rate than the growth in demand for electricity. ¹ While the price of silicon, the market leader PV material, has decreased in these recent years, the most cost-effective (\$/W) absorber material remains CdTe, which only requires nanometre-thin films to absorb light efficiently. Nevertheless, the toxicity of Cd and low abundance of Te remain potential issues for global deployment of the technology.

In this study, we examine another potential thin-film absorber material, antimony selenide. In our ab initio calculations, we have found that Sb₂Se₃ has an ideal pseudodirect 1.3eV band gap and shows a spectroscopically limited maximum efficiency² of 28% for a film thickness of 200nm, at which CdTe

would have a value of 20% - demonstrating its extremely efficient absorption. Cell efficiencies for Sb_2Se_3 have, however, historically been low, at close to 5%. In the past 2 years, however, a number of reports have pushed this efficiency to 7%, and discussed potential resistance to the negative effects of grain boundaries, however measured V_{oc} are still low in comparison with the band gap of the material.³⁻⁵ Here, together with our experimental collaborators at the University of Liverpool, we attempt to characterise the deep defect levels within Sb_2Se_3 that could be limiting its performance. We calculate the transition levels for all intrinsic defect environments in the structure using hybrid Density Functional Theory, and compare them to DLTS measurements performed on a 7.9% efficiency cell to identify detrimental recombination centres. From our results, we can propose a strategy to minimize the impact of these deep defects, and identify potential methods to passivate them and so allow Sb_2Se_3 to reach cell efficiencies that could compete with other champion solar absorbers.

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4:45 PM ET12.01.09

Device Model for Intermediate Band Materials Eduard C. Dumitrescu, Matthew Wilkins and Jacob J. Krich; Physics, University of Ottawa, Ottawa, Ontario, Canada.

High concentrations of deep-level forming defects in semiconductors can produce an intermediate band (IB) [1,2]. Such a band deep inside the standard semiconductor bandgap supports sub-gap optical transitions from the valence band and to the conduction band as well as carrier transport. IB materials have potential to produce highly efficient solar cells and photodetectors [3,4].

All efficient devices rely on careful design and modeling tools, but there are no existing device modeling tools for IB materials. We present for the first time a coupled Poisson and drift-diffusion device model with ability to simulate both standard semiconductors and IB materials, based on the finite element method (FEM), implemented using the FEniCS platform [5]. The model supports 2D and 3D devices. Semiconductor device models generally face challenges due to the large dynamic range needed to represent carrier concentrations and often need to use extended-precision arithmetic, implemented at the software level, to attain reliable results. We demonstrate high quality, well-converged results using standard 64-bit floating point numbers, allowing high-speed operation and efficient use of memory resources. Performance of the solver is demonstrated for standard semiconductors through comparisons with other simulation tools including TCAD Sentaurus.

We use this new device model to explore the optimization of an intermediate band solar cell, showing how to optimize device performance given fixed material quality, elucidating important figures of merit and design rules.

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- [2] Ertekin et al., *Phys Rev Lett* **108** 026401 (2012)
- [3] Okada et al., *App Phys Rev* **2** 021302 (2015)
- [4] Mailoa et al., *Nature Comm* **5** 3011 (2014)
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SESSION ET12.02: Design and Control of Functional Defects in Halide Perovskites for Solar Harvests
Session Chairs: Annamaria Petrozza and Rama Vasudevan
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 313

8:00 AM *ET12.02.01

Managing Defects in Metal Halide Perovskite Thin Films Vladimir Bulović; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Use of metal halide perovskites in practical solar cells and LEDs hinges on understanding, controlling and minimizing the parasitic non-radiative charge carrier recombination losses in thin films of these materials. In contrast to perovskite single crystals, which exhibit very low charge trap concentrations, a controlled growth of perovskites into polycrystalline thin film device layers often inadvertently introduces defects, with consequently reduced efficiency of active device structures. The talk will focus on the recent developments of methods for reducing the charge-trap density of polycrystalline perovskite films, and the demonstration of high-efficiency devices with improved perovskite films.

8:30 AM *ET12.02.02

Which Defects Matter in Perovskite Photovoltaics? Joanne Etheridge¹, Wei Li², Mathias Rothmann³, Yen Yee Choo⁴, Amelia Liu¹, Ye Zhu⁵, Udo Bach⁶ and Yi-Bing Cheng²; ¹Monash Centre for Electron Microscopy, Monash University, Clayton, Victoria, Australia; ²State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, China; ³Department of Physics, University of Oxford, Oxford, United Kingdom; ⁴Department of Materials Science and Engineering, Monash University, Clayton, Victoria, Australia; ⁵Department of Applied Physics, The Hong Kong Polytechnic University, Kowloon, Hong Kong; ⁶Department of Chemical Engineering, Monash University, Clayton, Victoria, Australia.

Photoactive perovskites show great potential for applications in solar cell devices, achieving remarkable power conversion efficiencies while using relatively low cost, low temperature solution chemistry for production. However, there remain many challenges, from stability in air and under photon irradiation to current density-voltage hysteresis.

In order to exploit the full potential of photoactive perovskites, it is critical to understand how macroscopic device performance depends on structure, from the micron to the atomic scale. Compared with the rigid diamond structure of silicon, the intrinsically flexible and versatile perovskite structure provides an entirely different structural landscape upon which to manipulate properties, such as optical bandgaps. Furthermore, it can accommodate a different class of structural defects which can influence and even enhance performance.

Here we investigate the relationship between local crystal structure, defect structure and device performance in strategically chosen perovskite photovoltaic devices using carefully devised low dose electron microscopy methods correlated with cathodoluminescence, photoluminescence and device characterisation. (We emphasise that special low dose transmission electron microscopy (TEM) methods and dry, ion-free TEM specimen preparation is imperative if an undamaged structure is to be observed [1,2].)

We characterize and compare structure-property relationships in two photovoltaic systems: the mixed organic mixed cation perovskite $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$ (with methylammonium, $\text{MA} = \text{CH}_3\text{NH}_3^+$ and formadinium, $\text{FA} = \text{NH}_2\text{CH}=\text{NH}_2^+$ and $x=0, 0.15, 0.5, 0.8, 0.9$ and 1) [3] and the more structurally stable pure inorganic $\text{CsPbI}_{(1+x)}\text{Br}_{(2-x)}$ [4].

We reveal the different crystal structures and defect structures induced by varying composition and identify how these in turn impact upon charge carrier recombination and device performance, providing insights into the structural environments necessary to optimise device performance.

[1] Rothmann MU, Li W, Zhu Y, Liu A, Ku, Bach U, Etheridge J, Cheng YB; *Advanced Materials* 1800629 (2018)

[2] Rothmann MU, Li W, Etheridge J, Cheng YB *Advanced Energy Materials* 7 23 (2017)

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9:00 AM ET12.02.03

Understanding Perovskite PV Materials from a Defect Perspective Yi-Yang Sun; Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China.

Being a new class of materials achieving commercially competitive efficiency in an amazingly short period, the halide perovskites have set a new horizon for photovoltaic (PV) research. The success has been largely attributed to the unusual defect properties of the halide perovskites. In particular, the materials exhibit surprising defect tolerance even when synthesized by low-cost solution-based methods. The common understanding has been that the halide perovskites are “free” of deep defect levels which usually serve as efficient carrier recombination centers and are detrimental to the solar cell efficiency. While density functional theory calculations using semi-local functionals without including spin-orbit coupling (SOC) support this view, high-level calculations such as those using a hybrid functional including SOC suggest the existence of deep levels. Another puzzle is that the solution-produced halide perovskites exhibit high resistance suggesting an ultralow concentration of the shallow defects, which is at odds with the low formation energy of these defects. In this talk, we attempt to address these puzzles by a systematic comparison of the calculated defect transition levels and formation energies for hybrid halide perovskite, pure inorganic halide perovskites, as well as chalcogenide perovskites using different levels of methods. It is expected that the results will shine a light on the understanding of the role of defects in the perovskite PV materials.

9:15 AM ET12.02.04

Heterovalent Doping and Defect Formation in Metal Halide Perovskite Material Pabitra Nayak¹, Michael Sendner³, Bernard Wenger¹, Zhiping Wang¹, Kshama Sharma², Robert Lovrincic³, P. K. Madhu² and Henry Snaith¹; ¹University of Oxford, Oxford, United Kingdom; ²TIFR Centre for Interdisciplinary Sciences, Hyderabad, India; ³InnovationLab, Heidelberg, Germany.

Optoelectronic devices based on intrinsic Pb halide perovskites (HaP) based semiconductors have shown wide applications in the recent past. There have been several attempts to introduce heterovalent metal ions (e.g., Li^{+1} , Bi^{+3} , Sb^{+3} etc.) in the perovskites in an attempt to induce electronic doping and increase the charge carrier density in the semiconductor. It has been reported that inclusion of heterovalent metal such as Bi^{+3} decreases the bandgap of the material considerably. However, contrary to the earlier conclusions, despite a definite change in the appearance of the crystal as observed by eye, here we show that bandgap of MAPbBr_3 crystals does not change due to the presence of Bi^{+3} in them. Formation of optically active defects states in the band gap region and use of very thick samples for the transmission measurements erroneously give the impression of bandgap shift. Moreover, we find that all the claims regarding the bandgap narrowing in single crystals reported in many reputed journals in the past are also incorrect. Our finding also eliminates the ambiguity regarding the range of bandgap values reported for a single type of perovskite material. We find the bandgap values for the thin film and crystals for a MAPbI_3 is same. In the Bi^{+3} doped crystals, we find that the microstrains and the density of sub-bandgap state (defects) increase due to the inclusion of Bi ions in the crystal. These bandgap states also act as non-radiative recombination centers in the crystals. Our findings give a clear indication of the impact of heterovalent (Bi^{+3}) doping and also highlights the challenges which need to be resolved for this to be of real use. This latter aspect is of critical importance to reach the perovskite research community so that researchers can be mobilized to investigate how to dope HaP materials effectively.

9:30 AM ET12.02.05

Passivation and Photo-Brightening in Metal Halide Perovskites Bernard Wenger, Julian Godding and Henry Snaith; University of Oxford, Oxford, United Kingdom.

Lead halide perovskites show impressive optoelectronic properties as demonstrated by their high radiative efficiencies and power conversion efficiencies in photovoltaic devices surpassing 20%. Since this is rather exceptional for materials synthesized directly from precursors in solution with simple coating techniques, the quality of semiconducting lead halide perovskites has sometimes been attributed to their “defect tolerance”. [1] However, substantial improvements of radiative efficiency can be obtained by various post-deposition treatments. The effectiveness of such passivation techniques demonstrates clearly that these materials do suffer from defects and, moreover, that these defects are likely to be localised at the surface of grains in polycrystalline films.

In this contribution, we investigate several passivation strategies, compare them and also combine them for the model MAPbI_3 perovskite as well as for high performing mixed cation, mixed halide perovskite such as $\text{FA}_x\text{Cs}_{1-x}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$.

First, we discuss the effect of passivation by the addition of Lewis bases, such as pyridine and related organic molecules. Then, we investigate the effect of

several monovalent cations salts (e.g. K^+) which have been recently shown to improve massively the photoluminescence efficiency of triple cation (MA/FA/Cs) perovskites and allowed for the fabrication of highly efficient thin film solar cells [2]. Finally, we compare (and combine) the addition of passivation agents with the photo-brightening effects obtained when exposing the perovskites to light in air in the presence of moisture.

Combining optical, electronic and materials characterisation techniques, we propose a detailed mechanism leading to passivation and demonstrate a new approach to further improve the radiative efficiency by a simple post-deposition treatment.

References

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9:45 AM BREAK

10:15 AM *ET12.02.06

Defect Photochemistry of Lead-Halide Perovskites Filippo De Angelis; CNR-ISTM, Perugia, Italy.

An outstanding property of lead-halide perovskites is the incredibly low band-gap to open circuit voltage loss, which in optimized devices is close to the thermodynamic limit (1.6 eV gap; 1.3 V voltage, loss 0.3 V).[1] The high open circuit voltage is extremely attractive for both photovoltaics and water splitting. These observations suggest an apparently low density of carrier traps in MAPbI₃, contrary to the expectedly high defect density of a low-temperature, solution-processed material, suggesting that metal halide perovskites are inherently defect tolerant due to dominant defects introducing only shallow traps in the material band-gap.[2]

We present an overview of first-principles computational analyses devoted to understanding the outstanding optoelectronic properties of lead-halide perovskites. We show that despite the fairly high defect density due to Pb- and MA-related defects, less abundant iodine defects introduce deep electron and hole traps in MAPbI₃. [3-5] The peculiar iodine redox chemistry leads, however, to kinetic deactivation of filled electron traps, leaving only short-lived hole traps as potentially harmful defects. [6,7] Hole traps can be eventually converted to electron traps under mild oxidizing conditions, clarifying the surprising material defect tolerance.

Exposing the material to light may initiate light-induced annihilation of iodine defects, that may explain the reversible enhanced PL quantum yield repeatedly observed. Under high irradiation intensity of short wavelength, however, bimolecular photochemical transformations of such iodine defects may start to prevail, leading to PLQ quenching and eventually to material degradation. [8]

Identifying the key factors underlying defect photochemistry in lead-halide perovskites may allow to further improve the material optoelectronic quality and can represent the basis for development of new materials with similar target characteristics, possibly avoiding the environmental risks posed by lead.

References

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10:45 AM ET12.02.07

Broadband Excitonic and Trap-Assisted Emission in Cs₃Bi₂I₉ Nanocrystals Giuseppe M. Paternò², Nimai Misra¹, Alex J. Barker², Zhiya Dang¹, Guglielmo Lanzani², Liberato Manna¹, Annamaria Petrozza² and Daniele Cortecchia²; ¹Nanochemistry, Istituto Italiano di Tecnologia, Genova, Italy; ²Center for Nanoscience and Technology, Istituto Italiano di Tecnologia, Milano, Italy.

In the recent past, lead-based perovskite nanocrystals (NCs) have received significant attention for their unique optical and electronic properties¹. This lead-based perovskite nanostructures with chemical formula APbX₃ (A: Cs, CH₃NH₃ (MA), X=Cl, Br, I) have been reported with high PL quantum efficiency (PLQE), tunable quantum confined emission, large absorption cross section, and low-threshold for lasing. However, the toxicity of the lead² and stability in air limits its practical application³.

Here, we present a study on ligands-capped lead-free Cs₃Bi₂I₉ nanocrystals showing unprecedented structured and broadband (200 nm) emission. We attribute such features to the recombination of self-trapped excitons mediated by ligand vibrations and to the emission from trap-states. Given these interesting features, we envisage application of these materials in solid-state lightning.

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11:00 AM ET12.02.08

Tailoring the Broadband Emission Properties of 2D Perovskites Through Synthetic Design Daniele Cortecchia¹, Tetiana Borzda¹, Stefanie Neutzner¹, Benny Febriansyah², Jason England³ and Annamaria Petrozza¹; ¹Centre for Nano Science and Technology, Istituto Italiano di Tecnologia, Milan, Italy; ²Energy Research Institute @ NTU(ERI@N), Nanyang Technological University, Singapore, Singapore; ³Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore.

Two-dimensional (2D) perovskites are attracting increasing interest for application in photonic and light emitting devices. These low dimensional structures are characterized by great synthetic versatility which allows the incorporation of a wide range of organic cations for the fine-tuning of their optoelectronic properties. The excitons confined in these quantum-well-like structures strongly interact with the highly polar perovskite lattice and determine their characteristic optical properties. [1] Through careful material's engineering, it is possible to modulate the emissive properties from narrowband luminescence with high colour purity, to ultrabroad and highly Stokes shifted luminescence. Such broadband emission is generally attributed to trap states with wide energy distribution originating from exciton-self trapping phenomena. [2,3] Although recent progresses suggest that broadband emission is favoured in case of strong distortion of the inorganic lattice [2,4], a full understanding of the interplay between the material's structure and

defectivity/luminescence properties is still missing, urging the synthesis and analysis of a broader range of materials.

In this work, we report the study of a series of novel 2D perovskites combining temperature dependent and time resolved spectroscopic measurements with structural characterization. We exploit the templating properties of different organic cations to control the structural arrangement of the inorganic motif and show that increased distortion of the octahedral coordination promotes the exciton self-trapping process enhancing the contribution of broadband photoluminescence. On the other hand, we demonstrate that optoelectronically active organic cations (e.g. naphthyl and pyrene based organic molecules) can be used to further tune the luminescence properties of the hybrid perovskite.

Our findings extend the understanding of the processes underpinning broadband luminescence in 2D perovskites and provide fundamental guidelines for the synthetic design of efficient emitters with tunable luminescent properties.

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11:15 AM ET12.02.09

Investigation of Structural and Compositional Defects in Hybrid Organic-Inorganic Triple Cation Perovskite Films and their Effect on Optoelectronic Properties [Tiarnan Doherty](#)¹, Stuart Macpherson¹, Duncan Johnstone⁵, Andrew J. Winchester², Mojtaba Abdi Jalebi¹, Julia Parker⁴, Paul Quinn⁴, Giorgio Divitini⁵, Paul Midgley⁵, Keshav Dani², Hugh Simons³ and Samuel D. Stranks¹; ¹Cavendish Lab, University of Cambridge, Cambridge, United Kingdom; ²Femtosecond Spectroscopy Unit, Okinawa Institute of Science and Technology, Onna, Japan; ³Technical University of Denmark, Fysikvej, Denmark; ⁴Diamond Light Source, Oxfordshire, United Kingdom; ⁵Department of Materials, University of Cambridge, Cambridge, United Kingdom.

Metal halide perovskites are exceptional candidates for inexpensive next generation optoelectronic devices. State-of-the-art perovskite photovoltaic devices exhibit performance characteristics competitive with other thin film technologies (i.e., power conversion efficiencies exceeding 22%). The passivated embedded semiconductor layers demonstrate > 90% internal photoluminescence quantum efficiency; results that are remarkable given their short development timeframe. This pace of development has been so extraordinary in fact, that empirical device improvements have outpaced the complete physical understanding of the materials. For example, the nature of the defects contributing to parasitic non-radiative losses and hindering device performance remains unclear. Understanding the origin of these defects, structural or otherwise, and how to advantageously exploit them will enable the fabrication of devices approaching their theoretical limits.

In this talk we will detail a multiscale approach to determine 1) the nature of the defects, 2) their effect on the electronic properties of (MA,FA,Cs)Pb(I_{0.8}Br_{0.2})₃ thin films and 3) how a number of the most promising passivation strategies modify defects on the nanoscale and subsequently reduce trap state densities. We spatially correlate high-resolution nano x-ray diffraction and nano x-ray fluorescence maps obtained on the I14 nanoprobe beamline at Diamond Light Source, with scanning electron diffraction, scanning transmission electron microscopy - energy dispersive x-ray, photoluminescence, and photoemission maps to reveal that strain related structural defects have a significant impact on the nanoscale and microscale optoelectronic properties of perovskite thin films.

Our work reveals important information on the relevance of defects in the operation of state-of-the-art perovskite optoelectronic devices, which is critical to inform future defect engineering and passivation strategies. We also detail correlated multimodal characterisation techniques with nanoscale spatial resolutions that are applicable to a wide range of inherently beam sensitive materials.

11:30 AM ET12.02.10

Compensation of Intrinsic Point Defects by Extrinsic Substitution in Lead-Based Mixed Halide Hybrid Perovskites [Arun Kumar Mannodi Kanakkithodi](#)¹, Ji-Sang Park², Duyen H. Cao¹, Nari Jeon¹, Alex Martinson¹ and Maria K. Chan¹; ¹Argonne National Laboratory, Lemont, Illinois, United States; ²Imperial College London, London, United Kingdom.

An issue of critical importance in lead-based halide perovskites, much sought-after class of semiconductors in photovoltaics (PV) research, is defects; “deep” defect levels can prove catastrophic for PV performance by causing non-radiative carrier recombination^[1], whereas impurity induced energy levels in the band gap could lead to increased absorption of sub-gap photons which can enhance efficiencies^[2]. While experimental detection of defects is non-trivial and identification of the origin of defect states is usually impossible, density functional theory (DFT) calculations have been widely applied to accurately predict defect formation energies and transition levels^[3]. In this work, we use DFT to study various intrinsic and extrinsic point defects in mixed bromide/chloride MAPbBr_{3-y}Cl_y perovskites (MA = methylammonium) with varying compositions (y = 0, 0.75, 1.5, 2.25, 3), where the calculated band gap increases from ~ 2 eV for y = 0 to ~ 2.6 eV for y = 3. We simulated all vacancy, self-interstitial and anti-site defects, as well as several transition metal substitution defects at the Pb site and calculated their formation energies in different charged states as a function of the chemical potential of relevant species and the Fermi level in the semiconductor as it moves from the valence band maximum (VBM) to the conduction band minimum (CBM). Our results revealed that in MAPbBr₃, vacancy defects (V_{MA}, V_{Pb} and V_{Br}) are dominant acceptor and donor defects and only create shallow transition levels (i.e., close to the VBM or CBM), while higher energy defects create deeper levels; this is in good agreement with the computational literature^[4]. The equilibrium Fermi level changes from inside the VB (very p-type conductivity) to mid-gap (intrinsic conductivity) on going from Br-rich to Pb-rich chemical potential conditions. Upon adding Cl to the system, it is seen that vacancy defects are again the lowest energy defects and the equilibrium Fermi level follows the same trend as in MAPbBr₃, but halogen vacancies (V_{Br} and V_{Cl}) create deeper levels in the band gap the higher the value of y, indicating that in mixed Br/Cl or pure Cl perovskites, there is a danger of non-radiative recombination of carriers owing to deep defect levels. Further, several extrinsic substituents like Se, Y, Zr, Nb and Hf are shown to compensate for the dominant intrinsic defects in MAPbBr₃, MAPbBr_{1.5}Cl_{1.5} and MAPbCl₃ by creating lower formation energy defects and shifting the equilibrium Fermi level towards the CBM, thus making the semiconductor conductivity more n-type. These substituents can not only help overcome the adverse effect of deep intrinsic defects, but their mid-gap states can potentially be exploited for intermediate band PV applications^[2].

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11:45 AM ET12.02.11

Polarization, Mixed Conductivity and Deep Level Defects in Organometallic Halide Perovskites Artem Musiienko², Pavel Moravec², Roman Grill²,

Igor Vasylenko², Jakub Pekarek², Katka Ridzonova², Belas Eduard², Jeremy Tisdale¹, Bin Hu¹, Eric Lukosi³ and Mahshid Ahmadi¹; ¹Joint Institute for Advanced Materials, University of Tennessee, Knoxville, Tennessee, United States; ²Institute of Physics, Charles University, Prague, Czechia; ³Nuclear Engineering, The University of Tennessee, Knoxville, Tennessee, United States.

Understanding the type, formation energy and capture cross section of defects is one of the challenges in the field of organometallic halide perovskite (OMHP) devices. In more matured semiconductors like Si, the knowledge of defects was one of the major factor in successful technological implementation. This knowledge and its control can make a paradigm in development of OMHP devices. Yet there is limited information on the properties of defects in OMHPs and controversy on the nature and role of these defects. Several studies explained that main intrinsic defects are only shallow level defects leading to long carrier diffusion length and carrier life time coupled to efficient OMHP devices suggesting a class of materials with low concentration of defects and/or highly defect tolerance¹. Recently, it was revealed that the performance of OMHP devices is mainly limited by Shockley-Read-Hall recombination confirming that defects are dynamic elements and have a critical role in development of OMHP devices^{1,2}. Therefore, deep localized defects exist and limit the operation of highly efficient OMHP devices. It is crucial to fundamentally understand how deep levels can explain the long carrier life time and how this characteristic can be used practically in development of OMHP devices. The non-radiative defect assisted carrier recombination is particularly important in operation of solar cells for higher Voc and in detectors for high charge collection efficiency. In this work, we provide a profound insight into crucial electrical and transport properties of OMHPs based on single crystal MAPbBr₃ device. The space charge dynamics associated with charged deep level defects was studied by time-of-flight technique (ToF) driven by pulse voltage bias. We have previously shown that current waveform (CWF) used in ToF technique is sensitive to space charge near the contacts³, which deforms the electric field inside the device and enables evaluation of the space charge parameters. Such modification of ToF allows us to determine the effect of deep levels on material transport properties such as lifetime, carrier mobility, and electric field profile. Using CWF ToF measurements and polarization theory, we explored polarization dynamic and transport properties of MAPbBr₃ single crystals. In order to determine deep level activation energy and capture cross section, for the first time photo-Hall effect spectroscopy (PHES) with enhanced illumination in both steady and dynamic regimes was used. Using these measurements with tunable photon energies, we revealed the inner-bandgap electrical structure of MAPbBr₃ single crystals and the activation energy and capture cross section of deep level defects was estimated.

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SESSION ET12.03: Elucidating Roles of Defects in Operating Fuel Cell Materials and Devices
Session Chairs: Daniele Cortecchia and Panchapakesan Ganesh
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 313

1:30 PM *ET12.03.01

Surface-Terminating Grain Boundaries as Active Sites for Oxygen Electrochemical Reactions Sossina M. Haile¹, Ichiro Takeuchi² and Robert E. Usiskin³; ¹Northwestern University, Pasadena, California, United States; ²Materials Science and Engineering, University of Maryland, College Park, Maryland, United States; ³Max Planck Institute for Solid State Research, Stuttgart, Germany.

Lanthanum strong manganite is the canonical cathode for solid oxide fuel cells. It offers a valuable balance between electrochemical activity, chemical stability, and thermomechanical compatibility with the widely used electrolyte, yttria stabilized zirconia (YSZ). Despite its widespread implementation, questions regarding the reaction pathway for oxygen electroreduction on this material remain open. Here, a fundamental study of the reduction mechanism is carried using thin film methods. Libraries of (La_{0.8}Sr_{0.2})_{0.95}MnO_{3+δ} (LSM) thin film microelectrodes with systematically varied thickness or growth temperature were prepared by pulsed laser deposition, and a novel robotic instrument was used to characterize these libraries in automated fashion by impedance spectroscopy. All impedance trends are consistent with a reaction pathway involving oxygen reduction over the LSM surface followed by diffusion through the film and into the electrolyte substrate. The surface activity is found to be correlated with the number of exposed grain boundary sites, which decreases with either increasing film thickness (at constant growth temperature) or increasing film growth temperature (at constant thickness). These findings suggest that exposed grain boundaries in LSM films are more active than exposed grains towards the rate-limiting surface process, and that oxygen ion diffusion through polycrystalline LSM films is faster than several prior studies have concluded.

2:00 PM *ET12.03.02

Dopant and Vacancy Distribution in Doped Ceria and Its Influence on the Oxide Properties—Theoretical Approach Natalia Skorodumova^{1,2}; ¹Materials Science and Engineering, The Royal Institute of Technology (KTH), Stockholm, Sweden; ²Physics and Astronomy, Uppsala University, Uppsala, Sweden.

Transition metal oxides are often doped in order to tune their performance for particular applications. It is generally known that the properties of doped oxides are sensitive to the details of dopant distribution and its dynamics, however, reports demonstrating exact structure – properties relations are still rare. Here, taking Gd-doped ceria as an example, we show how the ordering of dopants and oxygen vacancies varies with temperature and concentration. The phase diagram for the Gd-doped ceria has been determined by means of a combined Density Functional Theory (DFT), cluster expansion and lattice Monte Carlo approach. In the thermodynamic equilibrium, we observe two transitions: an onset of oxygen-vacancy ordering at ~ 1300K–3300K for concentrations xGd = 30 – 100% and then, below ~ 1000 K, a phase separation into CeO₂ and C-type Gd₂O₃ for the whole concentration interval (xGd = 0 – 100%). We also observe that the immobilisation of cations below 1500 K does not prevent the oxygen-vacancy C-type order from forming. We demonstrate that this oxygen-vacancy ordering transition noticeably influences the lattice parameter, bulk modulus and elastic moduli of Gd-doped ceria as well as its oxygen-ion conductivity.

2:30 PM ET12.03.03

Atomic-Scale Structure and Stability of Dopant-Defect Complexes at Misfit Dislocations in CeO₂/MgO Heterointerfaces Pratik P. Dholabhai; School of Physics and Astronomy, Rochester Institute of Technology, Rochester, New York, United States.

Complex oxide heterostructures and thin-films have emerged as promising candidates for diverse applications, wherein interfaces play a critical role in

influencing novel properties not present in individual components. In Solid Oxide Fuel Cells (SOFCs), oxide thin films and heterostructures have found applications as advanced electrolytes. Lattice-mismatched epitaxial growth of oxide films on substrates above a critical thickness lead to the formation of misfit dislocations, which influence vital material properties. We have employed atomistic simulations to investigate the influence of misfit dislocations on dopant-defect complexes at CeO₂/MgO heterointerfaces. In this case, the experimentally observed (110)_{CeO₂}|| (100)_{MgO}|| interface orientation relationship has been utilized. For ionic conductivity applications, trivalent dopants are generally added to CeO₂, as they have a net effective charge that affects the electroneutrality condition, which lead to the formation of oxygen vacancies. In bulk electrolytes, at low temperatures, dopants and oxygen vacancies form complexes that influence oxide ion conductivity. However, at misfit dislocations, the role of dopant-defect complexes is not well understood. We find that the complexes shaped by trivalent dopants and oxygen vacancies have diverse structures at the heterointerfaces. We have considered various scenarios wherein the nearest-neighbor bonding environments within the complexes are altered for different trivalent dopants. As opposed to the grain interior, the thermodynamic stability of oxygen vacancy is found to be sensitive to the dopant arrangement at the heterointerface. Stability of extended dopant-defect structures at the misfit dislocations reveal that such complexes would influence ionic transport at heterointerfaces. Overall, our results offer a fundamental atomic-scale perspective of the dopant-defect behavior in the neighborhood of misfit dislocations at complex oxide heterointerfaces.

2:45 PM ET12.03.04

Decoding the Surface Instability of Perovskite Oxides at the Atomic Level—Sr Segregation in La_{1-x}Sr_xMnO_{3±δ} SOFC Electrodes Franziska Hess and Bilge Yildiz; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

One of the most important and best-studied perovskite materials for energy conversion applications is La_{1-x}Sr_xMnO_{3±δ} (LSM). It is a promising material for Solid Oxide Fuel Cell (SOFC) electrodes that exhibits superior electronic conductivity, oxygen reduction kinetics and thermal stability. As the oxygen exchange at the surface is typically rate-limiting, tuning of the electrode surface is a key aspect in the development and optimization of materials for energy conversion applications. Sr-doped perovskite materials form passivating Sr-rich layers and particle on the surface due to segregation of the dopant strontium ions. This surface layer inhibits the oxygen exchange at the surface, thus increasing polarization resistance and reducing the energy efficiency of the SOFC.

Although the basic features of the LSM defect chemistry have been well-understood for at least 20 years based on experiments, the more detailed aspects (such as antisite defects and A/B ratio) and their possible implications for Sr segregation are not understood. Due to the large variety of defect species, the surface and bulk defect chemistry of LSM (as well as other perovskites) have not been explored in detail with computational methods in the past. As a consequence, there is little consensus in the literature about the nature and driving force of Sr segregation.

We assess the stability of LSM over a wide range of T and p(O₂) using a combination of DFT calculations on the GGA+U level and DFT-based thermodynamics. We apply these methods to examine the stabilities of the LSM(001) surface and the LSM bulk. We find the clean LSM(001) surface to be unstable and prone to reconstructions and defect segregation.

Considering a wide variety of near-surface defects, as well as the growth of SrO as clusters, particles or homoepitaxial layers, we come to the conclusion that Sr segregation should be self-limiting because the surface dipole moment is removed by SrO overlayers that do not cover the entire surface. These surface terminations are stable and not prone to further segregation of Sr.

Experimental studies report the formation of SrO particles on the surfaces of Sr-doped perovskites after annealing, while our findings suggest that these large quantities of Sr cannot come from the surface. We considered the formation of a SrO phase as a new type of defect reaction in a new defect model for LSM that considers all of the defects mentioned above. We find that the equilibrium Sr content in LSM varies considerably within the relevant range of T and p(O₂), which can effortlessly explain the experimentally observed formation of SrO under SOFC operating conditions, as well as the experimentally observed onset temperature of Sr segregation.

These results allow us to develop a knowledge-based doping strategy that prevents Sr segregation in LSM. Our modeling strategy and principle findings are transferable to other perovskite oxides.

3:00 PM BREAK

3:30 PM *ET12.03.05

A Protonated Brownmillerite Electrolyte for Superior Low-Temperature Proton Conductivity Pu Yu^{1,2}, ¹Tsinghua University, Beijing, China; ²RIKEN, Wako, Japan.

Design novel solid oxide electrolyte with enhanced ionic conductivity forms one of the Holy Grails in the field of materials science due to its great potential for energy applications. Conventional solid oxide electrolytes typically require elevated temperature to activate the ionic transportation, while it has been increasing research interests to reduce the operating temperature due to the scientific and technological importance. In this talk, I will introduce our recent efforts to design a conceptually new solid oxide electrolyte, H₂SrCoO_{2.5}, which shows an enhanced proton conductivity at low temperature region. Combining both the experimental results and corresponding first-principles calculations, we attribute these intriguing properties to the extremely-high proton concentration as well as the well-ordered oxygen vacancy channels inherited from the novel crystalline structure of H₂SrCoO_{2.5}. These results provide a novel strategy to design solid oxide electrolyte with excellent proton conductivity for energy-related applications.

4:00 PM ET12.03.06

Tuning Brownmillerite Phase Stability—Bottom Up and Top Down Le Wang, Zhenzhong Yang, Yingge Du, Mark Bowden and Peter V. Sushko; Pacific Northwest National Laboratory, Richland, Washington, United States.

Recently, brownmillerite (BM) phase oxides are of particular interest as they accommodate a large number of ordered oxygen vacancies on regular perovskite lattice sites. Such vacancies produce both oxygen-ion conduction and electronic conduction, and the former could be exploited in electrolytes in solid-oxide fuel cells and in oxygen-separation membranes. So a better understanding the BM phase formation and evolution process will give us further insight into the oxygen-diffusion paths of solid oxygen-ion conductors. Here, we report on the epitaxial growth of high quality SrFeO_{3-x} (SFO) single crystalline films on LaAlO₃ (001) substrates by pulsed laser deposition. By tuning the deposition oxygen pressure and post-annealing, the orientation of the oxygen vacancy channels (OVCs) in the BM-SFO structure can be converted from a horizontal to a perpendicular direction related to substrate surface direction via the XRD and STEM measurements. For the BM-SFO films deposited under 0.01 mTorr, all the OVCs are along the horizontal direction while a certain portion of the perovskite phase SFO (P-SFO) still exists near the SFO/LAO interface, which contributes some electrical conductivity and optical non-transparent characteristic. The proportion of this P-SFO portion increases and some perpendicular direction OVCs appear when increasing the deposition oxygen pressure. However, for the BM-SFO film deposited under 300 mTorr and postannealed under 0.01 mTorr, most of the OVCs are along the perpendicular direction. In-plane transport and ellipsometry measurements confirm that the BM-SFO with perpendicular OVCs shows the higher resistivity and larger optical transition energy. Our theoretical calculations provide certain insights into the exceptional BM phase formation process for the SFO films grown on LAO substrate, which is in good agreement with our experimental observation. Our results display a comprehensive experimental study on how the deposition oxygen pressure and postannealing control the brownmillerite phase formation and evolution and then influence the structural, optical and electronic properties of SFO films.

4:15 PM ET12.03.07

Defect Engineering of Bulk Al₂O₃ and the Al₂O₃/Al Interface to Enhance Its Hydrogen Permeation Barrier Properties Vrinda Somjit and Bilge Yildiz; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Hydrogen is a promising clean fuel. A key bottleneck to its widespread utilization is the susceptibility of the materials used in hydrogen storage and transport infrastructure (typically steels) to embrittlement and failure. This necessitates the use of permeation barriers to prevent hydrogen ingress into the steel. Al₂O₃ has been established as a popular hydrogen permeation barrier material, due to its low hydrogen solubility and diffusivity. The goal of this study is to further enhance the permeation resistance of Al₂O₃ by two means: point-defect engineering of the Al₂O₃ bulk, and space-charge engineering of the Al₂O₃/Al interface, to reduce the overall hydrogen solubility and diffusivity of the system.

To evaluate the performance of the Al₂O₃ bulk, a combination of first principles calculations and thermodynamic concepts were used to obtain defect concentrations in undoped and doped Al₂O₃. Our findings aid in the identification of suitable dopants that result in superior hydrogen permeation resistance of bulk Al₂O₃. Donor dopants like Ti, Si, Fe or Cr drastically reduce the concentration of free hydrogen interstitials (the primary diffusible defect under room temperature H₂ gas transport conditions) to negligible amounts, with majority of the total hydrogen concentration trapped at aluminum vacancy sites with high binding energy (~3 eV). Hydrogen is thus rendered immobile, with reduced diffusivity in Al₂O₃. In addition, Fe and Cr doping aid in decreasing the overall hydrogen solubility to 1/4 and 1/2 that of the undoped case respectively.

To evaluate the performance of the Al₂O₃/Al interface, first principles methods and continuum modeling were used to establish and tune the nature of the interfacial core and space-charge layer to lower the hydrogen solubility and diffusivity. Accounting for the interfacial band offset and variation in the local environment through defect segregation energies, Poisson's equation is self-consistently solved to obtain the defect equilibria at the interface. Moreover, dopants have a large tendency to segregate to the Al₂O₃/Al interface, and thus are used to regulate the nature and extent of this space charge. This study thus aids in the atomic-level understanding of the impact of the Al₂O₃/Al interface on overall hydrogen permeability of the coating. This study also helps rationalize experimental findings that multilayer coatings of Al₂O₃/Al have superior permeation resistance than a single layer of Al₂O₃ of the same thickness.

It is emphasized that the results of this study can also be extended to other systems where the metal/oxide interface (and interphase formation) affects device efficiency, such as the electrode/electrolyte interface in resistive switching devices and the metal/dielectric interface in MOS devices.

4:30 PM ET12.03.08

Discovery of Proton-Conducting Ceramic Fuel Cell Materials Using Genetic Algorithm Yeong-Cheol Kim¹, Ki-Yung Kim¹, Yurie Kim², Jason Kim² and Jun-Yeong Jo¹; ¹School of Energy Materials and Chemical Engineering, KoreaTech, Cheonan, Korea (the Republic of); ²Department of Creative IT Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of).

BaCeO₃ and BaZrO₃ have been the most studied electrolyte materials for proton-conducting ceramic fuel cells for the last four decades. BaCeO₃ shows high conductivity and good sinterability, but poor stability under CO₂ atmosphere. BaZrO₃ shows good stability, but poor sinterability and low conductivity at grain boundaries. Mixing these two materials to take advantage of the merits of both materials have been a trend, and recently BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O₃ (BZCYYb4411) was introduced as a best electrolyte, replacing BZCYYb1711 [1]. Y and Yb are dopants to generate oxygen vacancies in the electrolyte materials.

As researchers have increased the number of components to improve the material properties, they had to invest more time and money to investigate the vast materials composition space. We used genetic algorithm to save time and money in searching the vast structure space for better materials. We converted structures into chromosomes and applied crossover, mutation, and compensation to generate next-generation chromosomes. Based on the best chromosomes, we added water molecules to fill the oxygen vacancies. Genetic algorithm was applied again to find optimum configurations of protons in the structure. This technique was also applied to air electrode materials to find optimum solid solution configurations.

Reference

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4:45 PM ET12.03.09

Control of Oxygen-Vacancy Distribution and Intergranular Amorphous Phases to Boost the Ionic Conduction in Perovskite-Oxide Electrolytes Sung-Yoon Chung; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

ABO₃-type perovskites are one of the oxide families where various ionic defects can be created by changing the oxygen partial pressure and adding proper dopants. Among many notable physical properties and transport phenomena observed in perovskites, aspects of high proton conductivity have been intensively investigated in zirconates and cerates over the past three decades in efforts to elucidate the precise conduction mechanisms and further improve the ionic conductivity for real applications as electrolytes in solid-oxide fuel cells operated at intermediate temperature. In the first part of this presentation, we demonstrate that the proton conductivity can be notably enhanced by the association of acceptor dopants and oxygen vacancies in BaZrO₃ and BaCeO₃. The acceptor-vacancy clustering is verified to be remarkably efficient against proton trapping by theoretical DFT calculations and experimental measurements based on impedance spectroscopy along with atomic-scale direct visualization (*Angew. Chem. Int. Ed.* **55**, 13499 (2016)). In addition to the impact of defect association, we clarify that a nanometer-thick amorphous phase at grain boundaries in proton-conducting BaCeO₃ polycrystals is responsible for substantial retardation of proton migration in the second part of the presentation. By a combination of atomic-scale chemical analysis and physical imaging along with consideration of straightforward phase equilibria, it is demonstrated that highly densified BaCeO₃ polycrystals (>98% in relative density) free of a grain-boundary amorphous phase can be easily fabricated by a conventional ceramic process and show sufficiently high proton conductivity (order of 10⁻² S/cm at 600°C) and significantly improved chemical stability (*Nano Lett.* **18**, 1110 (2018)). These findings emphasize the value of direct identification of lattice defects and subsequent manipulation of their distribution in ion-conducting oxide polycrystals.

SESSION ET12.04: Poster Session: Harvesting Functional Defect in Energy Materials

Session Chairs: Panchapakesan Ganesh and Hua Zhou

Tuesday Afternoon, November 27, 2018

8:00 PM - 10:00 PM

Hynes, Level 1, Hall B

ET12.04.01

Preparation of Sol-Gel ZnO Layer Under Various Humidity for Organic Solar Cell Application Hyojin Song, Dongwook Ko, Seobum Chu and Jongbok Kim; Kumoh National Institute of Technology, Gumi, Korea (the Republic of).

The organic solar cells which convert incident light into the electricity comprises photoactive layer to absorb incident light, transport layer with charge selectivity, and the electrodes to collect the charges. Among them, it is very important to choose appropriate transport layer because transport layer suppresses charge recombination and enhances power conversion efficiency by blocking the holes(electrons) and transporting the electrons(holes) in electron(hole) transport layer. The zinc oxide (ZnO) with high electron mobility and hole blocking ability is a common material as an electron transport layer in organic solar cells. Such ZnO layer can be prepared various deposition approaches including magnetron sputtering and sol-gel process. People generally prefer to adopt sol-gel process because it is solution process, cheap and fast process. To deposit ZnO layer via sol-gel process, the humidity is very important because it affects hydration phenomena. However, it is not clear how much the humidity affect the characteristics of ZnO layer and their effects on organic solar cells.

Here, we investigated the characteristics of ZnO layer prepared in different humidity and then explored their effects on the actual devices of organic solar cells. Specifically, the humidity was adjusted from 15% to 80% to coat the ZnO layer. As a result of comparing efficiency of organic solar cell devices using these ZnO layer, it showed the highest efficiency of 8.30% at 25% of humidity. In order to confirm the effect on the efficiency change, the surface characteristics, optical characteristics and defects were analyzed. To investigate the effect of humidity on the thickness and roughness of the ZnO thin film, the Alpha step and AFM were analyzed and the optical characteristics were analyzed by measuring the transmittance. The defects in the organic solar cell were defective through XPS and PL because the charge recombination reduced the efficiency. From the efficiency of organic solar cell device and analysis results, It is thought that ZnO produced at 25% humidity is most suitable as ETL layer of organic solar cell.

ET12.04.02

Hydration of $\text{BaCe}_{1-x-y-z}\text{Zr}_x\text{Y}_y\text{Yb}_z\text{O}_{3-\delta}$ Using Genetic Algorithm Ki-Yung Kim¹, Yurie Kim², Jason Kim², Young-Bok Kim¹, Jun-Yeong Jo¹, Dong-Gung Shin¹, In-Gyu Choi¹ and Yeong-Cheol Kim¹; ¹School of Energy Materials and Chemical Engineering, KoreaTech, Cheonan, Korea (the Republic of); ²Department of Creative IT Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of).

Oxygen-conducting solid oxide fuel cells (SOFCs) have been actively studied as an alternative power source because they have high energy conversion efficiency and no use of precious metal catalysts. The high operating temperatures (800-1000°C), however, hinder durability and low fabrication costs of the SOFCs. Proton-conducting FCs is an alternative solution due to their low operating temperatures (400-600°C) [1].

Recently, $\text{BaCe}_{1-x-y-z}\text{Zr}_x\text{Y}_y\text{Yb}_z\text{O}_{3-\delta}$ that can be fabricated by mixing BaCeO_3 and BaZrO_3 with Y and Yb as dopants was introduced as an excellent electrolyte material [2]. $\text{BaCe}_{1-x-y-z}\text{Zr}_x\text{Y}_y\text{Yb}_z\text{O}_{3-\delta}$ can take advantage of the strong points of BaCeO_3 and BaZrO_3 ; BaCeO_3 shows high conductivity but low stability, while BaZrO_3 shows good stability but low grain boundary conductivity [3]. The material, however, shows many different configurations of Ce, Zr, Y and Yb atoms in the B site of the ABO₃ perovskite structure.

In this study, we employed genetic algorithm and lattice dynamics to find an energetically favorable $\text{BaCe}_{1-x-y-z}\text{Zr}_x\text{Y}_y\text{Yb}_z\text{O}_{3-\delta}$ solid solution structure. We also investigated the hydration process by adding water molecules to fill the oxygen vacancies that reside in the solid solution structure. The distribution of protons after hydration will be discussed based on the results of genetic algorithm and lattice dynamics.

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ET12.04.03

Equilibrium Space Charges Effect at Halide Perovskite Interactions—The Role of the Ionic Charge Conductions Gee Yeong Kim, [Alessandro Senocrate](#) and Joachim Maier; Max Planck Institute for Solid State Research, Stuttgart, Germany.

Methylammonium lead iodide (MAPI) is the archetype of the halide perovskites that are currently in the focus of photovoltaic research not only because of high conversion efficiencies but also because of intriguing long-time behavior. In this contribution we discuss equilibrium space charge effects at MAPI interfaces and concentrate on the implications for MAPI/TiO₂ and MAPI/Al₂O₃ contacts. Irrespective of polarization phenomena building up under operation, already the equilibrium situation is dominated by space charge effects. While such space charge effects are only considered as a consequence of electronic charge carrier redistribution, we will apply a generalized picture that discusses both ionic and electronic redistribution. In fact, we will show that the space charges are ionically dominated, in a sense that ions dictated the space charge potential and electrons follow the established field (fellow-traveler effect). Our analysis is based on the measurement of electronic and ionic conductivities in MAPI-TiO₂ and MAPI-Al₂O₃ composites, a technique that has been successfully applied in solid states Ionics [1-3]. The results are corroborated by Hall effect experiments.

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ET12.04.04

Fano Defect Induced Resonant Thermoelectric Transport in Metallic Nanowires [Chumin Wang](#), Fernando Sanchez and Vicenta Sanchez; Universidad Nacional Autonoma de Mexico, Mexico City, Mexico.

Fano defects consist of atomic chains attached to a low-dimensional system and produce rich wave interferences in its conductivity spectra [1]. Recently, we have analytically proved the existence of a novel ballistic conduction state in two-dimensional belts with a non-periodic arrangement of atoms in both its cross section and along the Fano plane defect [2]. Moreover, enhancements to the ballistic alternating current (AC) conductivity are reported when quasiperiodically placed Fano defects are introduced to a periodic chain or nanowire [3]. On the other hand, the direct conversion between thermal and electrical energies by thermoelectric devices has become an important alternative for the clean energy generation. Low-dimensional materials seem to be promising candidates, whose efficiency is determined by the dimensionless thermoelectric figure-of-merit (ZT) that can be calculated by using the Boltzmann formalism. The inherent correlation between the thermoelectric quantities, such as electrical and thermal conductivities, makes difficult to improve the value of ZT.

In this work, we study the thermoelectric properties of metallic nanowires with periodic and quasiperiodically placed Fano defects by means of a real-space renormalization plus convolution method [4] developed for the Kubo-Greenwood formula, in which tight-binding and Born models are respectively used for the study of electric and lattice thermal conductivities [5]. We analytically demonstrate the existence of a significantly improved ZT due to the Fano defects [6]. In addition, the numerical results suggest that the quasiperiodicity could be another important ZT enhancing factor, since it highly diminishes the thermal conduction of long wavelength acoustic phonons, which are responsible of the phononic conductivity at low temperature and not easy to block their transmission since they do not feel local defects neither impurities [7].

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SESSION ET12.05: Harvesting Functional Defects for Photoelectrochemistry
Session Chairs: Joanne Etheridge and Hua Zhou
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 313

8:00 AM *ET12.05.01

Effect of Surface and Bulk Defects on Hot Carrier Transport in Ultra-Thin Metallic Films Jeremy N. Munday; University of Maryland, College Park, Maryland, United States.

Photon absorption in metal films can result in the excitation of hot carriers, i.e. electrons and holes with kinetic energy in excess of their thermal distribution. For hot carriers generated within a diffusion length of the surface, opportunities arise for extraction of these energetic carriers, which can perform tasks not achievable by thermal electrons including modification of chemical reaction rates, charge injection into nearby semiconductors for current generation, etc. However, one of the key limitations on carrier transport and collection is defects. Both surface and bulk defects can cause carrier relaxation and forfeit their original benefits. Here we will discuss our recent work on excitation and collection of hot electrons from thin metal films and our attempts to mitigate the harmful effects of defects. We will show energy conversion and photodetector devices that can operate over both the visible and near-IR based on injection of hot carriers either into semiconductors or across insulating barriers into an adjacent conductor. We will also discuss future applications of this work for tailoring photon absorption and carrier lifetime.

8:30 AM ET12.05.02

Precise Design of Photocatalyst Heterostructure with Controllable Photo-Generated Carrier Behaviors for Solar to Fuel Conversion Kan Zhang^{1,2}; ¹Nanjing University of Science and Technology, Nanjing, China; ²Yonsei University, Seoul, Korea (the Republic of).

Solar-driven hydrogen (H₂) evolution has been considered as a clean, green and efficient strategy to solve the energy shortage and ameliorate environmental pollution. Heterogeneous photocatalysts comprising an excitable semiconductor and a H₂ evolution co-catalyst (HEC) are regarded as a standard configuration to drive efficient photocatalytic H₂ reaction. However, photocatalytic H₂ generation requires both efficient charge separation and redox steps to occur simultaneously. Loading a HEC on photocatalyst is an efficient means of extracting photogenerated charge carriers, host active sites for catalytic H₂ evolution and improve stability by suppressing photo-corrosion. However, H₂ generation in photocatalyst remains limited by the electron/hole mutual Coulomb interaction, which seriously inhibits spatial charge separation. When HECs are near the charge generation region of CdS, both electrons and holes can be localized via Coulomb interaction. This localization determines the wavefunction overlap with the HECs and trap states and retards the electron transfer rates. In this sense, generating a long-lived charge-separated state for delocalized electrons is crucial for efficient H₂ evolution while accelerating hole consumption by hole scavengers. In this talk, I will discuss how to control photo-induced electrons that successfully deliver to HECs sites towards highly efficient solar hydrogen evolution through structure design of nanomaterials.

8:45 AM ET12.05.03

Dispelling the Myth of Passivated Codoping in TiO₂ Benjamin A. Williamson^{1,2}, Nicholas P. Chadwick^{1,3}, Sanjayan Sathasivam¹, Claire J. Carmalt¹, Ivan P. Parkin¹ and David O. Scanlon^{1,2,4}; ¹Department of Chemistry, University College London, London, United Kingdom; ²Thomas Young Centre, University College London, London, United Kingdom; ³Bio Nano Consulting, London, United Kingdom; ⁴Diamond Light Source Ltd., Diamond House, Didcot, United Kingdom.

Modification of TiO₂ to increase its visible light activity and promote higher performance photocatalytic ability has become a key research goal for materials scientists in the past two decades. One of the most popular approaches to achieve this is “passivated co-doping”, whereby an equal number of donor and acceptor dopants are introduced into the lattice, producing a charge neutral system with a reduced band gap. From the multitude of codoped systems, [Nb+N] and [Ta+N] are widely regarded as the “archetypal” codoping pairs of doped anatase, however the literature results rarely claim 1:1 passivated codoping. Using state-of-the-art hybrid density functional theory, and using the [Nb+N] and [Ta+N] codoped systems as examples, we show that fully passivated TiO₂ is unrealisable due to the inherent doping asymmetry of anatase or any other n-type photocatalysts. This research critically discusses the future of passivated codoping as a mode of band gap modulation.

9:00 AM ET12.05.04

First Principles Modelling of Polaron Formation in TiO₂ Polymorphs Razak Elmaslman¹, Matthew Watkins² and Keith McKenna¹; ¹University of York, York, United Kingdom; ²University of Lincoln, Lincoln, United Kingdom.

We present a computationally efficient and predictive methodology for modelling the formation and properties of electron and hole polarons in solids.[1] Through non-empirical optimization of the fraction of Hartree-Fock exchange (α) in a hybrid functional, we ensure the generalized Koopmans' condition is satisfied and the self-interaction error is minimized. Our previous work in model systems has shown that accurate densities and energies can be obtained from such an optimization.[2] The approach is applied to model polaron formation in known stable and metastable phases of TiO₂ including anatase, rutile, brookite, TiO₂(H), TiO₂(R) and TiO₂(B). Electron polarons are predicted to form in rutile, TiO₂(H) and TiO₂(R) (with trapping energies ranging from -0.02 eV to -0.35 eV). In rutile the electron localizes largely on a single Ti ion, whereas in TiO₂(H) and TiO₂(R) the electron is distributed across two neighboring Ti sites. Hole polarons are predicted to form in anatase, brookite, TiO₂(H), TiO₂(R) and TiO₂(B) (with trapping energies ranging from -0.16 eV to -0.52 eV). In anatase, brookite and TiO₂(B) holes localize on a single O ion, whereas in TiO₂(H) and TiO₂(R) holes can also be distributed across

two O sites. We find that the optimized α has a degree of transferability across the phases, with $\alpha=0.115$ describing all phases well. We also note the approach yields accurate band gaps, with anatase, rutile and brookite within six percent of experimental values. We conclude our study with a comparison of the alignment of polaron charge transition levels across the different phases. Since the approach we describe is only two to three times more expensive than a standard density functional theory calculation, it is ideally suited to model charge trapping at complex defects (such as surfaces and interfaces) in a range of materials relevant for technological applications, but previously inaccessible to predictive modelling.

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9:15 AM ET12.05.05

Anomalous Conductivity Tailored by Domain Boundary Transport in Crystalline Bismuth Vanadate Photoanodes Wenrui Zhang¹, Danhua Yan¹, Jun Li¹, Qiyuan Wu², Jiajie Cen², Lihua Zhang¹, Alexander Orlov², Huolin Xin¹, Jing Tao¹ and Mingzhao Liu¹; ¹Brookhaven National Laboratory, Upton, New York, United States; ²Stony Brook University, The State University of New York, Stony Brook, New York, United States.

Carrier transport in semiconductor photoelectrodes strongly correlates with intrinsic material characteristics including carrier mobility and diffusion length, and extrinsic structural imperfections including mobile charged defects at domain boundaries, which collectively determines the photoelectrochemistry (PEC) performance. Here we elucidate the interplay between intrinsic carrier transport, domain-boundary-induced conductivity and PEC water oxidation in the model photoanode of bismuth vanadate (BiVO₄). In particular, epitaxial single-domain BiVO₄ and c-axis oriented multi-domain BiVO₄ thin films are fabricated using pulsed laser deposition to decouple the intrinsic and extrinsic carrier transport. In addition to the low intrinsic conductivity that is due to the small polaron transport within BiVO₄ domains, we identify anomalously high electrical conductivity arising from vertical domain boundaries for multi-domain BiVO₄ films. Local domain boundary conduction compensates the inherently poor electron transport by shortening the transport distance for electrons diffused into the domain boundary region, therefore suppressing the photocurrent difference between front and back illumination. This work provides insights for engineering carrier transport through coordinating structural domain boundaries and intrinsic material features in designing modulated water splitting photoelectrodes.

9:30 AM BREAK

10:00 AM *ET12.05.06

Tuning Catalytic Properties for Water Splitting with Functional Defects Xiaolin Zheng; Stanford University, Stanford, California, United States.

Defects, such as vacancies and dopants, offer rich opportunities to tune the catalytic properties of crystals. In this talk, we will present three examples on using defects to optimize the catalytic activity for water splitting and all examples are supported by density functional theory calculations and experimental results. The first example is related to the well-known hydrogen evolution reaction (HER) catalyst, MoS₂. For MoS₂, the perfect basal plane is chemically inert, but it can be activated by creating S-vacancies. In addition, the activity of the S-vacancy can be further tuned by either strain or transition metal modification. The second example is also related to another HER catalyst: WS₂. I will explain how the basal plane activity of WS₂ is activated and optimized by tuning Co doping configurations. The third example is switched to the water oxidation side for water splitting. I will demonstrate how rare earth doping enhances the activity, selectivity and stability of BiVO₄ towards H₂O₂ production.

10:30 AM DISCUSSION TIME

10:45 AM ET12.05.08

Enhancing Water-Splitting Performance of Hematite Photoanodes via Hydrogenation Induced Defects Hariom Jani^{1,2}, Mengyuan Zhang⁵, Lydia H. Wong^{4,5} and Thirumalai V. Venkatesan^{1,2,3}; ¹NanoCore, Singapore, Singapore; ²NUS Graduate School of Integrative Sciences and Engineering, National University of Singapore, Singapore, Singapore; ³ECE, National University of Singapore, Singapore, Singapore; ⁴Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, Singapore, Singapore; ⁵School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore.

Hematite (α -Fe₂O₃), is a photoanode material candidate for Oxygen Evolution Reaction in a Photo-Electro-Chemical cell (PEC). It has an optical bandgap (~2.1eV) which straddles the water oxidation and reduction potentials, allowing it to drive water splitting by absorbing solar radiation. Its chemical resistance, non-toxicity and low cost, make it a promising material to manufacture hydrogen in an environmentally friendly way. Unfortunately, its poor electrical conductivity, carrier transport dynamics and absorptivity, yield low solar-to-hydrogen conversion.

In my talk, I will present how we have used a special hydrogen treatment to systematically enhance the bulk electronic transport in Hematite Nanorods. We observe that hydrogen doping increases the electronic conductivity of α -Fe₂O₃, without changing its optical bandgap or its structural properties. Consequently the PEC performance of treated photoanodes is much higher than their pristine counterparts.

The novel hydrogenated phase of α -Fe₂O₃ is characterised by X-Ray Diffraction, Raman and UV-Vis Spectroscopy, Electron Microscopy and Impedance Spectroscopy. The physics underlying the electronic changes are elucidated by Ultrafast Optical-Pump Probe techniques, X-Ray Absorption and Ab-Initio calculations. Our work paves way to utilizing novel hydrogen induced defect states to systematically enhance functionality of oxide photoanodes.

11:00 AM ET12.05.09

Minimizing the Grain Boundary Effect by Dopant Segregation on Hematite Photoelectrodes for Solar Water Oxidation Aryane Tofanello¹, Andre Luiz M. Freitas^{1,2} and Flavio L. De Souza¹; ¹University Federal-ABC, Santo Andre-SP, Brazil; ²University of California, Santa Cruz, Santa Cruz, California, United States.

This work describes the effect of nitrogen atmosphere and chemical addition of different metal transition elements (M = Sn, Ti or Mn) on the hematite surface electrode and its impact on the photoelectrochemical performance (PEC). For comparison, undoped [Air or N₂-Fe₂O₃] and modified [Air or N₂-M-Fe₂O₃] hematite electrodes were prepared by aqueous solution precursor method under hydrothermal condition at low temperature and at fixed synthesis time (at 2 hours). The as-prepared materials were subjected to additional thermal treatment at 750 °C for 30 min in air and nitrogen (N₂) atmosphere. The undoped electrodes obtained after 2 hours of synthesis exhibited the columnar morphology with thickness around 300 nm. In case of undoped electrodes, treatment in nitrogen atmosphere (N₂-Fe₂O₃) promoted the oxygen vacancies formation (evidenced by X-ray photoelectron spectroscopy) leading to a better photocurrent response at 1.3 mA.cm⁻² at 1.23 VRHE. The chemical addition of metal transition elements (M = Sn, Ti or Mn) followed by the thermal treatment and monitored by top-view scanning electron microscopy (SEM) shows significant changes in the morphology. Additionally, to the morphology changes the “dopant” insertion seems to drastically reduce the grain growth, which increases the number of interfaces and surface area. Although the

surface area available for chemical reaction increases with the reduction of grain size, the increased number of interfaces or grain boundaries in hematite normally is a problem to the charge separation by acting as recombination sites. Surprisingly, the chemical addition of Sn and Ti, which was found to be segregated in the hematite grain boundaries, seems to reduce the energy in between grains facilitating the electron transport and enhancing the overall electrode performance. The impedance spectroscopy (Nyquist plot) data revealed that the combination of N₂ atmosphere with chemical addition of Sn or Ti significantly reduce the electrical resistance increasing the hematite performance for water oxidation assisted by sunlight independent of the final morphology.

11:15 AM ET12.05.10

The Role of Fluorine Doped Tin Oxide Substrate-Hematite Electrodes Interface in the Solar Water Oxidation Performance [Andre Luiz M. Freitas¹](#), Renato V. Goncalves² and Flavio L. De Souza¹; ¹UFABC, Santo Andre, Brazil; ²IFSC, USP, São Carlos, Brazil.

Despite the hematite fulfills most of the requirements as photoanode in a photoelectrochemical cell, some limitations still prevent its commercial application. The poor electron-hole separation is the major issue in hematite being responsible for the low photoelectrochemical performance. In fact, the extensive charge recombination in hematite mainly occurs at the interfaces such as substrate-hematite layer and hematite-hematite grains. This work describes the impact of the substrate-hematite interface in the overall photoelectrochemical performance. The thermal treatment has an important role not only to provide the phase transformation from precursor oxy-hydroxide phase but also on surface activation for the chemical reaction. The study was conducted firstly evaluating the influence of the temperature of thermal treatment in the fluorine-doped tin oxide (FTO) substrate and then, at the FTO-hematite interface. Considering all the techniques and data analysis, it was found that the fast annealing at 750°C for 30 minutes has achieved a synergy among to the resistance to charge transport, the optimal amount of Sn-diffused (a ratio Sn:Fe of 0.17) from the substrate that leads to a suitable reduction in the recombination rate at FTO-hematite interface. The observed photoelectrochemical performance for 750-fast annealing showed an improvement of photocurrent response achieving 0.54 mA cm⁻² at 1.23 V_{RHE} and shifting onset potential around 200 mV. It is worth mentioning that the overall improvement of the hematite electrode observed after the annealing process was attributed to a more efficient charge separation that does not compromise the properties of the FTO substrate (surface roughness and electronic conductivity). Therefore, more investigation is underway in the laboratory to increase even more the FTO-hematite interface since the optimized annealing process was found.

11:30 AM ET12.05.11

Defect Engineering in 1D Ti-W Oxide Nanotube Arrays and Their Correlated Photoelectrochemical Performance [Nageh K. Allam](#); American University in Cairo, New Cairo, Egypt.

Understanding the nature of interfacial defects of materials is a critical undertaking for the design of high-performance hybrid electrodes for photocatalysis applications. Theoretical and computational endeavors to achieve this have touched boundaries far ahead of their experimental counterparts. However, to achieve any industrial benefit out of such studies, experimental validation needs to be systematically undertaken. In this sense, we present herein experimental insights into the synergistic relationship between the lattice position and oxidation state of tungsten ions inside TiO₂ lattice, and the respective nature of the created defect states. Consequently, a roadmap to tune the defect states in anodically-fabricated, ultrathin-walled W-doped TiO₂ nanotubes is proposed. Annealing the nanotubes in different gas streams enabled the engineering of defects in such structures, as confirmed by XRD and XPS measurements. While annealing under hydrogen stream resulted in the formation of abundant Wⁿ⁺ (n<6) ions at the interstitial sites of the TiO₂ lattice, oxygen- and air-annealing induced W⁶⁺ ions at substitutional sites. EIS and Mott-Schottky analyses indicated the formation of deep-natured trap states in the hydrogen-annealed samples, and predominantly shallow donating defect states in the oxygen- and air-annealed samples. Consequently, the photocatalytic performance of the latter was significantly higher than those of the hydrogen-annealed counterparts. Upon increasing the W content, photoelectrochemical performance deteriorated due to the formation of WO₃ crystallites that hindered charge transfer through the photoanode, as evident from the structural and chemical characterization. To this end, this study validates the previous theoretical predictions on the detrimental effect of interstitial W ions. In addition, it sheds the light on the importance of defect states and their nature on tuning the photoelectrochemical performance of the investigated materials.

11:45 AM ET12.05.12

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis [Burcu Akata Kurc^{1,2}](#) and Duygu Kuzyaka²; ¹Central Laboratory, Middle East Technical University, Ankara, Turkey; ²Micro and Nanotechnology Department, Middle East Technical University, Ankara, Turkey.

The development of visible-light effective photocatalysts allows low cost degradation of toxic non-biodegradable organic pollutants. Vanadium, present in a specific oxidation state within the structure of SiO₂ matrix could open up the gateway to investigate and tailor the defects created for such photocatalytic applications. Vanadosilicate AM-6, which is a large pore microporous material containing semiconducting monatomic ...V-O-V-O-V... chains embedded in a silica matrix has recently been demonstrated to exhibit photocatalytic activity in the visible light range. Pore regularity, control of defects, and the presence of stoichiometric amounts of in AM-6 allows one to create alternative materials in visible-light photocatalysis. Accordingly, vanadosilicate AM-6 thin films with controlled defect sites were produced by tailoring the V⁵⁺/V⁴⁺ ratio within the thin film structure. Furthermore, the effect of changing molar composition and vanadium source used for the secondary growth was also investigated systematically. V⁵⁺/V⁴⁺ ratio was tailored systematically by controlling the defect concentration of seed crystals during the film growth and vanadium source with alternating V⁵⁺ concentration. It was found that vanadosilicate AM-6 films with higher amount of V⁵⁺ ions arising from different synthesis conditions possess better photocatalytic activity under visible light irradiation for the degradation of MB, which can be attributed to the presence of V⁵⁺ cation within the framework of AM-6. Photocatalyst production in the form of thin film provides integration of the material to device-oriented applications and also accelerates the degradation kinetics between the pollutant and the photocatalyst due to the controlled defect formation leading to enhanced photocatalytic activity under visible light.

SESSION ET12.06: How Functional Defects Dictate Semiconductors
Session Chairs: Panchapakesan Ganesh and Ekaterina Pomerantseva
Wednesday Afternoon, November 28, 2018
Hynes, Level 3, Room 313

1:30 PM *ET12.06.01

Dopability of Semiconductors in Relation to Chemical Composition and Crystal Structure Vladan Stevanović; Colorado School of Mines, Arvada, Colorado, United States.

Controlling electric transport in a semiconductor material via doping is essential for a range of important applications. These include standard microelectronics, which is almost entirely enabled by the ability to dope silicon both p- and n-type, but also the less established technologies such as thermoelectric and transparent (invisible) electronics. However, unlike silicon, many materials cannot be doped at all and those that can, often exhibit strong doping asymmetry favoring only one doping type, i.e., either p or n, but not both. The latter is particularly evident in wide band gap semiconductors such as SnO₂ or ZnO, which are known as exclusively n-type dopable, but the strong asymmetry is also observed in many systems with smaller gaps such as Zintl thermoelectrics (e.g. ZnSb), which are ubiquitously p-type. In this talk, I will present and discuss our recent efforts in modeling point defects in semiconductors, in particular in relation to understanding and predicting their dopability. The focus of the work is on establishing quantitative relationships between the dopability of semiconductors on one side, and their chemical composition and crystal structure on the other, with the main purpose to advance design and discovery of novel optoelectronic and thermoelectric materials. In addition, I will examine more closely our recent prediction of bipolar dopability in the metastable, high-pressure rocksalt phase of ZnO, and discuss significant prospects it implies to overcoming doping asymmetry of semiconductors through polymorphism.

The work is supported by the US National Science Foundation.

2:00 PM ET12.06.02

Predictive Design of Defects in Non-Ideal Ternary Nitrides—Off-Stoichiometry, Contamination and Disorder Jie Pan¹, Jacob Cordell^{1,2}, Andriy Zakutayev¹, Adele Tamboli¹ and Stephan Lany¹; ¹National Renewable Energy Laboratory, Golden, Colorado, United States; ²Colorado School of Mines, Golden, Colorado, United States.

II-IV-V₂ ternary nitrides offer many advantages in enhancing functionality for optoelectronic applications. For example, ZnSnN₂ (ZTN) is a promising absorber material for photovoltaic (PV) applications and ZnGeN₂ (ZGN) can be used in light emitting devices. However, the properties of multinary compounds strongly depend on the materials nonidealities, e.g., disorder, stoichiometry, and impurities. For example, in practice, the growth of ZTN thin film incorporates a non-trivial amount of oxygen. The excess amount of oxygen can lead to cation off-stoichiometry, i.e., Zn excess, and disorders in the material. The conventional dilute-defect model does not capture these non-ideal conditions. In this contribution, we present a predictive defect model of these complex ternary nitrides with disorder, off-stoichiometry, and oxygen contamination, e.g., Zn_{1+x}Sn_{1-x}N_{2-2x}O_{2x}, and their effects on materials properties, such as band gap, carrier localization, absorption coefficients, and defect equilibria. The disordered structures were created by Monte Carlo (MC) simulation with simplified Hamiltonians, such as motif-Hamiltonian and cluster expansion. The MC generated structures were then passed on to electronic structure calculations for disordered and off-stoichiometric structures. These calculated changes in the band structure were then fed back to the materials property predictions, such as net doping, defect equilibrium.

2:15 PM ET12.06.03

Effect of Extended Defects on Electrical Properties in Earth Abundant Inorganic Materials Ji-Sang Park¹, Sunghyun Kim¹, Maria K. Chan² and Aron Walsh¹; ¹Imperial College London, London, United Kingdom; ²Argonne National Laboratory, Lemont, Illinois, United States.

In diamond and zinc-blende structure semiconductors, the stacking sequence can be altered by a missing layer or an additional layer and combinations of them. These extended defects, which is termed as stacking faults, can be regarded as local wurtzite phase in the zinc-blende host, and the material properties are affected accordingly. In a material with at least two types of cation, anti-site domain boundaries, which are periodic arrays of anti-site defects, can be formed as well. We have investigated the extended defects in Cu₂ZnSn(S, Se)₄ and Si to obtain a general understanding of the defects [1,2].

Cu₂ZnSn(S, Se)₄ based solar cells have attracted much attention for achieving terawatt scale photovoltaics. While the problem of the open-circuit voltage deficit has not been resolved yet, spatial fluctuations of the band edges by disorder have been regarded as the origin of the deficit. Our hybrid density functional theory calculations indicate that the extended defects also have a role in the lower photovoltaic efficiency [1]. The anti-site domain boundaries, another type of disorder, lower the conduction band. The fact that the anti-site domain boundaries act as electron capture can be understood by the formation of metastable polymorphs or Sn anti-site defects. On the other hand, stacking faults in the material act as electron barriers, while their formation is more likely than the anti-site domain boundaries which formation was experimentally observed. Cation substitutions can promote or suppress the formation of stacking faults.

We also found that the stacking faults affect the stability of point defects. It is known that stacking faults are formed in Si solar cells after the potential induced degradation of shunting type happens. Our calculation shows that the Na interstitials are more stable at the stacking faults where the Na becomes less mobile [2]. Based on the calculation results, we suggest that Na atoms are accumulated at the stacking faults after a long time of operation because of the segregation. Effect of the stacking faults on the device will be discussed.

References

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Acknowledgement

J.-S.P. thanks the Royal Society for a Shooter International fellowship. The work at ICL received funding from the European H2020 Framework Programme for research, technological development and demonstration under grant agreement no. 720907. See <http://www.starcell.eu>. The work at ANL was supported by Laboratory Directed Research and Development (LDRD) funding under Contract No. DE-AC02-06CH11357. Use of the Center of Nanoscale Materials was supported under Contract No. DE-AC02-06CH11357.

2:30 PM BREAK

3:30 PM *ET12.06.04

Oxygen Vacancy in Complex Oxides—The Good, the Bad and the Ugly Ho Nyung Lee; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Functional ionic defects, such as oxygen vacancies, play a central role in the performance of many advanced information and energy materials. While of immediate benefit for low temperature energy production and storage devices and sensors, the ability to artificially control oxygen vacancy content in any environment is also crucial for variety of functional materials, such as high-temperature superconductors, colossal magnetoresistors, memristors, and

spintronic devices. On the other hand, for some of functional materials, such as ferroelectrics, the formation of oxygen vacancies is highly detrimental for the performance and endurance of the ferroelectric polarization. However, achieving deliberate control of the oxygen stoichiometry in the oxide thin films has not been much studied, albeit critical for the performance. In this presentation, I will review a synopsis of the major developments and achievements in formation, control, and understanding of oxygen vacancies in correlated oxides. This includes the oxygen sponge SrCoO_{3-d} (Jeen et al., *Nature Mater.* **12**, 1057 (2013)), Petric et al., *JACS* **138**, 7252 (2016); *Adv. Funct. Mater.* **26**, 1564 (2016)), oxygen diode formed in LaNiO_3 (Guo et al., *Adv. Mater.* **2018**, 1705904), strain control of oxygen kinetics in the Ruddlesden-Popper oxide $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-d}$ (Meyer et al., *Nature Commun.* **9**, 98 (2018)), and metal-insulator-transition by oxygen stoichiometry control in VO_2 (Sharma et al., (unpublished)). Overall, these results summarize the role, importance, and challenge in film growth for the right stoichiometry as well as strain utilization for developing next generation energy and functional materials and devices.

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.

4:00 PM ET12.06.05

Drastically Improved UV Photoluminescence from ZnO Nanowires by Selective Introduction of Surface Oxygen Vacancies Danhua Yan¹, Wenrui Zhang¹, Jiajie Cen² and Mingzhao Liu¹; ¹Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States; ²Department of Materials Science and Chemical Engineering, Stony Brook University, The State University of New York, Stony Brook, New York, United States.

Zinc oxide nanowire arrays (ZnO NWs) have been extensively studied for their versatile applications in optical and optoelectronic devices, such as light-emitting diodes (LEDs), photodetectors, optical modulator waveguides, and photoelectrochemical anodes. Among various techniques that have been used to fabricate ZnO NWs, the wet-chemical approach becomes the most widely adopted method for its simplicity, as well as its capability to synthesize well oriented single crystalline ZnO NWs over various types of substrates in a scalable manner. However, ZnO NWs grown by the wet-chemical process usually feature a high density of defects, which suppress near band edge emission and contribute to broad defect state emission in the photoluminescence (PL) spectra.

Here, we demonstrate, counter-intuitively, that the near band edge emission may become dominant by selectively introducing surface oxygen defects to ZnO nanowires *via* surface engineering. Specifically, near band edge emission (NBE) is effectively enhanced after a thermal annealing that removes most *bulk* defects and a low pressure O_2 plasma treatment that sputters off surface oxygen species to produce a reduced and oxygen vacancy-rich surface. Through a combined study by low-energy electron microscopy (LEEM) and ultraviolet photoelectron spectroscopy (UPS), we discover that the effect is attributed to the lowered surface valence band maximum of the reduced ZnO surface that creates an accumulative band bending, which screens the photo-generated minority carriers (holes) from reaching or being trapped by the surface defects.

4:15 PM ET12.06.06

Passivating Defects in Sn-Based Oxides— SiO_2 Replaces Thermal Treatments Monica Morales-Masis^{2,1}, Esteban Rucavado¹, Migle Grauzinyte³, Jose A. Flores-Livas³, Quentin Jeangros¹, Federica Landucci¹, Stefan Goedecker³, Aicha Hessler-Wyser¹ and Christophe Ballif¹; ¹Ecole Polytechnique Federale de Lausanne, Neuchatel, Switzerland; ²MESA+ Institute of Nanotechnology, University of Twente, Enschede, Netherlands; ³Universität Basel, Basel, Switzerland.

Tin (Sn)-based metal oxides have been of high technological importance for decades, with applications ranging from photovoltaics, sensors, displays and smart windows. For Sn-based oxides, oxygen deficiencies and undercoordinated Sn atoms result in extended densities of states below the conduction band edge. While shallow states provide free carriers necessary for electrical conductivity, deeper states inside the bandgap create absorption centers affecting the transparency in the visible spectrum range.

Using two Sn-based transparent conductive oxides as model systems, i.e. amorphous zinc tin oxide (a-ZTO) and polycrystalline tin oxide (SnO_2) the origin of these subgap defects and routes for their passivation were studied. Previously we have demonstrated that in a-ZTO, the overall optoelectronic properties can be improved by defect passivation via annealing at high temperatures in oxygen-rich environments. Yet, the high thermal budget associated with such treatment is incompatible with many applications such as devices requiring temperature-sensitive materials or fabricated on polymer-based substrates. As an alternative low-temperature passivation route, we propose co-sputtering Sn-based TCOs with silicon dioxide (SiO_2). In-depth optoelectronic characterization of the co-sputtered SnO_2 - SiO_2 (or a-ZTO- SiO_2) films and density functional theory simulations indicate that the SiO_2 contribution is two-fold. First, oxygen from SiO_2 passivates the oxygen deficiencies that form deep defects in SnO_2 and a-ZTO. Secondly, the ionization energy of the remaining deep defect centers is lowered by the presence of silicon atoms. Remarkably, these ionized states do not contribute to subgap absorbance while still providing free electrons maintaining the high conductivity of the film. This simple passivation scheme with SiO_2 significantly improves the optical properties without affecting the electrical conductivity, and it is independent of the microstructure of the films, hence overcoming the known transparency conductivity trade-off in Sn-based TCOs.

E. Rucavado et al. *Physical Review B*, **95**, 245204 (2017)

E. Rucavado et al. *Journal of Physical Chemistry C*, *under consideration*

4:30 PM ET12.06.07

Probing Defects in Au- and Te-Hyperdoped Si with Deep Level Transient Spectroscopy and Carrier Lifetime Measurements Shao Qi Lim¹, Christopher Tao-Kuan Lew², Brett Johnson², Philippe K. Chow³, Senali Dissanayake⁴, Meng-Ju Sher⁴, Quentin Hudspeth³, Jeffrey M. Warrender³ and Jim S. Williams¹; ¹Electronic Materials Engineering, Research School of Physics and Engineering, Australian National University, Canberra, Australian Capital Territory, Australia; ²Centre for Quantum Computing and Communication Technology, School of Physics, University of Melbourne, Melbourne, Victoria, Australia; ³US Army ARDEC - Benet Laboratories, Watervliet, New York, United States; ⁴Physics Department, Wesleyan University, Middletown, Connecticut, United States.

Developing a technology that can allow Si to efficiently absorb light in the mid infrared region can open-up important applications in fibre-based communications as well as facilitating the fabrication of Si-based infrared (IR) imaging arrays. In this context, recently Mailoa et al. demonstrated that by hyperdoping Si with Au by ion implantation and pulsed-laser melting (PLM), a Si-based photodetector can absorb into the IR up to 2200 nm [1]. The thin Au surface layer (~150 nm) so produced contained up to 1 atomic % Au that was almost all in solid solution at concentrations far exceeding the solid solubility limit for Au in Si. Spectroscopic data suggest that the observed enhanced absorption was associated with the Au deep donor level in the Si bandgap [1].

Enhanced sub-bandgap absorption of Si hyperdoped (HD) with Ti, S, Se and Te [2-4] have also been demonstrated. However, despite considerable literature on the physical, optical and electrical characterization of HD Si, there is a lack of characterization of defect states that lie in the Si bandgap as well as the related carrier lifetime data of such materials. This study aims at using deep level transient spectroscopy (DLTS) and carrier lifetime

measurements with THz spectroscopy [5] to investigate the nature of defects present in Au- and Te-HD Si and thus better understand how these defects contribute to the overall photodetector performance.

Several variations of the DLTS method was performed on the Au-HD Si photodiodes from [1], revealing the presence of defects as deep as 1-2 μm from the surface, well beyond the HD region. The defect identities currently remain undetermined due convoluted hole and electron trap signals and other experimental complications. However, current efforts have been successful in overcoming such barriers, and concentration depth profiling of individual trap components via small-pulse DLTS will further elucidate the role of each type of defect in the Au-HD diodes. On the other hand, carrier lifetime measurements made on Te-HD Si revealed the presence of both short (picosecond) and long (microsecond) lifetime components. These DLTS and carrier lifetime results will be discussed in terms of defects emanating from the PLM processing of HD Si, as well as its implications for photodiode properties.

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4:45 PM ET12.06.08

Role of Vacancy-Type Defects in Au-Hyperdoped Si Fabricated by Ion Implantation and Pulsed Laser Melting Wenjie Yang¹, Naheed Ferdous², Philippe K. Chow³, James M. Gaudet⁴, Peter Simpson⁴, Austin Akey⁵, Jeffrey M. Warrender³, Michael J. Aziz⁵, Elif Ertekin² and Jim S. Williams¹; ¹Australian National University, Canberra, Australian Capital Territory, Australia; ²University of Illinois at Urbana-Champaign, Champaign, Illinois, United States; ³U.S. Army ARDEC- Benet Laboratories, Watervliet, New York, United States; ⁴University of Western Ontario, London, Ontario, Canada; ⁵Harvard University, Cambridge, Massachusetts, United States.

Ion implantation followed by pulsed laser melting can produce hyperdoped Si with a highly non-equilibrium impurity concentration, giving rise to sub-band gap optical absorption that holds potential in Si-based photovoltaics and infrared light detection. [1, 2] In particular, a Si-based infrared photodetector has been successfully demonstrated on Au-hyperdoped Si, motivating a detailed study on the role of substitutional Au and other related defect complexes that arise from the non-equilibrium hyperdoping process. [3]

In this study, the atomic location of Au in hyperdoped Si is determined using Rutherford backscattering spectrometry combined with ion channelling (RBS/C) and triangulated angular scans. Additionally, the local lattice environment around the Au atoms is examined using a combination of techniques, including high-resolution transmission electron microscopy (HRTEM), high-resolution x-ray diffraction (HRXRD) and positron annihilation spectroscopy (PAS). Surprisingly, the incorporation of large Au atoms into the Si lattice appears to contract rather than expand the lattice. We show that vacancies are trapped following pulsed laser melting, and, with the aid of density functional theory (DFT) calculations, propose that the vacancy trapping process is consistent with the local minimisation of lattice strain around the large Au atoms. Finally, we explore the thermal stability and sub-band gap optical activity of these vacancy-type defects. This vacancy trapping process may be global in other laser-melted hyperdoped Si systems with large-size impurities and may affect their efficacy as infrared absorbers.

References:

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- [3] J. P. Mailoa, et al., *Nature Communications*, 5:3011 (2014)

SESSION ET12.07: Functional Defects in Electrochemical Energy Storage and Conversions

Session Chairs: Marina Leite and Petro Maksymovych

Thursday Morning, November 29, 2018

Hynes, Level 3, Room 313

8:00 AM *ET12.07.01

Complex Dynamics of Novel Polyborane Solid Electrolytes Joel B. Varley; Lawrence Livermore National Laboratory, Livermore, California, United States.

Rationally motivated computational discovery and optimization of solid electrolytes for all-solid-state batteries require the development of reliable descriptors for ionic conductivity. However, many of the fundamental motivations for superionic behavior in solids remain enigmatic, which has generally slowed progress in screening electrolyte candidates, as well as in tuning existing materials for maximal ionic conductivity. I will discuss how high-performance computing has been applied to perform extensive simulations of ionic conductivity in model classes of solid electrolytes. Focusing primarily on a relatively new class of closoborane-based materials ($\text{Li}/\text{NaB}_{10}\text{H}_{10}$, $\text{Li}/\text{NaB}_{12}\text{H}_{12}$, and derivatives), I will show how computational “experiments” can systematically isolate factors such as stoichiometry, strain, alloy composition, and crystal structure in the determination of ionic conductivity. The findings point to the importance of highly correlated motion and dynamical fluctuations in the broader structural environment. They also reveal the universal importance of frustration, which lowers the barrier for ionic mobility and motivates the order-disorder transition to a superionic state. Such frustration may arise from factors such as off-stoichiometry, competition between interstitial site occupancies, and symmetry incompatibilities between local bonding character and lattice geometry. Physicochemical origins of the relevance of these factors for cation mobility will be explored, with a view towards developing design rules for engineering faster ionic conductors.

8:30 AM *ET12.07.02

1D, 2D and 3D Defect Dynamics in Li Intercalation Compounds Y. Shirley Meng^{1,2} and Minghao Zhang^{1,2}; ¹University of California, San Diego, La Jolla, California, United States; ²Sustainable Power and Energy Center (SPEC), La Jolla, California, United States.

Defects and their interactions often underpin material properties and functionality as they are decisive for stability, can result in enhanced and impeded ionic diffusion. Despite their importance, understanding of their presence in lithium ion electrode materials remains challenging, particularly in operando. Combining electron microscopy, coherent X-ray diffraction imaging and first principles computation, we will discuss and explain the observations on vacancy ordering, nucleation of a dislocation network both classical layered oxide and lithium-rich layered oxide (LRLO) materials during electrochemical

processes. These defects are dynamic and have profound effects on the performance of the energy storage devices.

9:00 AM ET12.07.03

The Ordering and Disordering of Functional Charged Point Defects in NaTMO₂ Xin Li; Harvard University, Cambridge, Massachusetts, United States.

Layered sodium transition metal oxide system of NaTMO₂ (TM=3d transition metal ions and their mixture) forms a unique materials platform for the study of transition metal, oxygen and sodium interactions. Specifically, Fe and Mn, which are not stable in LiTMO₂, become much more stable in NaTMO₂ due to increased alkaline layer distance. In this talk, we show the novel interplay between these TM ions and the charged point defects to modulate the electrochemical performance of Na_xTMO₂ through unique ordering and disordering phases. A combined in situ (synchrotron) XRD, atomic resolution (scanning) TEM, neutron diffraction and density functional theory (DFT) simulation techniques are used to understand the coupled sodium, TM charge and magnetic orderings and disorderings. For the Fe containing mixed transition metal system of Na(FeTM)O₂, a novel disordered phase at high voltage was developed due to the unique electronic property of FeO₆ octahedrons, while at low voltage it goes reversibly back to the ordered phase. For NaMnO₂ a unique superstructure evolution mechanism related to the Jahn-Teller activity of Mn³⁺ was found to dominate the electrochemical performance through the charged point defects in a special ordering pattern. The underlying connection between the two systems of Na(FeTM)O₂ and NaMnO₂ will be discussed to further facilitate the design of new battery cathode materials.

9:15 AM ET12.07.04

Defect-Enhanced Phase Transformation Kinetics in LiFePO₄ Ming Tang, Liang Hong and Kaiqi Yang; Rice University, Houston, Texas, United States.

Lattice defects such as antisite defects are commonly present in battery compounds and traditionally viewed as deleterious features. In this work, however, we use phase-field modeling and theoretical analysis to illuminate a mechanism of antisite defects accelerating phase transformation and hence enhancing the rate performance of battery particles for compounds with strong ion diffusion anisotropy. Using LiFePO₄ as an example, we show that the inclusion of antisite defects can increase the phase boundary velocity by orders of magnitude in the surface-reaction-limited phase transformation regime, which is closely related to the effect of antisite defects on reducing the Li diffusion anisotropy in LiFePO₄. As such, defect-rich LiFePO₄ particles can be (dis)charged much faster than defect-free particles especially at low overpotentials, where the metastable solid solution does not form. Based on the mechanistic understanding, criteria for optimizing the defect concentration are presented. This finding suggests defect engineering as a fruitful approach to enhance the rate performance of intercalation compounds.

9:30 AM ET12.07.05

Charge Storage and the Critical Role of Defects—Case Study of 2D Layered Delta MnO₂ and VO₂(B) Nanosheets Scott Misture, Peng Gao, Robert Koch, Madeleine N. Flint and Alec Ladonis; Alfred University, Alfred, New York, United States.

It has recently become clear that defects may be of great importance in developing new electrochemical energy storage materials. Herein we focus on two model systems, 2-D layered delta MnO₂ and 2-D VO₂(B) nanosheets, with controlled defect contents, and investigate the atomic-scale mechanisms of charge storage. Using a combined approach of high energy X-ray scattering and X-ray spectroscopy, we find that MnO₂ nanosheets possess a peculiar out-of-plane Mn³⁺ defect, forming a “surface Frenkel” defect. In our earlier work, we correlated the concentration of these defects (~20-30%) to the charge storage, where defects increase the overall capacitance from 200 to 300 F/g while decreasing the charge transfer resistance from ~15 to ~3 Ω. *In-situ* XRD and X-ray PDF studies show that in-plane expansion and contraction occurs in the nanosheets upon charge and discharge. *In-situ* XANES reveals a 31% change in the Mn oxidation state in the presence of 30% surface Frenkel defects, promoting ion intercalation and charge transfer. To test the hypothesis of charged defects controlling capacitance, Mn doping into layered VO₂(B) nanosheets has also been investigated. Addition of ~9 mol% Mn to the VO₂ results in 80% higher capacitance, as well as 2X smaller charge transfer resistance and 2X improvement in cyclability. PDF and X-ray scattering demonstrate distorted local structures with increased cation substitution, which may facilitate Na⁺ intercalation. The formation of more V⁴⁺ (~13% higher by XPS) and oxygen vacancies by Mn doping can also help relieve electrochemical strain and increase electrical conductivity. Through these model systems, we provide insight into engineering defects for the next generation of transition metal oxide nanosheet electrochemical supercapacitors.

9:45 AM ET12.07.06

Guiding Principles for Designing Highly-Efficient Metal-Free Carbon Catalysts Lipeng Zhang¹ and Zhenhai Xia²; ¹Beijing University of Chemical Technology, Beijing, China; ²University of North Texas, Denton, Texas, United States.

Carbon nanomaterials are promising as metal-free catalysts for energy conversion and storage. To accelerate the search for the highly-efficient catalysts, it is necessary to establish design principles for the carbon-based catalysts. This review focuses on theoretical analysis and material design of metal-free carbon nanomaterials as efficient photo-/electro-catalysts to facilitate the critical chemical reactions in clean energy technologies, including oxygen reduction reaction (ORR) in fuel cells, oxygen evolution reaction (OER) in metal-air batteries, hydrogen reduction/evolution (HER) in water splitting, Iodine reduction (IRR) in dye-sensitized solar cells, and carbon dioxide reduction (CO₂RR) in artificial photosynthesis. Intrinsic descriptors and design principles are analyzed and summarized, and future directions are discussed in development of efficient carbon-based catalysts for clean energy conversion and storage.

10:00 AM BREAK

10:30 AM *ET12.07.07

The Role of Chemically Preintercalated Cationic Species at the Interlayer Region of Layered Oxides in Electrochemical Energy Storage Ekaterina Pomerantseva; Drexel University, Philadelphia, Pennsylvania, United States.

Transition metal oxides with layered crystal structures favor reversible intercalation of ions at relatively high potentials and as a result are attractive for cathode application in lithium-ion batteries. However due to the concerns related to the abundance of lithium on Earth and a desire to reduce battery cost, the interest in developing beyond lithium ion energy storage systems fuels discovery of new electrode materials that would be efficient in reactions of intercalation of more abundant and therefore less expensive ions, such as Na⁺ and K⁺ ions. The larger size of these ions compared to that of lithium ion dictates the need for expanding the interlayer region of layered oxides to enable facile diffusion of the electrochemically cycled ions. This presentation will focus on new materials synthesis approach, called chemical pre-intercalation, which allows to tune the interlayer spacing of a model bilayered vanadium oxide phase from ~10 to ~30 Å. The effect of introducing inorganic and linear organic ions on charge storage properties in electrochemical systems with different charge-carrying ions will be discussed. Methods to control species in the interlayer region will be highlighted and correlated with functional properties of materials. This talk will also demonstrate that chemical pre-intercalation synthesis approach can be extended to synthesize new layered transition metal oxide phases beyond vanadium oxide. Overall, this presentation will shed some light on ways to chemically control interlayer content in

layered oxides to modify their structure and chemical composition with the aim to achieve enhanced electrochemical properties in energy storage applications.

11:00 AM *ET12.07.08

Tailoring Mobile Defects for Fast Ionic Conductors Yifei Mo; University of Maryland, College Park, College Park, Maryland, United States.

Fast ionic conductor materials are the key component in enabling a variety of electrochemical devices. It is crucial to understand why only a few materials exhibit faster ionic conduction than typical solids and how one can design fast ion conductors following simple principles. We perform ab initio modeling on a range of novel fast ion conductor materials as model systems. In lithium super-ionic conductors, we show that fast diffusion in super-ionic conductors happens through unique concerted migration mechanism of multiple ions with low energy barrier in contrast to isolated ion hopping in typical solids. We elucidate that low energy barriers of the concerted ionic diffusion are a result of unique mobile ion configurations and strong mobile ion interactions in these super-ionic conductor materials. Our theory provides a conceptually simple framework for guiding the design of super-ionic conductor materials. Using first principles computation, we demonstrate this strategy by designing a number of novel fast ion conducting materials. In addition, our computation studies in other ionic conductors will also be discussed, and newly discovered design strategies will be presented.

11:30 AM ET12.07.09

Tuning Bifunctional Oxygen Electrocatalysts by Changing A-Site Rare-Earth Element in Perovskite Nickelates Le Wang^{1,2}, Kelsey A. Stoerzinger¹, Lei Chang², Junling Wang² and Yingge Du¹; ¹Pacific Northwest National Laboratory, Richland, Washington, United States; ²Nanyang Technological University, Singapore, Singapore.

Perovskite-structured (ABO₃) transition metal oxides are promising bifunctional electrocatalysts for efficient oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). In this paper, we investigate a set of epitaxial rare earth nickelates (RNiO₃) thin films with controlled A-site isovalent substitution to correlate their structure and physical properties with ORR/OER activities. The ORR activity is shown to decrease monotonically with decreasing the A-site element ionic radius which lowers the conductivity of the RNiO₃ (R = La, La_{0.5}Nd_{0.5}, La_{0.2}Nd_{0.8}, Nd, Nd_{0.5}Sm_{0.5}, Sm, Gd) films, with LaNiO₃ being the most conductive and active. On the other hand, the OER activity initially increases upon substituting La with Nd and is maximal at La_{0.2}Nd_{0.8}NiO₃, in which oxygen vacancies (V_{OS}) start to form. Moreover, the OER activity remains comparable within error through Sm-doped NdNiO₃. Beyond that, we cannot reliably measure activity due to the potential voltage drop across the film. The improved OER activity is ascribed to the partial reduction of Ni³⁺ to Ni²⁺ as a result of V_{OS}, which increases the average occupancy of the e_g antibonding orbital to more than one. Our work highlights the importance of tuning A-site elements as an effective strategy for balancing the ORR and OER activities of bifunctional electrocatalysts.

11:45 AM ET12.07.10

Lifting Electrocatalytic Activity in LaNiO₃ Perovskite Films with Helium Jonathan Petrie¹, Thomas Zac Ward¹, Anthony Wong¹, John w. Freeland², Valentino Cooper¹ and Ho Nyung Lee¹; ¹Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ²Argonne National Laboratory, Argonne, Illinois, United States.

Complex oxides, such as ABO₃ perovskites, can catalyze oxygen reduction and evolution reactions essential for fuel cells, metal-air batteries, and other energy-related devices. Similar to noble metal films such as Pt, in-plane compressive strain was recently reported to generate significant enhancements in the electrocatalytic activity of LaNiO₃ (LNO) perovskite films epitaxially grown on different substrates. Greater amounts of in-plane compression induced by the substrate increases the out-of-plane (c) lattice parameter via the oxide's Poisson relationship. The increased tetragonality in turn improves the catalytic activity due to strain-induced splitting of the e_g orbitals in the film's NiO₆ octahedral units. However, this sole reliance on in-plane epitaxial strain to facilitate uniaxial changes in the c-parameter limits our ability to optimize the activity.

Recently, low energy helium (He) ion implantation was demonstrated as a means to directly control uniaxial c-axis lattice expansion in epitaxial perovskite oxides. Here, we show that this "strain doping" process presents an additional avenue towards manipulating catalytic activity in LNO films coherently grown on STO substrates. Through the introduction of controlled amounts of interstitial He atoms into the film, we can continuously adjust the c-axis lattice expansion that drives changes in the e_g orbital asymmetry essential for greater catalytic activity. Consequently, we can use these He point defects to raise the activity of LNO films by over an order of magnitude. Furthermore, the LNO activities seen surpass any yet found through straightforward substrate-induced epitaxial strain. The considerable enhancement in oxygen activity through the tailored incorporation of He into LNO demonstrates the emerging power of this 'defective' dial to enhance oxide functionality.

SESSION ET12.08: Mastering Functional Defects for Energy Efficient Ionic and Electronic Materials

Session Chairs: Xin Li and Hua Zhou
Thursday Afternoon, November 29, 2018
Hynes, Level 3, Room 313

1:30 PM *ET12.08.01

Designing Dopants for Higher Performance TCOs David O. Scanlon; University College London, London, United Kingdom.

The combination of electrical conductivity and optical transparency in a single material gives transparent conducting oxides (TCOs) an important role in modern optoelectronic applications such as in solar cells, flat panel displays, and smart coatings. The most commercially successful TCO so far is tin doped indium oxide (Indium Tin Oxide – ITO), which has become the industrial standard TCO for many optoelectronics applications; the ITO market share was 93% in 2013. Its widespread use stems from the fact that lower resistivities have been achieved in ITO than in any other TCO; resistivities in ITO have reached as low as $7.2 \times 10^{-5} \Omega \text{ cm}$, while retaining >90% visible transparency. In recent years, the demand for ITO has increased considerably, mainly due to the continuing replacement of cathode ray tube technology with flat screen displays. However, indium is quite a rare metal, having an abundance in the Earth's crust of only 160 ppb by weight, compared with abundances for Zn and Sn of 79000 ppb and 2200 ppb respectively, and is often found in unstable geopolitical areas. The overwhelming demand for ITO has led to large fluctuations in the cost of indium over the past decade. There has thus been a drive in recent years to develop reduced-indium and indium-free materials which can replace ITO as the dominant industrial TCO. In this talk I will outline a new doping mechanism, and a new TCO which should usurp ITO as the industry standard.

2:00 PM ET12.08.02

Controlling Surface Mobility and Step Barrier Heights in Oxide Film Growth [Arthur P. Baddorf](#)¹, Alexander Tselev¹, Rama K. Vasudevan¹, Anthony Gianfrancesco^{1,2}, Liang Qiao¹, Tricia Meyer¹, Ho Nyung Lee¹, Michael Biegalski¹ and Sergei V. Kalinin¹; ¹Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ²The University of Tennessee, Knoxville, Tennessee, United States.

Control of defects during nonequilibrium growth requires an understanding of surface mobilities and diffusion barriers, such as step barrier heights. We have explored these parameters and their influence on structure in epitaxial $\text{La}_{5/8}\text{Ca}_{3/8}\text{MnO}_3$ thin films grown with pulsed laser deposition by varying laser fluence, oxygen pressure, and substrate-induced strain. Films were examined in operando using reflective high-energy electron diffraction (RHEED) followed by in situ atomically resolved imaging with scanning tunneling microscopy (STM) and subsequently with ex situ X-ray diffraction (XRD). Regardless of the laser fluence, RHEED intensity oscillations were observed, characteristic of layer-by-layer growth. For SrTiO_3 substrates (and not the better lattice matched NdGaO_3) the envelope of the oscillations first drops with film thickness, then increases. Such RHEED behavior can be interpreted as first roughening of the film surface, then a decrease of the roughness and eventual conversion to a stable layer-by-layer growth. STM images confirm this interpretation. Remarkably, this indicates that the suboptimal layer-by-layer growth involving multiple exposed layers evolves into a nearly ideal layer-by-layer growth with the prototypical three exposed layers. At intermediate film thicknesses, atomically resolved images show that the surface consists of both A-, MnO, and B-site, (La,Ca)O, terminations with $(\sqrt{2}\times\sqrt{2})R45^\circ$ reconstructed surfaces. The A-site termination is clearly more highly ordered. As the film thickness increases, the less ordered B-site domain dominates and by 250 layers is the sole termination. This surface morphology is largely independent of the laser fluence, but layer-by-layer growth could be delayed by reducing the growth pressure. Rough growth is frequently associated with a Ehrlich-Schwoebel barrier for adatoms to descend steps resulting in a reduction of the downhill flux. This interpretation is confirmed by atomically resolved images with a high concentration of adatoms along the terrace edges. Image analysis and Monte Carlo simulations estimate the height of the Ehrlich-Schwoebel barrier to be 0.18 ± 0.04 eV for deposition at 750°C . Similarly, the evolution of adatom mobility can be inferred from STM images based on adatom island sizes and spacing. In the layer-by-layer regime, an increase in the adatom mobility with increasing thickness is accompanied by an increase in the out-of-plane lattice parameter. STM images reveal a pattern of extended nontopographic features over the cationically stoichiometric surfaces, which can be ascribed to subsurface defects created during growth. Research was sponsored the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division and the Office of Science Early Career Research Program. Research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

2:15 PM ET12.08.03

Non-Stoichiometry-Induced Metal-to-Insulator Transition in Nickelate Thin Films Grown by Pulsed Laser Deposition [Jongmin Lee](#)¹, Kyoung Soon Choi², Tae Kwon Lee³, Il-Seok Jeong¹, Sangmo Kim⁴, Jaesun Song¹, Chung Wung Bark⁴, Joo-Hyoung Lee¹, Jong Hoon Jung³, Jouhahn Lee², Tae Heon Kim⁵ and Sanghan Lee¹; ¹Gwangju Institute of Science and Technology, Gwangju, Korea (the Republic of); ²Korea Basic Science Institute, Daejeon, Korea (the Republic of); ³Inha University, Incheon, Korea (the Republic of); ⁴Gachon University, Seongnam, Korea (the Republic of); ⁵University of Ulsan, Ulsan, Korea (the Republic of).

The chemical stoichiometry in transition-metal oxides influences their physical properties due to the multi-valent nature of the transition-metal element. In perovskite rare-earth nickelates (RNiO_3 , except for $R = \text{La}$), which undergo metal-to-insulator phase transitions (MITs) with the decreasing temperature, the oxidation state of the transition-metal Ni^{3+} ion is very sensitive to the stoichiometry and the transport property becomes different relying on the Ni valence state. Thus, it has been extensively studied how off-stoichiometry in either bulk or thin-film RNiO_3 modifies the Ni oxidation state and then, affects the MITs eventually. However, the detailed study of the non-stoichiometry effect has been rare due to a difficulty in the systematic control of cation and oxygen contents. Herein, we manipulate the cation stoichiometry in RNiO_3 bilayer films ($\text{NdNiO}_3/\text{LaNiO}_3$ on $\text{SrTiO}_3(001)$) epitaxially grown by a pulsed laser deposition technique. Through a training process by laser irradiation, we can systematically control the R/Ni compositional ratio in RNiO_3 target. Interestingly, a Ni-excess RNiO_3 bilayer film shows MITs at around ~ 50 K. In contrast, a stoichiometric RNiO_3 bilayer film is metallic at all temperatures. Based on the first-principle calculations results, the possible origin of the non-stoichiometry-dependent transport behaviors will be discussed in conjunction with x-ray reflection (XRR) and x-ray photoemission spectroscopy (XPS) analyses.

2:30 PM *ET12.08.04

Machine Learning Guided Design of Functional Materials with Targeted Properties [Prasanna V. Balachandran](#); Department of Materials Science and Engineering & Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia, United States.

Computational strategies that enable identification of predictive design rules have the potential to rationally design materials for targeted applications. In this talk, I will discuss some of our recent works that have rationally guided experiments and computational codes (eg., density functional theory) towards promising regions in the vast design space of functional materials. The uniqueness of our approach lies in the integration of machine learning methods with experimental design in an adaptive feedback loop. The role of machine learning is two-fold: (i) to establish a relationship between the features and property of interest and (ii) to quantify uncertainties. Experimental design, on the other hand, uses the machine learning outcome to recommend the next experiment or simulation. I will demonstrate examples showing the efficacy of these approaches to design novel complex oxides and alloys with improved properties.

3:00 PM BREAK

3:30 PM *ET12.08.05

Neuromorphic Computing Based on Dynamic Control of Dopants in Organic and Inorganic Materials [A. A. Talin](#); Sandia National Laboratories, Livermore, California, United States.

Inspired by the efficiency of the brain, CMOS-based neural architectures and memristors are being developed for pattern recognition and machine learning. However, the volatility, design complexity and high supply voltages for CMOS architectures, and the stochastic and energy-costly switching of memristors complicate the path to achieve the interconnectivity, information density, and energy efficiency of the brain using either approach. In my talk I will describe a non-volatile redox memory (NVRM): a device with a resistance switching mechanism fundamentally different from existing memristors, based on the concept of reversible, electrochemical reduction/oxidation of a material to tune its electronic conductivity. The first type of NVRM that I will describe is based upon the control of Li vacancy concentration in $\text{Li}_{1-x}\text{CoO}_2$ through reversible Li-ion intercalation. Li vacancies act as positive dopants, resulting in linear, highly symmetric, and low voltage switching between hundreds of analog conductance states and achieving high classification accuracy when implemented in neural network simulations¹. The second type of NVRM I will describe operates on a similar principle but is based on the polymer system PEDOT:PSS, and utilizes the proton as the mobile ion to control the polaron carrier density in the channel². Plastic NVRMs are fabricated on flexible substrates enabling the integration of neuromorphic functionality in stretchable electronic systems.

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(2) van de Burgt, Y.; Lubberman, E.; Fuller, E. J.; Keene, S. T.; Faria, G. C.; Agarwal, S.; Marinella, M. J.; Talin, A. A.; Salleo, A. A non-volatile organic

electrochemical device as a low-voltage artificial synapse for neuromorphic computing. *Nature Materials* **2017**, *16*, 414.

4:00 PM ET12.08.06

Low Dimensional Sr_{1-x}Ti_yNb_{1-y}O_{3+δ} Nanoparticles for Defect-Induced Infrared Light Harvesting Tochukwu Ofoegbuna, Pragathi Darapaneni and James A. Dorman; Louisiana State University, Baton Rouge, Louisiana, United States.

The family of Sr_{1-x}Nb_{1-y}O_{3+δ} (SNO) metal oxides have attracted interest for their plasmonic and low-loss response making them promising materials for photovoltaic and photocatalytic devices. SNO metal oxides have been synthesized using thin-film deposition techniques to control oxygen concentrations which are responsible for the plasmonic response. However, electronic state modification can be further amplified via strain engineering which is limited to film/substrate lattice mismatch and deposition pressure. An alternative approach to induce strain within these systems is through size confinement and morphology control. This work focuses on utilizing wet-chemical processes to control defects (oxygen vacancies and dopant) to tune the optical response of a host nanocrystal (SrTiO₃, STO) doped with Nb ions, Sr_{1-x}Ti_yNb_{1-y}O_{3+δ} (STNO).

STNO nanoparticles were synthesized via a two-step co-precipitation/pressure-controlled molten salt technique. This low-pressure synthetic route limits available oxygen during the crystallization process allowing for systematic control of oxygen vacancies and dopant incorporation. The resultant particles have been identified as highly doped, cubic STNO nanostructures via TEM, EDX, and XRD. The average strain on the host matrix due to different dopant concentrations and oxygen pressures was calculated to be ~1%. Additionally, it is possible to induce the expected optical response by controlling the oxygen partial pressure and subsequent annealing processes. This optical response was confirmed to be due to the formation of Nb⁴⁺, as opposed to the more stable Nb⁵⁺ state, in the STO lattice using X-ray photoelectron and X-ray absorption spectroscopy. These results on low dimensional Nb-doped SrTiO₃ nanoparticles demonstrate a capacity for infrared light harvesting which has the potential for applications in optical communication, remote sensing, spectroscopy, and thermal imaging.

4:15 PM ET12.08.07

Exploring Defect-Coupled Polarization Dynamics in Ferroelectrics via Multimodal X-Ray Imaging Qian Li¹, Ben Xu², Bo Wang³, Joshua Agar⁴, Hua Zhou¹, Nouamane Laanait⁵, Lane W. Martin⁴, Long-Qing Chen³, Sergei V. Kalinin⁵ and Haidan Wen¹; ¹Advanced Photon Sources, Argonne National Laboratory, Lemont, Illinois, United States; ²School of Materials Science and Engineering, Tsinghua University, Beijing, China; ³Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States; ⁴Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; ⁵Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

It is broadly acknowledged that oxide ferroelectric materials inherently contain significant amounts of defects, such as oxygen vacancies, that form during fabrication due to thermodynamic defect equilibria. These defects are also known to interact with ferroelectric polarization, though in many cases leading to adverse effects such as polarization fatigue. It is thus crucial to understand the configuration and dynamical behavior of defects in order to enhance the functional properties of ferroelectric materials. Diffuse scattering is one of a few widely applicable methods that gives microscopic insights about defects, with its quantitiveness, nondestructiveness and high sensitivity. Here at the Advanced Photon Source, we have developed a new materials characterization instrument which combines scanning probe microscopy (SPM) *in-situ* with nano-focused X-ray diffraction imaging (XDM). We have devoted the initial application of this development to an examination of the defect-coupled polarization dynamics in Pb(Zr,Ti)O₃ ferroelectric epitaxial thin films. This model system has been found to show mechanical switching behavior, that is, the polarization can be switched under mechanical pressure exerted by an SPM tip. We have performed XDM around such mechanically written regions and observed remarkably enhanced diffuse scattering in these regions, which nonetheless preserve the pristine average structure. Defect scattering modeling based on the classical Huang theory and phase-field modeling based on the Landau-Ginzburg theory, both informed by atomistic simulations of the defect (oxygen vacancy) configuration, have been performed to obtain a deep understanding of the pertinent dynamic processes. Altogether, they lead to a coherent picture that the tip pressure drives a redistribution of ionized oxygen vacancies in the films due to the Vegard strain coupling; slave to this process, the polarization switching occurs due to the electrostatic coupling. While our discovery substantially challenges the prevailing belief that flexoelectricity drives the mechanical switching, it points to a fundamentally different route to manipulate ferroelectric polarization at the nanoscale and prompts a rethinking of the functional roles of oxygen vacancies. Beyond ferroelectrics, this methodology may well be applied to a wide range of condensed matter systems where oxygen vacancies and the-like ionic defects modulate electronic transport, magnetism and other physical properties.

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4:30 PM ET12.08.08

Mapping Potential Energy Landscapes via Electron Beam Induced Atomic Impurity Dynamics Maxim Ziatdinov¹, Ondrej Dyck¹, Feng Bao², Ali Yousefzadi Nobakht³, Rick Archibald¹, Kody Law⁴, Stephen Jesse¹ and Sergei V. Kalinin¹; ¹Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ²Department of Mathematics, The University of Tennessee at Chattanooga, Chattanooga, Tennessee, United States; ³The University of Tennessee, Knoxville, Tennessee, United States; ⁴The University of Manchester, Manchester, United Kingdom.

Atomic fabrication of materials remains the ultimate goal of nanotechnology. The modern-day scanning transmission electron microscope allows to simultaneously image and manipulate matter at the atomic scale and is therefore considered one of the most promising tool for building new forms of matter from the atom up. Accomplishing this goal requires detailed understanding of the mechanisms of beam-induced transformations. Here we show that moving atomic impurity under beam excitation can be used to map atomic scale potentials in solids and determine beam-induced effects on chemically-relevant time scale. We first used stochastic reconstruction of molecular dynamic simulations to extract information on the random force exerted by the beam on Si dopant in graphene (arxiv:1804.03729). We then extended our approach to recover the potential along step edge of graphene nanohole with multiple impurities and to study cooperative effect between substrate reconstruction and 1D crystallization-like behavior under electron beam irradiation. Our study paves the way towards controllable electron beam induced transformations of matter.