Flexible Hybrid Electronics promises to deliver high performance and reliable systems in novel forms and functions. It is achieved by utilizing high performance silicon based semiconductor devices assembled on flexible (flex) substrates using optimized materials and additive processes. Integration of electronic devices on flexible substrates is starting to enable dramatically new approaches to traditional applications including: information displays, lighting, sensors, solar energy conversion and diagnostic medicine. The course will look at the fundamental aspects of three approaches: coating and printing (Mastropietro), chip-on-flex and micron scale thin-film devices on flex (Poliks) and sub-micron scale self-assembled/imprinted device based coatings on flex (Watkins).

1:30 PM
Coating and Printing Michael A. Mastropietro; ACI Materials

Selecting the right print method for additively manufactured circuits require a fundamental understanding of performance metrics of printed conductors and functional materials. The selection of the appropriate printing method is also key. This section will review the fundamentals of direct write methods: ink-jet, aerosol-jet, extrusion, micro-dispensing; printing methods requiring a master: screen printing, flexo, gravure, gravure offset; and coating methods: slot-die and Meyer rod, as well as the technical challenges of drying and curing functional inks.

3:00 PM BREAK

3:30 PM
Chip-on-Flex and Micron Scale Thin-Film Devices on Flex Mark D. Poliks; Binghamton University, The State University of New York

In the second section emerging methods for integration of thin semiconductor devices, sensors and transducers, including creation of thin die, thin die handling, die attach, interconnection and encapsulation on flexible substrates will be presented. Die function can also be integrated into micron scale thin-film electronic device fabrication directly on flexible non-silicon-wafer surfaces. Engineered polymer films such as PET, PI, PEN, as well as thin flexible metal foils and glass are all viable substrates for this technology. Key substrate properties include: dimensional and thermal stability, low moisture uptake, ultra-low gas and moisture transmission rates and nano-scale surface roughness. This part of the talk will examine how some of the basic semiconductor manufacturing processes can be adapted for use with flexible substrate materials and suggest a means for roll-to-roll manufacturing of flexible hybrid electronics. Advancements in manufacturing processes such as roll-to-roll handling, slot-die coating, vacuum deposition, photolithography and wet processing will be described.

4:15 PM
Sub-Micron Scale Self-Assembled/Imprinted Device Based Coatings on Flex James J. Watkins; University of Massachusetts-Amherst

The third part of this course, will discuss emerging technologies in printed and flexible electronics that can enable next generation performance. Nano-scale fabrication techniques, including the self-assembly of hybrid (inorganic/organic) materials and imprint patterning using polymers, hybrid polymer/inorganic resists and crystalline nanoparticle ink systems, can resolve challenges associated with large area production of sub-micron device features leading to very high integration densities as well as cost-effective production of functional device components. Applications include printing of 2-D and 3-D crystalline inorganic structures for light and energy management, printed micron scale transistors and printed microfluidic sensors. In addition, printing of functional structures to modify the performance and behavior of adjacent components.
Growing attention has been given to solution deposition techniques, considered as one of the promising deposition procedures for roll-to-roll process due to its properties of a continuous and large-scale deposition processing. However, further research is needed to apply a solution process into roll-to-roll process because of its several drawbacks such as inferior electrical characteristics of solution-grown electronic materials as thin film transistors compared to vacuum-processed ones. To date, various efforts have been made on eliminating causes of lowering electrical performance such as impurities and a small number of orbital overlap. While the outcomes exhibit a moderate increase in electrical characteristics, their performance still does not reach that of vacuum-processed thin film transistors. In order to address this issue, thin film transistors with double-stacked layers hold great promise among other approaches because of their superior electrical performance. Recent studies have proposed heterojunction transistors showing an average high field effect mobility of 30 cm²V⁻¹s⁻¹, an analogous performance with devices made by vacuum process. However, further development of double-stacked transistors is hindered by limitations particularly with regards to their turn-on voltage of -40 V which is unsuitable for the switching devices. Herein, we overcome this restraint by proposing a renovated structure called homojunction thin film transistors consisting of a channel layer and a channel electron modulation layer. Not only do we achieve the highest field effect mobility of approximately 50 cm²V⁻¹s⁻¹, but a turn-on voltage of the device can also be effectively controlled from -80 V to 0 V through modifying each layer. Moreover, this exceptional electrical performance of homojunction transistors are maintained more than 50 days under ambient conditions, and other device traits such as uniformity and reliability are validated. Through five analyses, including x-ray diffraction, atomic force microscopy, x-ray reflectivity, x-ray photoelectron spectroscopy and transmission electron microscopy, the solution-grown thin films in our structure have few electron trap sites and thus afford fast electron transportation, showing unprecedented field effect mobility and excellent hysteresis characteristics. These outstanding results are attributed to the high film quality of oxide films with a thickness less than 6 nm, its properties of a continuous and large-scale deposition processing. However, further research is needed to apply a solution process into roll-to-roll process techniques including roll-to-roll process.
8:45 AM *PM03.01.03
High-Speed, High-Resolution Printing of Inorganic Devices Vivek Subramanian and William J. Scheideler; University of California, Berkeley, Berkeley, California, United States.

In recent years, there has been increased interest in printed inorganic devices. This has been driven by the high performance that has been demonstrated in these systems, with field-effect mobility >10 cm²/V-s having been achieved in several solution-processed FETs based on inorganic semiconductor materials. Some of these materials are additionally attractive due to their optical transparency. Printing is a key issue in these systems. Due to the material constraints of these systems, inks formulated from these materials are often limited in their rheological tenability. Here, we review our work developing materials and processes for printing of inorganic devices, and present the resulting device data showing the achievement of high-performance devices using a range of high-speed and high-resolution printing techniques. We have realized transparent conductors and fully transparent FETs using these techniques. We have also developed material sets and inks that enable fabrication of such devices at low-temperature, enabling the use of a wide range of substrates.

We report on our development of printed thin film transistors, conductors, and sensors based on these materials.

9:15 AM *PM03.01.04
Zone-Cast Printed Crystalline Organic Thin-Film Transistors and Circuits with High Mobility Paul Heremans1, 2, Robby Janneck1, 2, Dimitrios Karagiannis1, 3, Thomas Nowack1, 2, Hany Ali1, 3, Florian De Roose1, 3, Jan Genoe1, 3 and Cedric Rolin1, 3; imec, Leuven, Belgium; ESAT, KU Leuven, Leuven, Belgium; 2KU Leuven, Leuven, Belgium.

We develop a meniscus-guided printing technique for organic transistors with high mobilities. In our zone-casting technique, a solvent meniscus with dissolved organic semiconductor is formed, that coats a crystalline thin-film of semiconductor in a continuous way. We acquire in-depth understanding of the process by modeling the film formation for different solvents,olute concentrations, temperatures and printing speed, and correlating the results with experimental findings for two different small molecules C8-BTBT and TIPS-pentacene. Next, printed crystalline films of C8-BTBT with charge carrier mobility exceeding 5 cm²/Vs are used to fabricate TFTs, both in top contact geometry and in bottom contact geometry. We show a reproducible and accurate process for patterning the semiconductor by photolithography and etch down to channel lengths of 3 micron. The patterning process does not impact the transistor performance. Using the bottom-contact geometry, robust 19-stage ring oscillators with 5-micron transistors are shown that comprise 80 TFTs, having an operating frequency of 6.30 Hz at an operating voltage of 10 V.

9:45 AM BREAK

10:15 AM *PM03.01.05
Horizontal Alignment of Carbon Nanotubes Using Roll to Roll Processing Ken R. Carter; University of Massachusetts Amherst, Amherst, Massachusetts, United States.

One-dimensional objects which have aspect ratios greater than 5 such as carbon nanotubes (CNTs), microtubes nanowires, microwires, fibers, nanorods, nanorods, whiskers, and the like, are generally bundles or entangled into aggregates or agglomerates when disposed on a surface. It is difficult to separate these objects and to orient them because their high aspect ratios permit them to overlap with one another when they are stored. This overlapping is generally random and often results in entanglements which produce the aggregates and agglomerates. The entanglements make it difficult to separate the one-dimensional objects from one another and to orient them in any particular direction. Oriented one-dimensional objects can find utility in a variety of applications in electronics, conductive plastics, catalysts and the like. It is therefore desirable to find a method of orienting one-dimensional objects. We report a method where CNTs can be directed to horizontally align when coated on a patterned substrate. A dispersion of one-dimensional objects in a liquid mixture is deposited on a substrate that has channels create by NIL or Roll-to-Roll NIL techniques. The CNTs orient in a direction that is perpendicular to the walls of the channel. By changing the shape of the channel, different orientations of the one-dimensional object can be obtained. The orientation of the one-dimensional objects can therefore be controlled by controlling the shape of the channels. Using this method, large areas of horizontally aligned CNTs can be fabricated with ease and high throughput.

10:45 AM *PM03.01.06
Metallicity-Based Sorting of Single-Walled Carbon Nanotubes M. B. Chan-Park; Nanyang Technological University, Singapore, Singapore.

Carbon nanotubes have attractive electronic properties for sensors, FET, etc. However, the mixture of metallic and semiconducting carbon nanotubes in almost all synthesis routes prevent their widespread use. We have developed a facile high yield sorting technique based on electron transfer to metallic nanotubes as we tune the pH. We have now extended the sorting technique to various carbon nanotube sources.

11:15 AM PM03.01.07
Dynamic Spray-Gun Deposition Method for New Generation of Graphene Based Devices Fabricated by Roll-to-Roll Paolo Bondavalli1, Alkaterini-Flora A. Trompet1, Gregory Pogon1, Konstantinos Charitidis1 and Elias Kounoulou1; 1Thales Research and Technology, Palaiseau, France; 2Research Unit of Advanced, Composite, Nano Materials & Nanotechnology, National Technical University of Athens, Athens, Greece.

This contribution deals with the fabrication of devices based on graphene based nanomaterials using dynamic spray-gun deposition method implemented rough roll-to-roll. We used this technique to fabricate supercapacitors, flexible memories and conformable Electro-Magnetic Shielding (EMS) layers. In the first case we exploited the nanostructuretization of mixtures of graphene and carbon nanotubes to achieve electrodes for supercapacitors. Indeed the carbon nanotubes (Multi-Walled Carbon Nanotubes that are metallic and so conductive) are used as sort of spacers to avoid the restacking of graphene. Thanks to that we can exploit the huge surface of graphene to store charges and at the same time we create channels between the layers allowing the rapid charge and discharge of the device. The use of high quality graphene (<5 layers) and MWCNTs, with a diameter of around 20nm, also improve the conductivity for the electrodes and allowed us obtaining an impressive specific power value of around 100kW/Kg using an industrially suitable technique and not only a lab based one. In order to increase the energy storage we have used ionic liquid, which are more viscous, having larger charges. In this case as spacers we have used carbon nanofibbers with larger diameters (10nm-100nm). The spray-gun deposition method has been also implemented in the fabrication of Graphene Oxide and Carbon Nanofibers Oxidized based memories. In this case we case spray nanomaterials water based suspensions on a flexible layer previously metallized. The total thickness is around 100nm. After contacting the top with metallic contacts we are able to achieve flexiblenon volatile memories for examples in RFID tags or in packages. Finally, we have achieved EMS architectures using nanostructuretization of graphene, MWCNTs and carbon nanofibbers between polymers layers in order to exploit the Maxwell-Wagner effects to absorb X-band frequencies. Thanks to this
nanostructure we are able to trap the charges in sort of micro-capacitors created in the layers. This is a real breakthrough considering that usually heavy metal based layers are used and that in this case nm based non-absorbable layers can be obtained opening the route for new kinds of applications. Also in this case the fabrication will be implemented by roll-to-roll fabrication. During the presentation we will show all the details on the first characterization of devices and we will show also perspectives for other potential field of applications.

11:30 AM PM03.01.08
Chemical and Mechanical Substrate Modification to Improve Printing of Functional Materials Stefan Schliske1,2, Tobias Rödlermeier1,2, Martin Held1,2, Silvia Menghi1,2, Alessandra Hausmann1,2, Kathleen Fuchs1,2, Marta Ruscello2, Uli Lemmer1,3 and Gerardo Hernandez-Sosa1,2; 1Light Technology Institute, Karlsruhe Institute of Technology, Karlsruhe, Germany; 2InnovationLab, Heidelberg, Germany; 3Institute of Microstructure Technology, Karlsruhe Institute of Technology, Karlsruhe, Germany.

The deposition of solution processable functional materials with printing techniques offers the possibility to prepare low-cost electrical devices like organic light emitting diodes (OLED) or organic field-effect transistors (OFET). These devices are to be deposited on non-porous and non-ink-absorbing substrates. Therefore, the interaction between the ink and the substrate has a strong influence on the wetting behavior, pinning effect and film formation during the drying process which magnitude is determined by the surface free energy (SFE) of the substrate and surface tension (ST) of the ink. Additionally, this interaction mainly affects the contact angle (CA) of a single drop and thus the smallest possible printed feature size. For these reasons a particular ink is usually developed for a particular set of surface properties and generally has to be reformulated when changing the substrate. In this work, we introduce a controlled nanoscale roughness onto the substrate surface to define wetting and pinning properties without changing the ink formulation. The roughness was transferred via soft imprinting onto spin coated polymeric layers resulting in increased pinning of test fluids and commercial inkjet inks. Additionally, we developed a siloxane substrate pretreatment which enables a complete control of the SFE. Siloxanes, with their huge variety of sidechains and their substrate independent ability to form self-assembled monolayers, allow to adjust the SFE of different types of substrates, like glass, metal, silicon or plastics. By mixing different silanes the SFE could be tuned from 47 mN/m down to 13 mN/m independently of the substrate. The influence of different fluorinated and non-fluorinated functional groups on the SFE as well as on the printing resolution was examined by static and dynamic CA measurement and by assessing the pattern quality of inkjet printed Ag structures. Furthermore, we show that the siloxane treatment increases the printing resolution by reducing the printed drop size up to 70%. This enabled us to increase the electrode density per area of OFETs without negatively affecting the device properties.

11:45 AM PM03.01.09
Increasing Organic Semiconductor Crystal Width with the Dimensions of Inorganic Polymer Micropillar Jeongchan Lee and Steve Park; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Solution coating process using organic semiconductors (OSC)s are a promising technique for large-area, low-cost and flexible transistor application. Therefore, a variety of solution coating processes have been developed over the past few decade such as spin coating, slot-die coating, inkjet printing and solution shearing. The key requirement of organic electronics is the formation of high quality organic semiconductor thin-film over a large area in a facile manner. However, the crystal orientation, crystallinity and crystal size of OSCs, which affects the performance of transistors, are difficult to control because of unmanageable nucleation and chaotic fluid flow. Therefore, the system is needed that controls the nucleation process during the solution coating. Herein, we demonstrate that organic crystal size can be manipulated simply by changing the shape and dimensions of the microstructures on the blade during solution shearing. We tuned the shape of the meniscus by tuning the micropillar shape and size, by which nucleation rate was controlled. The mobility of the thin-films increased with increasing crystal size to as high as 3.56 cm2/Vs. Such a new way to manipulate the crystal size adds another useful parameter that can be utilized to tune the property of organic thin-films and is potentially applicable to other materials systems. We also demonstrate for the first time the use of an inorganic polymer (AHPCS) as the microstructured blade for solution shearing. Currently, microstructured silicon is used, which is expensive and difficult to fabricate, and is very brittle. On the other hand, AHPCS can easily be microstructured via molding and is mechanically durable. Furthermore, unlike elastomers such as PDMS, AHPCS is highly resistant to various organic solvents. The use of AHPCS for microstructured blade is therefore highly advantageous for industrial applications where low cost and durability are of great importance. In summary, we demonstrate the crystal width of semiconductor increase with the dimensions of microstructure of shearing blade, which results in increasing the performance of field-effect transistors. Such a control of nucleation process by manipulating the meniscus line expands applicability of solution shearing to various printed electronics.

SESSION PM03.02: Nanoimprint and Structuring
Session Chairs: Nikos Kehagias and James Watkins
Monday Afternoon, November 26, 2018
Hynes, Level 1, Room 108

1:30 PM *PM03.02.01
Roll-to-Roll UV Nanoimprint Lithography for Large Area Manufacturing of Bionic Surfaces Dieter Nees, Johannes Goetz, Stephan Rutloff, Ursula Pfalzinger and Barbara Stadlober; Joanneum Research, Graz, Austria.

Roll-to-roll UV nanoimprint lithography (R2R-UV-NIL) gains increasing industrial interest for large area nano- and micro-structuring of flexible substrates because it combines nanometer resolution with many square meter per minute productivity. Beside the classical application fields of nanoimprint lithography like micro-electronics and micro-optics currently biomimetic micro- and nano-structured surfaces get increasing attention for viscous drag reduction (shark skin effect), water and dirt repellence (lotus effect) and anti-reflection (moth-eye effect) coatings. In this study we report the set-up of a custom made R2R-UV-NIL pilot machine which is able to convert 10 inch wide polymer web with velocities up to 50 m/min. For imprint as well as polymer working stamp material UV-curing resins based on urethane acrylates and thiol-ene chemistry were designed to meet the requirements of R2R-UV-NIL processes being strong adhesion to polymer substrates, fast curing speed and high imprint fidelity. The mechanical properties, surface chemistry and refractive index of these UV imprint resins can be tuned over wide ranges by choice and ratio of urethane acrylate oligomers and acrylate or thiol monomers – and surface active dopants. We have achieved Young’s moduli between 5 MPa and 5 GPa, refractive indices nD25 between 1.4 and 1.7 and surface energies between 15 mN/m and 60 mN/m. Furthermore, new strategies have been developed to achieve excellent abrasion resistance and utmost weathering stability of the nanoimprinted biomimetic polymer surfaces in harsh outdoor applications.
Thermal Nanoimprint Lithography, in its conventional implementation with heating plates acting as the source and sink of heat, suffers from several limitations such as low throughput, narrow range of suitable thermoplastic materials/resists and issues related to (differential) thermal expansion.

ThunderNIL has introduced the Pulsed Nanoimprint Lithography (Pulsed-NIL), an ultrafast NIL technology enabling the nanopatterning over large areas in ultra-short thermal cycles. This technique replaces bulky hot plates with heaters integrated into the stamps and buried just below their nanostructured surfaces. A single, short (<100 µs) intense current pulse results in the abrupt raise of the temperature at the stamp surface, leading to the melting of the resist film in contact with it. The process takes place in highly dynamic conditions with high heating/cooling rates (~10⁶ °C/ms) and very steep temperature gradients (~10³ °C/µm).

These conditions provide a few key advantages, not only related to the throughput, which can be enhanced by orders of magnitude (at least in principle, but limited in practice by the speed of substrate handling), but also improving the quality of the results, broadening the range of functional materials suitable to be processed and enabling a tight spatial confinement of material that is melted during the cycle, to regions in direct contact with the stamp.

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The seminar will present the working principle of the Pulsed-NIL technology, some aspects of polymer rheology under high temperature, high temperature gradients and high shear rates, and will show the specific advantages that the Pulsed-NIL technology has for the fabrication of 3D hierarchical nano/micro structures and for seamless tiling of large area with nanostructures in a Step & Repeat (SR) process mode.

The origination of large area nanostructures with seamless patterns by Step & Repeat (SR) process or the formation of hierarchical nanostructures for roll-to-roll applications will benefit from this special feature of the Pulsed-NIL process, enabling cost effect origination of complex 3D hierarchical nanostructures for use different applications domains of nanotechnologies.

R2R-UV-NIL as a Powerful Mean for Large-Area Fabrication of Optical Polymer Components in Lighting and Microfluidic Applications

Recently, R2R-UV nanoimprinting has proven to be very useful and unrivalled for the large-area fabrication of high-resolution, hierarchical structures at reasonable throughput for the realization of mechanically flexible functional surfaces useable in bionic applications like drag-reducing films or transparent conductive electrodes [1], [2].

Here we report on the utilization of UV-NIL for the manufacturing and upscaling of optical and conductive components in lighting and microfluidic applications. One key prerequisite for a versatile deployment of UV-nanoimprinting is the adjustability of the imprint resin towards the targeted application scenario. It should be tunable in terms of elasticity and surface tension to account for easy demolding and for low (water-repellent) as well as high (water-wicking) energy surfaces and it should have low enough viscosity to allow for large-area coating. Special requirements for the channel forming resin in microfluidics are a sufficiently high surface tension to allow for a fast and long distance filling of analytes, the ability to be bio-functionalized and low cytotoxicity. For optical polymer components such as free-form micro-lenses or light coupling/reflection structures the tenability of the refractive index is important as well.

Another important aspect is the master fabrication and its upscaling to large-area imprint tools. Here we introduce a Step & Repeat UV-NIL technique allowing for a high-precision nearly stitch-free multiplication of small scale masters onto polymer films resulting in large and flexible imprint stamps that are readily mounted around the imprint roller.

With these ingredients we R2R fabricate IVD chips for pathogen detection with double-side imprinting of microfluidic channels and light management structures. Due to the improved light outcoupling the chemiluminescence signal was increased by about 20% as tested in a portable read-out device of a commercial chip testing platform. Another example is the R2R fabrication of freeform micro lenses with small height that enable a homogeneous distribution of light from discrete LED sources in ultra-thin direct lit luminaires.


Acknowledgement:
Parts of this work have been performed within the H2020 EU-funded project “R2RBiofluidics”, Grant Agreement number 646260 and the RSA project Green Photonics (FFG Austria)

3:00 PM BREAK

3:30 PM PM03.02.03
R2R-UV-NIL as a Powerful Mean for Large-Area Fabrication of Optical Polymer Components in Lighting and Microfluidic Applications

Barbara Stadlober1, Dieter Nee2, Anja Haase3, Ursula Pfinger3, Ladislav Kuna1, Stephan Rutlloff4, Claude Leiner1, Christian Sommer1, Jan Hesse1, Max Soolteiner5, Daniel Thesen6, Mirko Lohse7 and Martin Smolka7; 1Joanneum Research Forschungsgesellschaft mbh, Graz, Austria; 2GenSPEED Biotech GmbH, Rainbach, Austria; 3Micro Resist Technology GmbH, Berlin, Germany.

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Wrinkling is a ubiquitous surface phenomenon that occurs at a wide range of length scales from kilometers to nanometers. Particularly, micro/nano-scale wrinkles have found applications in stretchable electronics, tunable optics and coatings with controlled wettability and adhesions [1,2]. Although various techniques including thermal treatment [3], swelling [4], mechanical stretching [5], and UV curing [6], have been developed for wrinkle fabrication, little attention has been paid for continuous manufacturing over large scale. Bearing this in mind, for continuous write wrinkle on a roller, both experimentally and theoretically, with the aim of developing a scalable roll-to-roll (R2R) manufacturing process. This technique takes advantage of the various geometrical shapes and curvatures defined by the 3D printed rollers to induce well-defined strain fields to manipulate the final wrinkle patterns on compliant polymer substrates. First, we study wrinkle formation on a thick polydimethylsiloxane (PDMS) film wrapped around a roller, followed by oxygen plasma. The wrinkle features show a strong dependence on the geometrical parameters of the roller, thickness of the film, and other processing parameters. We then explored to achieve continuous wrinkling under ambient conditions by applying a UV-curable polymer onto PDMS as the skin layer, followed by UV curing along with rotation of the roller. Based on this principle, we demonstrate one-dimensional (1D) gratings, two-dimensional (2D) herringbone and labyrinth patterns over large areas using different roller shapes, and the wrinkle wavelengths span from hundreds of nanometers to tens of microns. The use of rollers to control the generation of wrinkles paves the way for R2R manufacturing of surface wrinkles for a wide range of applications.


4:00 PM PM03.02.06 Transition to Superwetting for a Nanostructured Surface Nikolai K. Mandsberg1, Agnieszka Telecka1, Tao Li2, Emil Ludvigsen1, Sokol Ndoni1, Rosa Di Mundo1, Fabio Palumbo1, Jacek Fiotowski1, Serguei Chiriac2, Rafael Taboryski1, DTU Nanotech, Kongens Lyngby, Denmark; 1Dept. of Electronic and Electrical Engineering, University College London, London, United Kingdom; 2Dept. of Chemistry, Politecnico di Bari, Bari, Italy; 3NANOTEC, National Research Council, Bari, Italy; 4Mads Clausen Institute, University of Southern Denmark, Sonderborg, Denmark.

According to traditional Wenzel theory, superhydrophilicity emerge when introducing roughness on an intrinsically hydrophilic surface. However, recent studies have shown a deviation from this behavior [1]. Understanding the failure mechanism will aid the design of surfaces that exhibit superhydrophilic behavior. In particular, moderate hydrophilic materials, such as polymers and other low energy materials, need a careful design, as they are particularly prone to failure.

In this study, we employed block copolymer nanolithography [2] with a subsequent injection molding replication in poly(methyl methacrylate). Compared to the flat reference, the roughness increased the water contact angle (from 67.6° to 99.4°); a contraction to the traditional Wenzel theory. For moderately hydrophilic substrates, a nanoscopically pillar-built surface has a Laplace pressure barrier that prevents droplet spread. Increasing intrinsic hydrophilicity could lower the barrier to allow superwetting. Consequently, we characterized the transition by applying a low-pressure Argon plasma to increase the surface free energy in a continuous fashion. Using apparent contact angle to probe the transition, we found a threshold of 55°.

Furthermore, we demonstrate how macro- and microscopic wetting phenomena are interconnected. As an example of the barrier implications, we study the condensation of water on both sides of the threshold. While flat surfaces and untreated, structured surfaces both show indelible dropwise condensation, the plasma treated, structured surface gives rise to filmwise condensation. Using a transparent polymer and designing structures to be below the diffraction limit for visible light, the threshold defines the emergence of anti-fogging properties relevant to a plethora of optical applications such as endoscopy [3].

References:
[1] D. Kim et al., Wetting theory for small droplets on textured solid surfaces, Scientific Reports (2016) 6, 37813

4:15 PM PM03.02.07 Spirothiopyran Mediated 2 Color Super-Resolution Lithography for High Throughput Nanopatterning Harikrishnan Vijayamohanan, Edmund Palermo and Chaitanya K. Ullal; Rensselaer Polytechnic Institute, Troy, New York, United States.

Rapid, high throughput patterning in three dimensions with nanoscale resolution has long remained an elusive target for materials scientists. Optical interference lithography has been an attractive technique to cheaply and rapidly pattern three dimensional features in polymer photoresists despite both resolution and feature size being limited by diffraction. In the past few years, Stimulated Emission Depletion Microscopy (STED) inspired lithography schemes have shown the ability to direct-write features well below the diffraction limit using visible light. However, the high light thresholds required for effective photoinhibition renders them unsuitable to be used for interference lithography and limits their use to point by point writing. Recently, we have shown that combining the reversibly saturable photoisomerization of spirothiopyran with thiol-Michael addition chemistry can be used to formulate a super-resolution writing system with desired low light thresholds for photoinhibition, thus enabling them to be used for parallel patterning using interference lithography. Adapting the spirothiopyran writing chemistry for self-assembled monolayers on glass substrates allows us to fabricate switchable photosensitive surfaces that can be activated and deactivated for patterning with maleimide functionalized molecules using UV (365 nm) and green (532 nm) light respectively. By exploring the kinetics of photoisomerization of bound spirothiopyran and subsequently tuning their chemical environment, we experimentally demonstrate large area nanopatterning with sub-diffraction resolution and molecular thickness using a 2-color interference lithography setup. The lateral feature size of the written patterns is shown to be tunable by controlling the relative intensity of the initiation and inhibition wavelengths. The resultant nanopatterns formed are characterized using super-resolution microscopy. Secondary conjugation on regions patterned with bifunctional maleimide linker molecules can be used to tailor the nanostructured surfaces to desired chemical functionalities. These experiments demonstrate the versatility of spirothiopyran based writing systems for rapid high throughput nanopatterning. Efforts are currently underway in our
Flexible Nanogap Diodes for GHz Radio Frequency Energy Harvesting Applications

Akshita Mishra, Henam Sylvia Devi, Soumen Saha, Abhisek Dixit and Madhusudan Singh; Indian Institute of Technology Delhi, New Delhi, India.

Wearable and bio-implantable health monitoring applications require flexible memory devices that can be used to locally store body vitals prior to transmission or to support local data processing in distributed smart systems. In recent years, non-volatile resistive random access memories composed of oxide-based insulators such as hafnium oxide and niobium pentoxide have attracted a great deal of interest. Unfortunately, hafnium and niobium are not low-cost materials and may also present health challenges. In this work, we have explored the alternative of using titanium dioxide as the insulating oxide using a low-cost solution-phase deposition process. Aqueous sol deposited titanium dioxide thin films were deposited on standard RCA-cleaned commercial thermal silicon wafer (500 µm). Patterned bottom contacts Cr/Au (~200/300Å) using shadow masks were deposited on the substrate using successive DC sputtering, and thermal evaporation, respectively at 5 x 10^-4 Torr. A sol was prepared using titanium (IV) butoxide as precursor hydrolyzed under water and ethanol to form a colloidal solution (sol) at 50°C under constant stirring. Powder X-Ray Diffraction (XRD) scans of calcined (from sol at 750°C) nanoparticles show a mixture of anatase and rutile phases, confirming the composition of the material. The sol was slowly cooled to room temperature before being spin coated at low rotational speeds on to the substrate in multiple steps involving several spin coating and drying steps to form a uniform film. Top contacts (Ag) of thickness (~500Å) were deposited on the sol-deposited thin films using thermal evaporation. The resulting devices were coated with a thick layer of polydimethylsiloxane (PDMS) using a 10:1 ratio of base elastomer and curing agent respectively. After drying the PDMS, resistance measurements were carried out using Keithley 6514 electrometer. A high resistance state was detected prior to electroforming in the air at ~27 GΩ, which remains nearly unchanged (~24 GΩ) when dipped in a pH 7 buffer solution (equivalent to human blood’s pH (reference value ~7.4)). Unencapsulated devices were further characterized in air using a Keithley 4200-SCS semiconductor parameter analyzer in dual sweep mode to observe repeatable hysteresis behavior with a large difference between trace and retrace R-V characteristics (~50%-3% over a pristine device), which compares favorably with recent data in the literature on high-performance sputtered TiO2 memristors. Unchanged retention ratio using biocompatible device materials and encapsulation suggests that these devices can be used for biomedical implantable sensor electronics.

8:00 AM PM03.03.01
Flexible Nanogap Diodes for GHz Radio Frequency Energy Harvesting Applications

Kalaivanam Loganathan, Emre Yengel, Hendrik Faber, Zainab Felenben, Emre Yardali and Thomas D. Anthopoulos; Material Science & Engineering (MSE), King Abdullah University of Science and Technology, Jeddah, Saudi Arabia.

The emergence of the Internet of Things (IoT) device ecosystem is expected to impact many aspects of our daily lives including health via accurate sensing & monitoring of our environment, transportation, logistics, and entertainment, to name but a few. Despite the tremendous potential, however, numerous technological and economic barriers still exist. One such technology roadblock with significant economic implications is how to reliably power the myriad of these IoT devices without increasing the environmental impact (e.g. battery disposal/recycling). Among the various green options is harnessing the omnipresent radio frequency (RF) energy using Wireless Energy Harvesting (WEH) systems. The most crucial components of a WEH system is the rectifier circuits and the RF antenna as they determine the frequency of operation, operating distance, and ultimately the power conversion efficiency of the system. In order to satisfy these requirements, the rectifier circuit should be inexpensive to manufacture and able to operate at frequency ranges compatible with the widely available RF networks (>1 GHz). This is the reason why recently considerable effort focused on the development of diode technologies that can satisfy both the performance and cost requirements. Here, we report the development of sub-20 nm co-planar asymmetric nanogap electrode Schottky diodes manufactured on arbitrary substrate materials using adhesion lithography (a-Lith) as an alternative nano-patterning technique. As the semiconductor we employ different metal oxides as they combine solution-processability with excellent electron mobility while as the electron Ohmic contact we employ Ti as its native oxide (TiO2), which forms spontaneously upon semiconductor deposition, is thin (~2 nm) and semiconducting and as such does not compromise electron injection. For Schottky contacts, we find that both indium tin oxide (ITO) or Au yield large electron injection barriers and serve as good blocking materials. Using this rather simple nano-gap device architecture in combination with the attractive properties of metal oxides, we demonstrate diodes with operating characteristics significantly higher than 1 GHz. The manufacturing of the diodes can be further simplified through the use of an innovative photonic processing scheme that allows sub-10 second conversion of the metal oxide precursor to a highly polycrystalline semiconducting layer even on temperature sensitive substrates materials such as plastic, without compromising the diode’s performance. Our work paves the way to a radically new diode technology that has the potential to significantly impact the IoT device ecosystem.

8:15 AM PM03.03.02
Site-Specific Growth and In Situ Integration of Different Nanowire Materials on a Single Chip for Electronic Nose Applications

Guillem Domenech-Cuil1,2, Lukas Hrachowina1, Antonio Pardo1, Michael S. Seifner3, Isabel Gràcia1, Carles Cané1, Sven Barth3 and Albert Romano- Rodriguez1,2; 1University of Barcelona, Barcelona, Spain; 2In2UB, Barcelona, Spain; 3TUW, Wien, Austria; 4CNM, Bellaterra, Spain.

Many of our daily habits contribute to disperse toxic and harmful gases to the atmosphere, both in indoor and outdoor environments. For this reason, there is an increasing concern about the presence of these gases in the ambient and the need to fabricate systems to monitor them. There are many types of gas sensors for this application and among them, solid state gas sensors are an excellent choice. These sensors offer low manufacturing cost and low power consumption thanks to MEMs technology. Even though gas sensors based on semiconducting nanowires offer remarkable performances in terms of sensitivity and response time, they usually lack in selectivity, showing cross-sensitivities with environment conditions (e.g. humidity or temperature) and being only able to distinguish among oxidizing or reducing gases. A way to solve this issue is using pattern recognition from arrays of sensors with different materials or operating at different temperatures, giving rise to an electronic nose (e-nose) configuration. Based on a modification of the chemical vapor deposition method, a new procedure to site-selective synthesize nanowires on top of micromembranes has been developed. This method allows to grow the material with nanowire morphology and different compositions on one single chip surface and can be easily tailored offering an adjustable fabrication process for the direct integration of different nanowire-based resistive multi-functional devices. The use of
chemical vapor deposition techniques is compatible as a CMOS post-processing and, therefore, the impact of preparing gas sensors on any kind of chips for multifunctional devices is unimaginable.

In this work, we demonstrated for the first time the site-specific growth and in-situ integration of different materials in form of nanowires for sensing applications on a single chip in a well-defined geometry, with little interference on the growth parameters caused by the prior deposition of other nanostructured material. This proof-of-concept is exemplified by the deposition of SnO₂, WO₃ and Ge nanowires on the membranes of one single chip and their gas sensing responses towards different concentrations of CO, NO₂ and humidity diluted in synthetic air are presented. The measured responses allowed to discriminate between all three analytes using the well-known Principal Component Analysis (PCA) representation, as it allows gas separation and identification and, thus demonstrate that the system is suitable for environmental monitoring.

8:30 AM *PM03.03.03
Scalable Manufacturing for Flexible Hybrid Electronics

Benjamin Leever; Air Force Research Laboratory, Wright Patterson AFB, Ohio, United States.

Flexible Hybrid Electronics (FHE), which combine additive manufacturing processes with silicon chips, will enable applications such as wearable, assistive soft robotics, conformal and embedded sensors for condition-based maintenance, and wear-and-forget medical monitoring devices. The Department of Defense along with industrial and academic partners established NextFlex in 2015 to move these concepts from the lab to the manufacturing floor in the United States by developing or maturing key manufacturing processes in the areas of device integration & packaging and printing. This presentation will describe our roadmaps, which detail the capabilities identified by the FHE community over the next five years to enable the variety of envisioned applications. In addition, the presentation will highlight the FHE design and manufacturing flow through examples such as an FHE Arduino as well as specialized manufacturing tools developed through NextFlex projects such as modular systems that combine surface pre-treatment, inkjet printing, and encapsulation. Finally, the talk will address future prospects for applying roll-to-roll processes to FHE manufacturing.

9:00 AM *PM03.03.04
Hydration Sensor Patch for Human Performance Monitoring

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GE Global Research, Niskayuna NY 12309

Maintaining proper hydration is paramount for maximizing performance and minimizing health risks for laborers, warfighters, and athletes. Currently, there are no commercially high resolution solutions for accurate, non-invasive and continuous assessment of hydration in a wearable device format. Laboratory gold standards for hydration assessment are based on total body water and plasma osmolality under controlled conditions of stable and equilibrated body fluids. In practice, body mass losses are used as an indirect measure of fluid content, but continuous assessment of an individual's body mass fluctuations in the field during a mission is unrealistic. Similarly, blood (or urine) osmolality measurements are invasive and require sophisticated equipment and training for analysis. In this talk, we will present our approach towards developing a fully wearable system composed of bio-impedance and sweat sensors for dynamic and non-invasive assessment of hydration. The presentation will also include recent results from field testing of these devices at the U.S. Air Force Academy in Colorado Springs.

This work is sponsored by NextFlex, NBMC and AFRL and is a collaborative effort between GE Global Research, AFRL, UES, Dublin City University, University of Connecticut, University of Massachusetts, American Semiconductors Inc., and University of Arizona.

9:30 AM *PM03.03.05
Printed Image Sensors Based on Organic Phototransistors

Ana C. Arias; University of California, Berkeley, Berkeley, California, United States.

Image sensors are ubiquitous and used in a wide variety of applications ranging from consumer products to healthcare and industrial applications. The signal-to-noise ratio (SNR) of an image increases with larger pixels, which is costly to scale using silicon and wafer-based microfabrication. Solution-processed phototransistors can substantially advance the performance of image sensors. Phototransistors exhibit large photoconductive gain and a sublinear responsivity to irradiance, which enables a logarithmic sensing of irradiance that is akin to the human eye and has a wider dynamic range than photodiode-based image sensors. A solution-processed phototransistor composed of a heterostructure between a high-mobility organic semiconductor and an organic bulk heterojunction is presented here. The device efficiently integrates photogenerated charge during the period of a video frame then quickly discharges it, which significantly increases the signal-to-noise ratio compared with sampling photocurrent during readout. Phototransistor-based image sensors processed without photolithography on plastic substrates integrate charge with external quantum efficiencies above 100% at 100 frames per second. In addition, the sublinear responsivity to irradiance of these devices enables a wide dynamic range of 103 dB at 30 frames per second, which is competitive with state-of-the-art image sensors. The fundamental operation of image sensors using intra-pixel charge integration will be introduced and the figures of merit for these systems reviewed.

10:00 AM BREAK

10:30 AM PM03.03.06
Roll-to-Roll Fabrication of Conductive Copper Patterns on Flexible Substrates Using Maskless Lithography and Electroless Plating

U. Okoroanyanwu, S. Mehta, B. Brandso, A. Lepine, D. Morse and James Watkins; Department of Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States.

We report scalable roll-to-roll manufacturing processes for fabricating conductive copper patterns on flexible polyimide and PET substrates using a combination of maskless lithography and two approaches for patterning the seed layer, followed by electroless plating. A roll-to-roll processing platform comprising in-line surface cleaning, corona treatment, coating (gravure), and direct write lithography modules was used to pattern positive tone photosensitive coated polyimide and PET substrates. In the first approach, silver nanoparticle ink was deposited within the resist patterns and then sintered by photonic curing, to obtain silver seed layer for subsequent electroless copper plating steps. In the second approach, reactive Cu(II)-bearing ink and reducing ink were simultaneously deposited into the resist patterns and air-dried at room temperature to obtain a veritable reactive catalyst for subsequent electroless copper plating. Immersion of the silver seed layer and the catalyst bearing substrates into electroless copper plating baths resulted in deposition of conductive copper patterns over the lithographically defined silver seed layer and reactive copper catalyst patterns, respectively. Lastly, the photosensitive pattern was lifted off the substrate in acetone, resulting in well-defined copper patterns. The obtained copper patterns were characterized with optical and scanning electron microscopy, X-ray diffraction spectroscopy, and energy dispersive X-ray spectroscopy. The resistivity, solderability and adhesion strength of the copper patterns obtained with the two approaches were determined and compared, and will be presented, as will the performance of the copper patterns on an actual flexible hybrid electronic device.

10:45 AM PM03.03.07

*PM03.03.07
Novel Substrates for Applications of Roll-to-Roll Printed and Hybrid Functionalities

Jukka Hast, Markus Tuomikoski, Jussi Hiltunen, Marja Välimäki, Olli-Heikki Huttunen, Johanna Hietola-Keinänen, Marko Jurvansuu and Tiina Pöhler; VTT Technical Research Centre of Finland ltd, Oulu, Finland.

In this presentation, we discuss opportunities of novel substrate materials for roll-to-roll (R2R) printed and hybrid electronics and diagnostics applications as well as future production aspects. Traditionally standard substrates have been PET, PEN, PC, PMMA etc or stretchable polyurethane films. However, application requirements, especially wearable electronics and diagnostics, and sustainability issues are setting new demands for the future. Firstly, we present R2R thermal imprinting method to fabricate integrated polydimethylsiloxane (PDMS)-paper micro-fluidics for molecular diagnostics, which demonstrated in on-chip amplification of viral ribonucleic acid (RNA) with loop-mediated isothermal amplification (LAMP). Secondly, we discuss about new bio-based and recycled materials that include introduction of novel interactive cellulose fibre acoustic RGB-LED panel that is manufactured using R2R printing, chip assembly and foam forming technique. Moreover, to improve the sustainability, performance and consumer acceptance of printed and hybrid electronics we will introduce these functionalities on recycled, bio-based and biodegradable substrates and compare their functionality against traditional PET/PEN substrates. Third part of the presentation introduces PrintoNode industrial internet platform, which has been ramped-up recently. The aim of the PrintoNode is to explore challenges and solutions that allow to utilize collected process data in printed and hybrid electronics manufacturing and product lifetime towards novel data based business models.

11:15 AM *PM03.03.08
High Resolution Screen Printed Circuits for Low Cost Hybrid Systems

Goran Gustafsson1, Peter Andersson Ersmar1, Roman Lassnig1, Jan Strandberg1, Robert Forcheimer2, Deyu Tu2, Isak Engquist3 and Magnus Berggren1; 1RISE Acreo, Norrköping, Sweden; 2ISY, Linköping University, Linköping, Sweden; 3ITN, Linköping University, Norrköping, Sweden.

Printed electronics devices and systems built up from organic and inorganic electronic inks, promise for a low-cost technology platform that enables widely distributed electronics possible to add onto stickers, labels, posters, packages, smart cards, construction elements, solar cells etc. However, the functionality and reliability that can be achieved is still not enough for most products. Hybrid Printed - Si labels have the potential to fulfill the requirements above but are still aiming their breakthrough. One reason for its slow market evolution is that the price is too high for low margin products, e.g. packaging. There is a strong need for a strategy to make such hybrid integration cost effective. We will present a technology platform that merges Si-based components with printed electronics, aiming at twinning the benefits of the two. The technology includes printed, low voltage, devices and circuits such as drivers and MUX/DEMUX that release Si from expensive input/output circuitry, thus making Si-labels into a low-cost technology.

The technology platform is based on electrochemical devices such as transistors and displays printed at high resolution, by standard screen printing equipment. The major advantages of these printed electrolyte-based components are that the manufacturing can be performed outside the clean room facility that typically is used for most other transistor and display technologies. The resulting devices are operated at low voltages, less than 3 V, and are thereby compatible with printed batteries. The device manufacturing is further simplified by that only a small set of materials is employed, for instance the very same conducting polymer utilized as the active material in both the electrochemical transistors and the electrochromic displays. In the presentation we will describe this platform in detail and also hybrid product demonstrators at different levels of integration.

11:45 AM *PM03.03.09
Silver Nanowire Inks for Direct-Write Electronic Tattoo Applications

Nicholas Williams1, Steven Noyce1, Jorge Cardenas1, Matthew Catenecci2, Benjamin Wiley3 and Aaron D. Franklin2; 1Electrical and Computer Engineering, Duke University, Durham, North Carolina, United States; 2Chemistry, Duke University, Durham, North Carolina, United States.

Integrating electronics with biological systems is a critical step toward ubiquity for the ever-growing field of wearable electronics. The ultimate in custom integration will be to print functional electronics onto biological surfaces without any buffer or transfer layers – a directly written electronic tattoo. However, the development of such direct-write capabilities is severely limited by the absence of a conductive ink capable of printing directly onto biological surfaces. Current ink formulas typically require significant post-processing to achieve conductive traces, such as sintering at temperatures incompatible with living organisms (>40°C), ultraviolet curing, or rinsing with hazardous solvents. In addition, the electrical performance of printed traces designed for low-temperature curing generally degrades rapidly when the substrate is flexed, even when the curvature is minor. Silver nanowires offer a promising solution to these challenges as their high aspect ratio allows for the high conductivity of traces to be retained when the supporting substrate is flexed. In this work, we demonstrate room-temperature aerosol jet printing of highly conductive silver nanowire traces onto both biological and non-biological substrates, including Kapton and an oak leaf, with near-identical electrical performance on both substrates. The printed traces maintain a conductivity within 10% of its initial value when the substrate is completely folded (bending radius <0.1 mm). We also show that the resistance of the printed traces was independent of nanowire length. As a result of these unique characteristics, we demonstrate how our water-based, silver nanowire ink is capable of providing direct-write electronic tattoos on sensitive biological surfaces, such as the petal of a flower. These results open the way for the tattooing of functional electronic components, from antenna to circuits, directly onto the surface of virtually any organism, such as the skin of an animal.
various transparent conductors, includes flexible indium tin oxides (ITO) and indium zinc oxides (IZO), on thin (100μm) flexible glass substrates. Progress of scaling up perovskites to larger area, sheet-to-sheet and roll-to-roll, on flexible substrates will be reported. Insight will be given in module performance and the stability of such modules. For device structures of flexible glass/ITO/TiO2/mixed cation perovskites/Spiro-OMeTAD/MoOx/AI, a power conversion efficiency of 18% has been demonstrated.

2:30 PM *PM03.04.02
Flexible Glass Applications and Process Scaling Sean Garner, Sue Lewis, Gary Merz, Alexander L. Cuno and Iia Nikulin; Corning Research & Development Corporation, Corning, New York, United States.

Substrate choice is critical for overall flexible electronic device and process optimization. Flexible glass, ≤200m thick, offers several advantages for web manufacturing of electronic devices. Compared to alternatives, glass substrates offer advantages of dimensional and thermal stability, hermeticity, transparency, and surface quality. Similar to other web materials, flexible glass is appropriately conveyed through fabrication equipment using roller systems. This paper discusses flexible glass properties that enable high-performance devices using roll-to-roll (R2R) processes. With a specific focus on mechanical reliability, use of glass web has been demonstrated in key R2R building block processes such as: vacuum deposition, lamination, laser patterning, printing, photolithography, and solution coating.

A disruptive industry ecosystem for flexible glass manufacturing is emerging with new equipment sets being specifically optimized for glass R2R processing. This paper provides specific examples of scaled-up glass web processing at manufacturing widths, lengths, and conveyance speeds for glass web. New demonstrations of flexible glass R2R microreplication, flexographic printing, and high temperature vacuum deposition are discussed. These processes go beyond the previous lab scale activities and highlight glass web R2R processing at 1m-width, 100m-length, and 30m/min conveyance speed.

References


3:00 PM BREAK

3:30 PM PM03.04.05
Ambient Roll-to-Roll Slot-Die Fabrication of Flexible Organic Photovoltaics with Non-Fullerene Acceptor Yu-Ching Huang1, Hou-Chin Cha2, Yun-Ming Sung2, Tsui-Yun Chung2 and Cheng-Si Tsao1, 2; 1Ming Chi University of Technology, New Taipei, Taiwan; 2Institute of Nuclear Energy Research, Taoyuan, Taiwan; 3Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan.

Solution-processed organic photovoltaics (OPVs) have shown a dramatic progress in enhancing power conversion efficiency (PCE) by using non-fullerene acceptors. The non-fullerene based OPVs recently achieved over 14% PCE [1-3], and the promising PCE demonstrated the great potential of commercialization. One of the most attractive advantages of OPVs is the printable capability into large-area devices. The high throughput slot-die coating process is the most suitable candidate for the mass-production technology. Our previous study has developed a universal roll-to-roll (R2R) slot-die coating approach to fabricate high-PCE OPVs [4]. Here, we demonstrate the promising photovoltaic characteristics of flexible OPVs based on a combination of PBDB-T and non-fullerene ITIC. We successfully R2R slot-die coated the flexible OPVs devices with high PCE over 9% under irradiation of simulated sunlight (AM 1.5G, 100 mW/cm²). In this study, we present systematical research on the morphology evolution of PBDB-T:ITIC bulk heterojunction (BHJ) films deposited by spin and slot-die coating processes. Our results indicates that the processing parameters significantly affect the morphology and nanostructure of PBDB-T:ITIC BHJ film. These results provide significant insights into the essential knowledge towards highly-efficient OPVs for R2R slot-die process.

References

3:45 PM PM03.04.06
Meniscus Guide Slot-Die Coating for Roll-to-Roll Fabricated Perovskite Solar Cells Daniel Burkit, Peter Greenwood, David Richards, David Beynon and Trystan Watson; Swansea University, Swansea, United Kingdom.

Slot-die coating has been proposed as a potential fabrication method for many of the layers of perovskite solar cell stacks and a growing number of publications are emerging on this topic. Slot-die coating is a versatile coating technique able to coat a range of ink rheologies and as a pre-metered coating method slot-die coating results in little ink wastage. It is compatible with both flexible and rigid substrates and can be used in both roll-to-roll or batch processes, is capable of simple patterning, such as stripes or patches and can achieve considerable line speeds. The use of a meniscus guide as part of the slot-die head, to help bridge the gap between the coating head lips and substrate, has been reported to improve stripe definition [1] and has often been employed in the fabrication of both organic photovoltaic and perovskite devices. To help understand the role of the meniscus guide and how it’s dimensions impact on coating quality we have performed coating trials and produced process windows with a range of inks and assessed if the onset of coating defects, low flow limits- ribbing, discontinuous films, can be predicted using the visco-capillary model of slot-die coating proposed by Carvalho [2]. We also present observations regarding the onset of flooding/leaking for different meniscus guide lengths and how these can be used to control stripe definition under different coating conditions and ink rheology.

We present results of how this understanding is used to develop improved roll-to-roll slot-die coating methods for perovskite solar cells in a P-I-N configuration using a sequential deposition process for the perovskite layer. The lead iodide ink used in the perovskite layer is formulated in a non-toxic solvent and results in a film readily converted to perovskite through slot-die coating of methylammonium iodide without any other pre-treatments. The choice of solvent for the MAI ink is optimised by considering how the rheology and volatility of the formulation impact on the conversion to perovskite. Finally, these developments will be used to demonstrate how slot-die coating can be used to produce the full perovskite device stack in a continuous roll to roll process.
A Scalable Dry-Powder Spraying to Manufacture Lithium-Ion Batteries from Electrodes Towards the Entire Battery


scale, and finally aiming to achieve an integrated direct manufacturing of the entire energy storage devices (batteries) accustomed to flexible designs.


requirements. There is a significant need to understand how we can tailor the solid electrolyte to promote effective transport. Herein, we demonstrate a broadly fall into two material categories: (1) polymers and (2) ceramics. Polymer ionic conductors are advantageous because they can be manufactured easily into thin films, are mechanically robust, and flexible. However, polymer conductors have lower ionic conductivities when compared with their ceramic counterpart. Ceramic conductors boast outstanding ionic conductivities (>10 mS/cm) but processing the electrolyte into thin films (50-100 micrometer) for efficient device integration still remains a challenge because of the brittle nature of the ceramic. There have been a few studies which have investigated a hybrid approach which combines the polymer and ceramic into a composite electrolyte to achieve both processing and performance requirements. There is a significant need to understand how we can tailor the solid electrolyte to promote effective transport. Herein, we demonstrate a custom-made benchtop multi-material slot-die system that can print solid electrolytes with graded structures. Initial results have shown that the nano-scale interactions in the ink phase impact the macroscopic ink properties and the coating structure [1,2]. This work focuses on demonstrating the fine feature capabilities in slot-die coating system and understanding how pathways can be engineered for efficient transport.

References:


doi:10.1002/aic.690461003

4:00 PM PM03.04.07 Scalable Strategies to Enhance Mechanical Stability in Efficient, ITO-Free, R2R Printed OPV Devices Processed in Ambient Conditions on Flexible Substrates William Greenbank, Elodie Destouesse, Jani Lammimäki and Morten Madsen; The Mads Clausen Institute, University of Southern Denmark, Sonderborg, Denmark.

Organic photovoltaic (OPV) solar cells have been explored by research groups across the world as a promising form of next-generation solar energy technology. In addition to their potential to reduce the costs of PV solar energy, they also open up a range of new applications to solar energy. The major point of difference for OPV is that they can be fabricated using roll-to-roll (R2R) printing processes onto flexible substrates in ambient conditions, drastically reducing the energy payback time of the device. Despite all this promise, OPV are only just beginning to be commercialised on any significant scale, and efforts to scale up OPV production have been slow. Much of this stems from issues of low efficiencies and short lifetimes of devices particularly when attempts are made to replicate laboratory-scale studies at commercial scales. In recent years, laboratory-scale OPV device efficiencies as high as 15% have been reported, and while this represents remarkable progress, devices with such high efficiencies are often produced using techniques that do not translate well to commercial production, and do not retain their high efficiency over time. This is compounded when attempts are made to replace expensive components of the device like indium tin oxide (ITO), or deposit on flexible plastic substrates.

At the SDU NanoSYD nanoscience centre at the University of Southern Denmark we explore an integrated approach to OPV research, spanning the spectrum from highly controlled, small scale device studies, to medium-scale slot-die coated modules, to large-scale R2R printed modules. In this way our work aims to help bridge the gap between the laboratory scale and the industrial scale. This strategy has already proven successful. Recently we successfully produced ITO-free OPV devices incorporating non-fullerene acceptors (NFAs) that were entirely air-processed on flexible polyethylene terephthalate (PET) substrates with 6% PCE using scalable slot-die coating. These devices showed impressive stability when properly encapsulated, demonstrating a viable route for the implementation of a highly efficient polymer-NFA system in industrial-scale OPV production.

One of the key areas that we focus on is improving the lifetime of OPV modules, in particular the mechanical stability of flexible modules. This is often an under-researched area for OPV stability, but vitally important for many of the anticipated applications of OPV technology. Much of the mechanical instability in devices arises from poor adhesion between chemically-incompatible layers that then easily delaminate when only small amounts of stress are applied to the device. In our work we explore strategies to improve layer compatibility without compromising device performance that can be easily applied to commercial-scale production. Although our focus is principally on OPV devices, the techniques we employ have the potential to be applied to any solution-processed organic electronic device.

4:15 PM PM03.04.08 Scalable Manufacturing Platform of Multi-Material Solid Electrolytes for Solid State Battery Applications Kelsey B. Hatzell1 and Marm Dixit1; 1Vanderbilt University, Nashville, Tennessee, United States; 2Department of Mechanical Engineering, Vanderbilt University, Nashville, Tennessee, United States.

Recently, there has been a push toward all solid-state batteries to eliminate flammability issues in portable electronics. Several solid conductors exist and broadly fall into two material categories: (1) polymers and (2) ceramics. Polymer ionic conductors are advantageous because they can be manufactured easily into thin films, are mechanically robust, and flexible. However, polymer conductors have lower ionic conductivities when compared with their ceramic counterpart. Ceramic conductors boast outstanding ionic conductivities (>10 mS/cm) but processing the electrolyte into thin films (50-100 micrometer) for efficient device integration still remains a challenge because of the brittle nature of the ceramic. There have been a few studies which have investigated a hybrid approach which combines the polymer and ceramic into a composite electrolyte to achieve both processing and performance requirements. There is a significant need to understand how we can tailor the solid electrolyte to promote effective transport. Herein, we demonstrate a custom-made benchtop multi-material slot-die system that can print solid electrolytes with graded structures. Initial results have shown that the nano-scale interactions in the ink phase impact the macroscopic ink properties and the coating structure [1,2]. This work focuses on demonstrating the fine feature capabilities in slot-die coating system and understanding how pathways can be engineered for efficient transport.


4:30 PM PM03.04.09 A Scalable Dry-Powder Spraying to Manufacture Lithium-Ion Batteries from Electrodes Towards the Entire Battery Jin Liu1, Yan Wang1, Heng Pan2, Brandon Ludwig2, Yangtuo Liu1 and Zhenfeng Zheng1; 1Worcester Polytechnic Institute, Worcester, Massachusetts, United States; 2Mechanical and Aerospace Engineering, Missouri University of Science and Technology, Rolla, Missouri, United States.

An advanced power-based spraying technology was developed by us to fabricate electrodes for the lithium-ion batteries to analytically lower 20% of the manufacturing cost. Gas-driven spraying guns were chosen to address a direct dry-powder laminating of the electrode structures onto the current collectors without involving solvents. Through removing the usage of these organic solvents and related recycling procedures, the entire processing of electrodes is shortened and found to be more precisely controlled, which results in product electrodes with higher bonding strength, structural integrity, and materials homogeneity. We have demonstrated this technology with a wide range of compatibility on producing electrodes, including cathodes (LCO, LMO, NCM), anodes (Graphite), advanced architecture designs (Ultra-low binder recipe (<1%), high-energy thick electrodes (>280um), hierarchical micro-structured).

In addition, the flexible arrangement strategy of spraying guns promoted the development of hierarchical designs to be practically available to the lithium-ion market. Dry-powder sprayed electrodes with a multi-layered structure, outperformed single layer ones at electrochemical performance and mechanical properties. This technology is currently developing to be grafted onto the existing roll-to-roll fabrication of electrodes for lithium-ion batteries at the pilot scale, and finally aiming to achieve an integrated direct manufacturing of the entire energy storage devices (batteries) accustomed to flexible designs.

4:45 PM PM03.04.10 Roll-to-Roll Fabrication of High Performance Conformal Thermoelectric Generators Yining Feng1, 2, Zamaan Bagban1 and Na Lu1, 2, 4; 1Lyles School of Chemical Engineering, Purdue University, West Lafayette, Indiana, United States; 2Department of Mechanical Engineering, Missouri University of Science and Technology, Rolla, Missouri, United States; 3Department of Electrical and Computer Engineering, Virginia Tech, Blacksburg, Virginia, United States; 4Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

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of Civil Engineering, Purdue University, West Lafayette, Indiana, United States; 4Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana, United States; 5School of Aeronautics and Astronautics, Purdue University, West Lafayette, Indiana, United States; 6School of Materials Engineering, Purdue University, West Lafayette, Indiana, United States.

Thermoelectric generator (TEG) is a solid-state technology that can convert thermal energy directly into electricity through the Seebeck phenomenon. Over 2.5 quadrillion BTU/year of energy generated in US is wasted as a form of heat, which can be reclaimed as electricity using flexible TEG to power sensors and other microelectronics for civil communications and Internet of Things (IoT) technologies. Unfortunately, the current TEG technology is suffering from its rigid device structure, low efficiency and high cost in both device fabrication and installations.

In this work, a novel roll-to-roll production line of conformal thermoelectric generator (cTEG) will be reported. In-line fabrication includes several micro-deposition processes on a roll-to-roll equipment for a continuous manufacturing platform. The specific activities include: (a) depositing top metal contact layers using screen printing technique; (b) creating micro-porous channels on polymer substrates using pulsed laser irradiation system; (c) filling of micro-channels with p- and n-type TE materials using pipet dispensing systems or similar technique for nanoparticles depositions; (d) laser sintering of p- and n-type TE materials for in-situ crystallization with minimal thermal damage, followed by screen printing the top layer metal contacts to achieve high power output of conformal TEG as power sources for sensors. Thermoplastics with low thermal conductivity (i.e. kapton, PDMS, polyamide etc.) will be used as substrate and insulating materials between p-n legs.

The cTEG with polymer substrate and insulating materials lead to maximum heat gain to reach high efficiency at the device level for power generation. The performance of cTEG will be discussed with regards to the materials quality and manufacturing process. The fundamental science developed here will have a broad interest to flexible electronic and nanomanufacturing community.

SESSION PM03.05: Lighting and Optical
Session Chairs: Shelby Nelson and Barbara Stadlober
Wednesday Morning, November 28, 2018
Hynes, Level 1, Room 108

8:15 AM *PM03.05.01
Hybrid Roll-to-Roll Manufacturing of OLEDs
Pim Groen1, 2; 1Holst Centre, Eindhoven, Netherlands; 2Aerospace engineering, TU Delft, Delft, Netherlands.

Hybrid production methods offer the possibility to exploit the benefits of different technologies in a single manufacturing process. In this contribution, this strategy will be highlighted using the example of the roll-to-roll (R2R) production of large area organic light emitting diodes (OLEDs) on flexible polymer substrates. Two opposing strategies are available to deposit the functional layers in an OLED device stack: The “dry” approach uses vacuum based methods such as thermal evaporation and sputtering, whereas the “wet” approach relies on the coating and printing of functional inks. The R2R production of OLEDs based solely on vacuum techniques has been demonstrated and can provide efficient and stable devices. By contrast, preparing OLEDs exclusively by R2R “wet” methods is generally hampered by the limited materials purity and undesired interactions between the functional layers during deposition. A number of R2R production steps from solution, however, are already well established and allow the high throughput production with good control over the resulting layer quality. We have designed an OLED architecture which can be prepared in a hybrid manner by combining elements of wet and dry R2R processing technologies. Starting with a roll of barrier substrate, indium tin oxide (ITO) is first deposited uniformly by R2R magnetron sputtering as a transparent conductor. Hereafter, an insulator is applied from solution with patterned slot die coating to separate the electrodes. This eliminates the need to pattern the ITO. A conductive and semiconducting inks is then employed, to enable the external power supply and planarise the ITO surface, respectively. These steps have been demonstrated at web speeds of 10 m/min and above. The slot die coated planarisation layer allows the following step (R2R evaporation of the active OLED materials) to be carried out targeting significantly lower layer thicknesses, thereby saving precious materials and speeding up the entire process. At current state, the efficiencies of the hybrid OLEDs still lack behind compared to fully evaporated reference devices (20 vs. 45 lm/W at 1000 cd/m2), but with further process optimisation, it is foreseen that the increased process speed and more efficient materials use can compensate for a somewhat lower performance.

8:45 AM *PM03.05.02
OLED Manufacturing on Flexible Substrates Towards Roll-to-Roll
Christian Mayer; Fraunhofer FEP, Dresden, Germany.

Beside to display technology, OLED also has unlikely potential for lighting applications. Where extremely thin, flexible or transparent light sources are desired, OLED can exploit its potential as a supplement to the LED. The improvement of flexible OLED is currently the focus of worldwide research activities. Thin substrates of primarily barrier-coated polymer films, but also metal foils or ultra-thin glass, were tested for use in OLED production and have advantages and disadvantages. OLED prototypes on polymer substrates as well as ultra-bright glass were realized by Fraunhofer FEP. The main development areas are the improvement of device stability and brightness. This includes intensive work on encapsulation as well as the development of stacked OLED architectures on flexible substrates. Metal foils have also been utilized for several years as substrates for thin-film photovoltaics and batteries. Now metal foils are getting interest as substrates for flexible organic electronic devices. In contrast to substrate materials like glass or plastic web an extra smoothing layer on typically rough metal foils are necessary to reach sufficient device stabilities, in particular for large area OLED lighting. An advantage of metal foils in the organic electronics is the comparatively good electrical and thermal conductivity. This allows for homogenous large-area lighting surfaces with current densities of more than 10 mA/cm2. Additionally, metal foils can be applied as top encapsulation on OLED devices on glass or plastic substrate to improve the temperature management during device operation, combined with excellent barrier properties of metal foils. Those benefits of improved temperature management on the OLED device lifetime and better illumination homogeneity will be outlined in the presentation. First results on a full roll-to-roll process chain enabling later high throughput production will be presented.

In future, the focus will be on the development of integration solutions in functional devices and surfaces using established technologies. Fraunhofer FEP works on processes along the entire value chain to produce flexible OLEDs in both, sheet-to-sheet and roll-to-roll processes. The requirements for the materials and technologies as well as the associated challenges will be introduced using latest results by Fraunhofer FEP. Solutions and application possibilities will be presented.

9:15 AM *PM03.05.03
High Volume Manufacturing of Advanced Optical Elements
Theodor Nielsen1, Alicia Johansson1, Ilja Czolkos1, Niklas Hansson2 and Brian Bilenberg2; 1NIL Technology ApS, Kongens Lyngby, Denmark; 2NILT Sweden Filial, Gothenborg, Sweden.
Advanced optical element such as diffractive optical elements (DOEs) are expected to revolutionize the compact optics market for imaging and non-imaging systems by enabling low weight and low cost optical systems. Today we are in the beginning of a transition period when bulky optical systems consisting of classical lenses are going to be replaced by advanced optical elements using only a single flat optical element with an advanced micro- and nanostructured surface topography.

NIL Technology ApS specialises in supplying high-quality nanostructured masters and nanoimprinting solutions for customers worldwide. The key to high-volume and low cost production is replication and NILT are experts in replication techniques such as nanoimprint lithography, hot embossing and injection moulding.

Since 2010, NIL Technology has developed methods to implement advanced micro-and nanostructures on steel inserts for injection moulding of low cost polymer parts. The applications range from super-hydrophobic lenses to consumer products with structural colors and lab-on-chip systems. Over 100,000 nanostructured parts have been replicated by injection moulding without any degradation of the nanostructured mould surface which demonstrates the potential for production of very high volumes at low cost.

In this presentation, NIL Technology will demonstrate advanced multi-level DOEs replicated in low cost materials suitable for high volume applications. Methods for future in-line quality control will also be presented. Focus will be on nanostructured steel injection moulding tools made by nanoimprint and the tools use in injection moulding process.

9:45 AM

3D Printed Polymer Photodetectors

Ruitao Su, Sung Hyun Park and Michael C. McAlpine; Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota, United States.

Organic optoelectronic devices have witnessed significant advances in both material development and device performance over the past several decades. Recently, additive manufacturing has been applied to the fabrication of optoelectronic devices via utilizing various functional inks that are compatible with an extrusion-based 3D printing process. This has enabled the ability to additively print complex 3D optoelectronic architectures without the need for any traditional microfabrication processing techniques. Here, polymer photodetectors with high performance are fully 3D printed and thoroughly characterized. Specifically, functional inks are carefully selected for the constituent layers of the photodetector and semiconducting polymer ink is optimized for the active layer, achieving an external quantum efficiency of 25.3% and a specific detectivity of 8 × 10^12 cmHz^1/2/W. Significantly, these metrics are comparable to those of traditionally spin-coated counterparts, yet are fabricated solely via a one-pot custom built 3D printing tool housed under ambient conditions. The devices were integrated into image sensing arrays with high sensitivity and wide field-of-view, by 3D printing interconnected photodetector arrays onto flexible substrates and directly onto hemispherical surfaces. It is further demonstrated that this approach can be extended to create fully integrated multifunctional devices consisting of optically coupled photodetectors and light emitting diodes which are both fully 3D printed on a single platform, showing for the first time the multifunctional integration of multiple semiconducting device types on an integrated platform.

The 3D printed optoelectronic devices introduced here simplify fabrication procedures by eliminating the need for any conventional microfabrication facilities, enhancing the flexibility for the design and manufacture of next-generation wearable and 3D structured optoelectronics, and validating the potential of 3D printing to achieve integrated active electronic materials and devices.

10:00 AM BREAK

10:30 AM


Noah Strobel1, 2, Felix Lindheimer1, 2, Tobias Rödlmeier1, 2, Mervin Seiberlich1, 2, Stefan Schiltske1, 2, Manuel Pietsch1, 2, Uli Lemmer1, 2, and Gerardo Hernandez-Sosa1, 2; 1Light Technology Institute, Karlsruhe Institute of Technology, Karlsruhe, Germany; 2Innovation Lab, Heidelberg, Germany.

Organic photodiodes (OPDs) have in recent years reached a level of performance comparable to inorganic devices. This has considerably fueled the development of printing processes for the fabrication of single and multi-device systems. However, in order to achieve adequate rheological properties while maintaining optical and electrical device functionality, heavy investment into ink-formulation and process parameter evaluation is necessary even for small changes in material properties like the absorption range. For instance, in systems comprising a polymer donor and a fullerene acceptor the viscoelastic and optical properties are mostly defined by the polymer and are thus intrinsically coupled. To overcome this challenge, we are working with non-fullerene acceptors, which offer an additional adjustment screw to tune the optical properties of our devices without strongly affecting the viscoelastic behavior.

First, we present OPDs comprising poly(3-hexylthiophene) (P3HT) and the non-fullerene acceptor (NFA) IDTBR, having an indacenodithiophene core with benzothiadiazol and rhodanine flanking group. The devices show a photo-response up to 800nm and reach record responsivities of 400mA/W as well as cut-off frequencies surpassing 4MHz. To combine the gained spectral flexibility with the freedom of design, the fabrication is transferred to digital printing techniques (i.e. ink- and aerosoljet printing) to process opaque and transparent devices of comparable performance. Furthermore, we demonstrate successful decoupling of the optical and rheological properties by using visibly transparent polymer donors and color-selective non-fullerene acceptors. This approach offers spectral flexibility without the need for a variation in process parameters. By the selection of NFAs with energetic compatibility, we fabricated devices with color selectivity in the range of 400-600nm as well as 500-800nm.

10:45 AM

PM03.05.04

Novel and Scalable Concepts for Efficient, Bright and Low-Cost Light-Emitting Electrochemical Cells

Ludwig Edman; Umea University, Umea, Sweden.

The light-emitting electrochemical cell (LEC) features mobile ions in the active material, and it is the action of these ions that distinguishes the LEC from other light sources such as the OLED, and which enables for a number of attractive properties. For instance, it is possible to fabricate LECs from solely air-stable materials and employ a relatively thick single-layer as the active material.1 These attributes promise to pave the way for an unprecedented low-cost fabrication, and we have demonstrated functional LEC devices can be fabricated by slot-die coating,2 inkjet printing,3 and spray-sintering4 directly on a wide variety of substrates -- including paper,5 metal,6 and textile7 -- under uninterrupted ambient-air conditions. We have also performed a cost analysis that predicts that solution-based high-volume R2R fabrication methods can allow for the realization of flexible LEC patches at a low cost of ~11 €/m², which deliver bright light emission at 3.6 mW/m².7

The redistribution of the mobile ions during the initial operation of LEC’s causes electrochemical doping of the active material (p-type at the positive anode and n-type at the cathode), so that a light-emitting p-n junction forms at steady-state.8 It is this in-situ formed doping structure that allows for the simple device structure and the low-cost fabrication, but at the same time it has represented a significant challenge from both a conceptual and performance
Polychromatic Quantum Dot Light-Emitting Diode Array Fabrication Using Omni-Resolution Immersion Transfer Printing Technology

With excitons formed in the p-n junction region will result in a quenching of the exciton before light emission. Thus, it has been questioned whether an LEC ever can become efficient at strong light emission. However, in a recent study we have demonstrated that this issue can be resolved with a triplet-emitting host-guest active material, designed with equally deep electron and hole traps, a balanced hole and electron mobility, and an optimized concentration of mobile ions. Such a carefully designed single-layer LEC featuring air-stable electrode materials and equipped with an outcoupling structure delivers strong green luminance of 1910 cd/m² at a efficiency of 99.2 cd/A, which corresponds to a record-high external quantum efficiency of 27.5 %.¹

References

11:15 AM PM03.05.07
Inkjet Printing of Small Molecular Phosphorescent Emitters at the Controlled Surface of Confined Geometry
Yojuang Kang, Ji-hye Kim, Robert Bail and Byung Doo Chun; Polymer Science and Engineering, Dankook University, Yongin, Korea (the Republic of).

Significant progress has been achieved in the area of full color organic light-emitting diodes (OLEDs) in terms of their high performances. However, stable ink materials and accurate fine line patterning by printing is an essential core as an alternative candidate of expensive fine metal mask-aided RGB side-by-side patterning or multi-stack (tandem) high efficiency white technology for the large area OLEDs. We have prepared a suitable combination of soluble host material compounds with an effective ink functional technology. The bipolar phosphorescent host materials based on diphenyl phosphine oxide, pyridinolide, and carbazole-based structure were dissolved in a solvent mixture, and various conditions for the solvent composition and drying of films were examined. Homogeneous dot and line patterns with controllable surface condition at the confined geometries of light emitting pixels were obtained, where the precise pinning at the coverage of light emitting region was accomplished by use of the photo-patternable pixel define layer. Proper thickness and smooth surface were obtained from a mixture of chlorobenzene and other organic solvent with higher viscosity than chlorobenzene. During the inkjet process, several issues such as control of drop injection density, reduction of line-edge roughness, and the role of the mixed solvent properties were studied in detail. These results show the potential power of inkjet printing as a low-cost patterning method for low molecular weight emitters at high resolution or large area OLEDs.

11:30 AM PM03.05.08
Polymeric Quantum Dot Light-Emitting Diode Array Fabrication Using Omni-Resolution Immersion Transfer Printing Technology
Tae Won Nam and Yeon Sik Jung; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Diverse integration of depositing and patterning colloidal quantum dots (QDs) to demonstrate individual red-green-blue (RGB) QD pixels has been developed in past years to realize electroluminescent QD light-emitting diodes (QLEDs) as next-generation displays. Among numerous display products from televisions to mobile displays, the inception of virtual reality (VR) displays opened up demands for sub-micrometer pixel resolution due to the requirements of extremely high pixels per degree (PPD) far above those of the conventional displays. However, previously reported patterning technologies have limitations in demonstrating large area, full-color pixel arrays of sub-micrometer feature size with high fidelity and pixel quality such as edge-roughness. Here we present a novel transfer-printing technique which allows patterning and printing of QD array in omni-resolution scale; QD array in single-particle resolution to entire film can be fabricated and transfer-printed. Polymeric QD array with unprecedented resolutions up to 200 PPD is demonstrated by utilizing sequential aligning and printing of individual RGB pixel arrays. Conventional transfer-printing techniques adopt flexible polydimethylsiloxane (PDMS) mold on which topological pixel information is written; expensive high resolution patterning on flexible media cannot extend its functionality from prototype to industrial fabrication because the repeated use of soft PDMS transfer mold at pressure-assisted stamping step is not permanent due to accumulated deformation. Conversely, we insert pattern information on hard Si master template on which the deposition and patterning process of colloidal QDs occur in single step. After the ordered QD arrays are delivered to transfer media, hard master template can be reused permanently. Another advantage of using hard master is extremely low edge-roughness of QD pixels as the QDs are strictly confined in hard master trench with minimal edge-roughness when they undergo capillary-force self-assembly. At the final delivery stage of QD pixels, mere minimal contact between the pixels on transfer media and final substrate is necessary therefore avoiding pressure induced defect formation at QD solid. Our transfer-printing technique effectively reduces trade-offs of conventional QD patterning method thereby suggests possibilities for fabrication of full-color electroluminescent QLED displays in industrial scale.

11:45 AM PM03.05.09
Direct-Write Assembly of Freeform Colloidal Structures
Alvin Tan, Justin Beroz, Mathias Kolle and A. John Hart; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Evaporative self-assembly can be used to assemble colloidal building block particles with varying degrees of order and scale. These particles, when assembled into a solid, can attain emergent properties, such an electronic or photonic band gap. However, to date, self-assembly of colloidal materials is limited to planar films on substrates. Extending colloidal self-assembly to three dimensions would enable new applications uniquely enabled by macroscale colloidal crystals. Here, we demonstrate a direct-write technique capable of on-chip assembly of colloidal particles into centimeter-scale freestanding structures. Using a custom-built liquid dispense apparatus, we precisely extrude an aqueous polystyrene particle suspension from a fine needle onto a temperature controlled substrate. By balancing the rate of dispense with the rate of water evaporation, the polystyrene particles are continuously assembled into a crystalline solid. We propose that direct-write assembly has the potential to be adapted to a vast library of building blocks for building functional materials such as photonic crystals, quantum dot solids, and metamaterials.

SESSION PM03.06: Device Fabrication
Session Chairs: Mark D. Poliks and James Watkins
Stretchable Hybrid Packaging for Skin Electronics and Electronic Textile
 Takao Someya 1, 2, Hanbit Jin 1 and Tomoyuki Yokota 1; 1 Electrical and Electronic Engineering and Information Systems, The University of Tokyo, Tokyo, Japan; 2 RIKEN Center for Emergent Matter Science, Saitama, Japan.

In this talk, we will report recent progress of stretchable hybrid packaging for skin electronics and electronic textile. First, we have fabricated a skin display, which is an array of micro LEDs embedded in a thin rubber sheet. The display is stretchable by 45 percent of its original length. A skin display is much more durable to stretching and twisting than previous wearable displays. It is built on a novel structure that minimizes the stress resulting from stretching on the junction of hard materials, such as the micro LEDs, and soft materials, like the elastic wiring—which is a typical reason of damage in the past. Stretchable hybrid packaging is used to integrate rigid electronic components and stretchable wires on textiles for smart apparel. Finally, we will describe remaining issues and future prospects of stretchable hybrid packaging.

R2R Gravure as an Additive Manufacturing Technology for the Fabrication of Large Area Flexible and Inexpensive Devices
Gyounin Cho, Sunchon National University, Sunchon, Korea (the Republic of).

Over the last decade, roll-to-roll (R2R) printing has been pursued with the expectation of developing a commercially viable, high throughput technology to manufacture flexible, disposable and inexpensive printed electronics. However, in recent years, pessimism has emerged due to the barriers faced when attempting to fabricate and integrate thin film transistors (TFT) using R2R printing. In this presentation, for the first time, I will report a way of manufacturing TFT based large area, flexible and inexpensive devices via a fully R2R gravure printing process with Ag nanoparticle based conducting ink, BaTiO3 nanoparticle based dielectric ink and single walled carbon nanotubes (SWCNT) based semiconducting ink. Using R2R gravure system including those inks and poly(ethylene terephthalate) (PET) as the substrate, we obtained about a 92 % device yield in 15 x 0.25 m² PET roll with the printing speed of 6 m/min and extracted the scalability factors needed for a feasible manufacturing process. The R2R gravure printing process addresses several barriers in the fabrication and integration of printed TFTs, circumventing or surmounting challenges associated with the alignment of source-drain and gate electrodes, threshold voltage (Vth) shift, stability and overall device yield, proving that R2R printing is indeed a viable advanced manufacturing technology that can enable high throughput production of inexpensive smart packaging.

Flexible and Printed Organic Electronics Development for IoT Sensor Applications
Shizuo Tokito; Yamagata University, Yamagata, Japan.

Flexible and printed organic electronics technology has garnered increasing attention and resources in research and development because of its potential for low-cost, environmentally-friendly electronic devices. In particular, there is an immense need to deploy sensor frameworks for the so-called Internet of Things (IoT). These applications are envisaged as thin-film transistor (TFT) devices with various types of sensors fabricated using a variety of printing processes on thin plastic film substrates. Here, we report briefly on recent advancements in printable electronic materials, printed OTFT devices used in integrated circuits and IoT sensor applications. We have successfully fabricated pseudo-CMOS inverters using p-type OTFT devices, as well as NAND logic gates, which exhibited ideal characteristics at low operating voltages and high gains. True CMOS inverters using both p-type and n-type OSC materials are essential for low-power, high-speed operation, and for circuit designs with compact layouts. Using our newly developed n-type OSC material (TU-3) and a commonly used p-type OSC material (dif-TES-ADT), we successfully demonstrated a CMOS inverter that employed a stacked TFT device construction. Based on this CMOS inverter design, an operational amplifier, as well as ring oscillators and D-flip flop circuits, were also fabricated. To realize very short-channel OTFT devices and higher performance integrated circuits, we employed the reverse-offset printing method to form narrow channel lengths below 10 µm, resulting in good electrical characteristics. Pressure sensors based on ferroelectric polymer (PVDF-TrFE) materials are superior in detecting vital signs for the human body. We previously succeeded in the precise detection of pulse waves with a wearable patch-type sensor, which was fabricated on a plastic film substrate using printing methods. Our goal is to develop a smart sensor device that can be connected wirelessly to the Internet, which combines printed integrated circuits and one or more sensors. More recently, we are developing flexible hybrid electronic (FHE) devices, which use silicon-based LSI die for the signal processing and wireless communication circuits and integrated onto a flexible plastic film substrate. We patterned the sensor element, interconnect layer, and antenna with screen or inkjet printing methods, after which we mounted Si-LSI die and resistors on the same flexible film substrate, whereby we employed both Near Field Communication (NFC) or Bluetooth Low Energy (BLE) wireless communication protocols have. We successfully demonstrated a wearable temperature sensor using a PEDOT:PSS sensor element.

Rapid Production of Large-Area, Transparent and Stretchable Electrodes Using Metal Nanofibers for Wearable Electronics
Jiuk Jang, Sanggyoon Ji, Byeong Wan An and Jang-Ung Park; Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Recently emerging electronic devices, including displays, light-emitting diodes (LEDs), touch screens, smart windows, and heaters requires transparent electrodes with high optical transmittance (T) and low sheet resistance (Rs). Although the indium tin oxide (ITO) shows the excellent electrical and optical properties, its brittleness limits many potential applications in stretchable and wearable electronics. There are numerous studies for high-performance, stretchable and transparent electrode to substitute the ITO-based transparent electrode, however, most of them are virtually unavailable to the industry because of their low production rates, high process temperature and lack of reliability.

Here, we report the rapid electrospinning process that can directly form one-dimensional (1D), ultra-long Ag nanofibers (AgNFs) as a large-area, and continuous network for stretchable, transparent electrodes. The electrospinning process is simple and cost-effective because AgNFs can be formed directly on a substrate while minimizing the waste of functional inks. Since this process is based on a roll collector, it enables the roll-based rapid production of a large-area and transparent electrode film that is composed of AgNF network. In this work, the electrode film exhibits superb electrical characteristics (Rs, of ~1.3 ohm/sq) with high optical transmittance (~90%) in a visible regime and outstanding mechanical properties (90% stretchability and minimum bending radius of curvature of 70 µm). In addition, the annealing temperature of AgNF network relatively low (< 150 °C), suggesting that the polymer substrate such as polyethylene terephthalate (PET) can be used directly without any transfer process. For a continuous roll-to-roll process, a photonic annealing of functional inks has been utilized and the production speed was 4.5 to 12 m/min. As an application of this high-performance transparent electrode, we fabricated a stretchable and transparent heater in a large area (300 mm x 300 mm) using the roll-to-roll process. The heater presents high temperature (250 °C) at a low operating voltage and excellent temperature reliability under large strain. Furthermore, we integrated the heater with wireless operation system by connecting Bluetooth module so that the temperature is controlled directly using smart devices. According to the target purpose, temperature also can be automatically controlled by applying logic circuit to the micro-controller unit. We believe that this approach presents a promising strategy for
future wearable electronic devices.

4:15 PM PM03.06.05
Laser Patterning of Flexible Nanogap Schottky RF Diodes Via Adhesion Lithography Hendrik Faber, Kalaiyanan Loganathan, Zainab Felemban, Emre Yengel and Thomas Anthopoulos; King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

A major part of the envisioned Internet of Things device ecosystem will rely on wireless smart tags and sensor nodes for application areas as diverse as health care, wearables or logistics. All these devices rely on radio frequency (RF) signals for communication or wireless energy harvesting, and a crucial component for that are rectifying diodes capable of operating at the required frequencies typically beyond 1GHz. Therefore, developing novel manufacturing paradigms that successfully combine the ability to produce such RF diodes over large areas and flexible substrates, can truly make a substantial impact.

We have recently introduced adhesion lithography (a-Lith) as an innovative patterning technology that enables the fabrication of ultrafast planar RF Schottky diodes based on a variety of semiconductors [1-3]. A first metal layer (M1) is deposited and patterned via standard lithography procedures. Afterwards the M1 surface is treated with a self-assembled monolayer to weaken the adhesive forces towards a subsequently deposited second metal film (M2). Due to the weak adhesion, the second metal can then be peeled off where it overlaps M1 using a liquid glue or adhesive tape, resulting in the formation of a small inter-electrode gap of typically <15nm at the boundary between M1 and M2. Because of the nm-sized gaps and the possibility to use dissimilar metals for M1 and M2, a-Lith is perfectly suited to create fast coplanar Schottky diodes. Such devices have been demonstrated using solution processed ZnO in Al-Au nanogap electrodes, reaching cut-off frequencies well above 20MHz [2].

For a-Lith the most involved step is the use of photolithography to structure M1. In this work we therefore investigated an alternative patterning approach to streamline the whole diode manufacturing process. Using a commercial laser scriber system (λ=1080nm), the desired pattern is achieved by selectively removing areas of M1 via laser ablation with sub-50 micron precision. With optimized process parameters the metal film can easily be patterned according to digital designs that can be realised quickly followed by the a-Lith steps. Using this innovative combination of laser ablation and a-Lith 50nm-nanogap coplanar ZnO diodes with on-demand size and shape are realised. Despite the simplicity of the approach, resulting diodes are found to exhibit excellent operation including high current rectification (>10^3) and cut-off frequency (>1GHz). Most importantly, the proposed manufactured methodology is compatible with a wide variety of electrode materials including Al, Au, Ti, ITO, Cu, as well as substrate materials such as glass and plastic. The easy adaptability of the diode designs and compatibility with flexible substrates makes the combination of laser ablation and a-Lith an ideal tool to prototype advanced RF devices and circuitry.

References:

4:30 PM PM03.06.06
Wafer-Recyclable, Environment-Friendly Transfer Printing Methods for Fabricating Large-Scale Thin-Film Nanoelectronics Bongjoong Kim1,
Dae Seung Wie1 and Chi Hwan Lee1,2; 1Mechanical Engineering, Purdue University, West Lafayette, Indiana, United States; 2Biomedical Engineering, Purdue University, West Lafayette, Indiana, United States.

Thin film nanoelectronics that can offer performances beyond traditional bulk systems but on diverse substrates or surfaces in lightweight, low-cost, transparent, and/or flexible forms could enable many emerging applications. Example devices include flexible complementary metal oxide semiconductor (CMOS) systems, multifunctional nanosensors and optoelectronics, and high-speed nanowire circuits. Conventional approaches in transferring thin film nanoelectronics from their fabrication wafer to arbitrary surface of interests commonly requires chemical etching on the sacrifice of wafer, but also is limited by defects with a low yield. Here, we introduce a high-fidelity transfer printing process that enables the wafer-scale separation of high-performance thin film nanoelectronics from their fabrication wafer in a defect-free manner that allows multiple reuse of the wafer. This interfacial delamination is enabled through a controllable cracking phenomenon triggered by liquid at room temperature or electrochemical reactions. The physically liberated thin film nanoelectronics can be then pasted onto arbitrary places of interest, thereby endowing the particular surface with desirable add-on electronic features. Systematic experimental and theoretical studies reveal the underlying mechanics mechanism and guide manufacturability for the transfer printing process in terms of scalability, controllability, and reproducibility.

SESSION PM03.07: Poster Session
Session Chairs: Mark D. Poliks and James Watkins
Wednesday Afternoon, November 28, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

PM03.07.01
High-Speed OFETs S-parameters Characterization Michele Giorgio1,2 and Mario Caironi; 1Politecnico di Milano, Milano, Italy; 2Istituto Italiano di Tecnologia, Milan, Italy.

The willingness to fabricate transistors capable of high frequency operation is spurred by possible applications like high-resolution flexible displays or devices able to communicate via wireless. This, together with high throughput manufacturing methods such as roll-to-roll coating and inkjet printing, allow organic electronics to be an attractive viable way to make low cost electronics.

The maximum operational frequency of OFETs is going to increase thanks to constant improvements in polymers charge carrier mobility. Since the frequencies of transition that has been achieved nowadays are in the order of tens of MHz, the direct measurement of transistor performances becomes not trivial because of parasitic contributions or the occurrence of resonance.

In this work, a setup for scattering parameter measurement is installed, allowing reliable measurements up to 10 GHz. A process compatible with S-parameters measurement is demonstrated. OFETs are realized through a mask-less approach, combining a fs-laser process for the sintering of high resolution metal electrodes and suitable deposition technique of high mobility polymer semiconductor. OFET frequency behavior is characterized using S-parameters, highlighting the trend of the transition frequency as a function of the channel length.
Direct printed on curved surfaces is a newly emerging challenge in printed electronics due to the difficulties in developing the suitable inks and fabrication methods for highly curved surfaces. So far, very few efforts have been made to realize devices over a curved surface. Fabrication of optimized direct printing inks is highly significant for the production of high-quality printing on curved surfaces. The effect of solid, solvent, and dispersant on the printability and ink rheological properties such as viscosity, storage modulus, yield stress, thixotropy and viscoelasticity of various inks were tuned and investigated by rheological tests under steady and dynamic shear conditions. Here, for the first time, we demonstrate the direct printing of magnetic resonant coupled wireless power transfer (WPT) modules and ceramic layers directly onto the highly curved surfaces (hemispherical glass substrates with a radius of curvature ~ 50) with viscoelastic conductive, ceramic, and magnetic inks designed for the highly curved surface printing. WPT module consists of an inductor coil (Ag), and capacitors (Ag/βTiO2/Ag) are used to realize a parallel resonant LCR circuit. Furthermore, a soft ferrite layer (NiZn-Ferrite) directly printed on inductor coil, these soft ferrite layer in WPT module plays important roles in (a) enhancing magnetic coupling between the inductor coils transmitting and receiving the magnetic field, and (b) preventing the magnetic field from reaching any conductive object, electronic devices, or human bodies near the WPT module. Laser annealing using an IR laser with various laser fluences was applied to enhance the magnetic property of the soft ferrite layer printed on the highly curved surface. The performance of the printed WPT module on the highly curved surface was demonstrated by transmitting wireless power to various electronic devices through the magnetic resonant coupling. This work may find potential applications, including wearable electronics, optoelectronics, biomedical devices, sensors, and Three-Dimensional (3D) electronics.

Printing Colloidal Quantum Dot Spectrometer Using Nanoporous Flexography

Quantum dots (QDs) have excellent long-term stability and finely tunable absorption spectra across wide range of spectral wavelengths. In addition, the absorption spectra can be varied continuously over wavelengths ranging from ultraviolet to mid-infrared by changing the size, shape and composition of the QDs. Using a 195 color QD filter array, accordingly, a point spectrometer has been demonstrated to operate in the visible wavelength which would not have been possible with the state-of-the-art color filters. The device can be used for low cost, high resolution visible spectroscopy, which is highly attractive for drone-based crop field monitoring or food ripening detection. Despite such potential merits, existing printing technologies are not suitable for precision patterning of individual QD micropixels. Here, we use nanoporous flexography for printing high-resolution pixels and color filters for QD spectrometers. The method allows direct printing of electronic ink features with micron-scale lateral dimensions (~10 microns), submicron line edge roughness (~1 micron) and highly uniform thickness in the sub-100 nm range. We show that the printed QD filter dots with precisely controlled lateral dimensions and the uniform submicron thickness can achieve high resolution image with excellent spectral resolution. We also print a sub-array of different QD color pixels, called super pixels, and characterize the performance of the spectrometer.

Guided Ink Design for Aerosol Jet Printing

Aerosol jet printing (AJP) offers a promising digital, direct-write printing technology for device applications with broad materials compatibility, high resolution, and versatile integration capabilities. Despite its potential, ink design and printer operation for AJP has relied to date on empirical experimentation with limited theoretical understanding or guidance. Recent work has examined fundamental principles governing this technology, revealing general guidelines for ink and process design. This work leverages those findings, examining several case studies in guided ink design spanning organic and aqueous solvent systems for printing colloidal dispersions, polymer solutions, and UV-curable monomers.

In each case, general principles of ink design derived from a simple numerical model are applied to identify suitable solvent systems. Standard calibration routines are presented to systematically identify a processing window and optimal printing conditions for specific applications. This framework establishes a useful toolbox for translating basic principles of AJP into practical guidelines, achieving stable printing in several hours with controlled deposition rate and resolution. By analyzing several materials systems, including silver nanoparticles, polyimide, and UV-curable acrylates, general considerations for ink design are clarified. By leveraging an understanding of AJP mechanisms, more systematic and robust ink design and printer operation is realized with general utility for this promising technology.

Architected Porous Media Designed for Flexographic Printing

The development of printed and unconventional electronic devices to meet application-specific needs requires innovation in printing technologies. Flexography (flexo), a rubber-stamping method developed in the 19th century, has proven scalable (meters per second) for graphic arts but is underdeveloped for printed electronics, particularly transistor and transparent electrode applications, due to limited feature resolution (<50 µm).

Although much work has gone into understanding the structural and fluid mechanics of the ink transfer processes, little attention has been paid to the actual stamp, typically fabricated via polymer replication of a hard master. The elastomeric stamp is top-side inked and compressed on a substrate, a process that has inherent limits for materials transfer and results in uneven pixel quality (poor feature resolution) due to compression-induced spreading. However, consider a porous stamp that undergoes precise deformation such as negative Poisson’s ratio (NPR) during this process. Here, ink transfer could be controlled through the pore-space being the reservoir and the mechanical deformation being the “metering pump”. Moreover, a stamp that exhibits a slight NPR may allow for controlled expulsion and sharper transfer foot print (minimal line-edge roughness). Only recently it has been feasible to produce...
such engineered structures at high resolution, for example, using multiphoton-induced, direct laser writing (DLW). Here we investigate how precisely architected (e.g., NPR and a structured pore size distribution), 3D porous media can control the fluid saturation capillary pressure characteristics upon mechanical compression to enable high fidelity/metered material transfer for high speed printing. In this study, we systematically investigate the effects of porosity, pore size distribution and microstructure compression on flexographic ink transfer using iterative arrays of high-resolution (<1 μm feature size) DLW structures to converge on optimized forms. Fluid dynamics simulations of defined poroelastic media provide further insight into metering ink transfer during compression. Overall, this work illustrates the design flexibility and precision control of micro-features/fluid dynamics enabled using form-fabrication of flexographic forms.

**PM03.07.06**

**Engineered Nanocomposite Material Properties Through Embedding of Smaller Nanoparticles in a Polymer Matrix**

Sanju Gupta, Alex Henson and Brendan Evans; Western Kentucky University, Bowling Green, Kentucky, United States.

Organic and inorganic nanoparticle reinforcements have garnered widespread attention for polymer nanocomposites to yield properties enhancement useful for wide ranging modern technologies including photovoltaics, catalysis, optics, and renewable energy. Recent experiments and computational simulations revealed the macroscopic properties are governed by mesoscale structure and interfacial layer dynamics due to the interactions between the polymer matrix (host) and nanoparticle reinforcements (guest). However, a clear fundamental understanding of the role of size, shape, loading (volume fraction) in controlling the structure and dynamics of polymer-nanoparticle interfacial layer is limited. Moreover, ‘forward’ engineered polymer-nanoparticle composites targeting specific applications often require higher volumetric density and better dispersions remains a challenging task. We report on developing polymer nanocomposites engineered to minimize dielectric losses and investigating structure and dynamics of interfacial layer to predict macroscopic properties. The nanocomposites will consist of poly-(2-vinylpyridine) (P2VP) polymer matrix with (1) spherical silsesquioxane nanoparticles (~2-5 nm diameter) and (2) planar nitrogenated graphene nanoribbons (~20 nm wide), having dimensions comparable to polymer matrix characteristic length i.e. gyration radius (Rg ~5 nm). This approach will enable improved nanocomposites and identify key molecular parameters governing non-linear dielectric loss mechanisms while studying structure and dynamics using broadband dielectric spectroscopy and wider-angle X-ray scattering. The transmission electron microscopy will reveal microscopic structure and the lattice bonding, interfacial stress transfer and conjugation length will be determined from micro-Raman spectroscopy. The exact loading and glass transition temperature, Tg will be obtained using thermogravimetric analysis and differential scanning calorimetry, respectively. We will gain fundamental insights into the interfacial layer and diffusion dynamics above and below Tg and establish quantitative structure-property correlations, while predicting macro-scale properties. We acknowledge KY NSF EPSCoR REG subaward Grant.

**PM03.07.08**

**Polyaniline/Carbon Nano Hybrid Composites for Monitoring and Detection of Flexible Alkali Sensor**

Do Hun Kim, Jin Sun Yoo, O Hwan Kwon and Woo Seok Yang; Korea Electronics Technology Institute, Seongnam-si, Korea (the Republic of).

As the safety has been emerged as a major interest in chemical industry facilities, there have been many researches about sensors for detecting hazardous chemicals. In this study, especially, the sensor for detecting alkaline solution was developed and evaluated. The sensor was composed of carbon materials and polyaniline, which is a conductive polymer. The candidate carbon materials for sensor such as graphite and graphene nano platelet were examined. When graphene nano platelet was used, it showed insensitive reactivity to basic material. Also sensor films can better overcome sensor errors in moisture and water when using graphite than GNP. Finally, it was confirmed that the graphite was the best carbon material for the alkali sensor and it was coated on PET to enable flexible sensor.

**PM03.07.09**

**Enhanced Photo-Luminescence from Highly Interconnected Porous QD/BCP Nanocomposites Formed via Controlled Spontaneous Decomposition of Block Copolymer**

Geon Yeong Kim, Yeon Sik Jung and Duk Young Jeon; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

In this poster, highly interconnected porous QD/BCP nanocomposites was demonstrated in order to achieve enhancement of photo-luminescence. The QD/BCP nanocomposites with strong emission has the potential to be used in photo-luminescence devices of display application with simple and cost-effective fabrication method. Block copolymer (PS-b-P4VP) forms highly interconnected porous structure via the mechanism of spinodal decomposition during the evaporation of solution when dimethylformamide (DMF) and water exist together. Here, the composite film was fabricated by simple spin-coating process. The porous QD/BCP nanocomposites effectively enhanced absorption of quantum dots inside block copolymer matrix by the multiple light scattering and trapping effect inside film, resulting in enhanced photo-luminescence. A one of current obstacles towards high-performance QD devices is reducing energy transfer nearby quantum dots, which is called Fluorescence Resonance Energy Transfer (FRET). The quantum dot was functionalized with hydroxyl ligand for the conjugation with BCP. The hydrogen bonding between hydroxyl ligand and nitrogen atom of P4VP block was successfully established. Consequently, by the self-assembly properties of block copolymer, the dispersion of quantum dots was induced, which indicated reduced Fluorescence Resonance Energy Transfer (FRET) effect. With the synergetic effects of light scattering from porous structure and dispersion of quantum dots from conjugation effect, the 21-fold enhancement in photo-luminescence was achieved compared to reference quantum dot film.

**PM03.07.10**

**Fabrication of Robust Superhydrophobic Surfaces with Modified Siloxane Resin**

Kiboom Nam and Dong Yun Lee; Kyungpook National University, Daegu, Korea (the Republic of).

The superhydrophobic surfaces have received a significant attention for decades because of their wide spectrum of applications such as self-cleaning, anti-icing, separation of liquids, and anti-corrosion. We achieved durable water repellent surface through a spray coating method. This technique is possible to fabricate superhydrophobic surfaces with multiscale of roughness over large area. Spray coating is conducted by spraying the nanoparticles (NPs) onto the substrate with some binders in it; The NPs are gathered each other and form multiscale structures on the substrate and the binder which has low surface energy acts as an adhesive. This superhydrophobic surfaces has not only an excellent water repellency and superb solidity. In addition, it shows a heat resistance even at 300 celsius degree, and solvent resistance. To achieve such superhydrophobic surface through spray coating, we should consider various factors that influence on degree of superhydrophobicity, for example NPs size and content, binder content and the amount of coating solution. Especially, it is important to control the aggregated size of NPs in solution, that highly affect the surface morphology after coating process. The superhydrophobic surface means the surface that has high contact angle over 150° and low slide angle under 10°. It is well established that the superhydrophobic surfaces came from an association of low surface energy and multilevel of surface roughness (i.e., hierarchical structures). It is explained by two theoretical models (Wenzel and Cassie-Baxter); Both models explain a superhydrophobic surface that has rough surface with low surface energy. If liquid drops on Wenzel model, liquid fills up all grooves however, air pockets are formed between the surface and water droplet in Cassie-Baxter state. Because of such differences, they show different wetting properties, water droplet can be pinned on the Wenzel surface and do not roll off easily. By contrast Cassie-Baxter drops are fall form the surface because they sit partially on air. These structures are vulnerable to mechanical forces form the
surrounding like water impact, or finger touching. When the structures are demolished, it lost its hydrophobic property. However, we introduce a method for fabricating the mechanically durable superhydrophobic surfaces by spraying robust siloxane resin as a binder. The resin can be synthesized through hydrolysis-condensation reaction of silanes and cured with amino-silanes. Furthermore, surface morphology is controlled by adjusting distribution and mount of NPs in the coating solution.

PM03.07.11
Superhydrophobic Functionalization of Textile Surface Using Roll-to-Roll Chemical Vapor Deposition Mehmet Gursoy and Mustafa Karaman; Selcuk University, Konya, Turkey.

In most cases, functional polymeric thin films are essential parts for the production of many devices with electronic or other advanced functionalities, including transistors, memories, physical and chemical sensors, photovoltaic cells, photo detectors, energy storage devices, displays, lighting, biomimetic surfaces and flexible-hybrid electronic devices. Today, the interest in wearable devices is increasing rapidly; making it necessary to integrate device parts on flexible textile surfaces. Usually, the surfaces of textiles are not compatible with the other elements of the devices, which could be overcome by imparting a functional thin film on textile surface. The desired properties of a device-quality textile include flexibility, breathability, durability, ease-of-mass production and so on. The traditional wet finishing processes that textile industry depend on usually fail to meet such requirements. Initiated chemical vapor deposition (iCVD), on the other hand, offers the advantages of being an all-dry process, which has been efficiently applied to produce many different types of functional polymers at very low energy inputs. For commercialization, the all-dry nature of CVD has the potential to reduce environmental, health, and safety impacts associated with solvents as well as the economic costs associated with their use, recycling, or disposal. iCVD can also be easily scalable to achieve high-throughput production, making it suitable for mass production equipment such as roll-to-roll process. In this study, a pilot roll-to-roll iCVD system was designed and operated to produce thin films of poly(hexafluoro butyl acrylate) on bamboo fabric surfaces. In this way the surface of bamboo fabric, which was highly hydrophilic, was converted into superhydrophobic. Tert-butyl peroxide was used as an initiator, which increased the deposition rates, and decreased the activation energy required for the film-forming reactions. The structure and morphology of the as-deposited films were investigated using FTIR and SEM; and it was found that roll-to-roll iCVD produced chemically well-defined and highly conformable polymeric films. Effects of substrate temperature and roll-speed on the deposition rates were also investigated. The methodology developed in this study can be used to transfer many flexible device or sensor parts onto the textile surface, which requires hydrophobic surface properties. Besides, many other functionalities can be imparted on any kind of textile surface using the same roll-to-roll approach.

PM03.07.12
Direct Write of Micro-Circuitry via Micro Cold Spray Ryan Mocadlo1, Victor Champagne1, Jianyu Liang2 and Richard Sisson2; 1U.S. Army Research Laboratory, Aberdeen, Maryland, United States; 2Materials Science & Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Micro-cold spray (MCS) is a process that can achieve the solid-state deposition of metal powders through capillary focusing. In this process, metal powders are accelerated, using high pressure helium, through a capillary nozzle to impact on a substrate, and subsequently deposit in micrometer lines. Fine feature sizes have been a long-standing aspiration of the cold spray community, but have remained elusive despite extensive efforts. Recent developments in micro powder feeding has enabled the use of the MCS as a direct-write technology to deposit conductive materials for use in printed electronics. In addition, the MCS process has shown the ability to deposit materials on flexible substrates, allowing for the possible use in the fabrication of flexible electronics. This work describes the extensive effort on understanding the impact of nozzle design, and process gas temperature on the final deposition. Computational fluid models were employed in the preliminary design of the capillary nozzles, with the goal of maximize particle velocity, while minimizing the particle beam diameter. The insights gained through experimental studies were used to help optimize the computational models for future use.

PM03.07.13
Transparent Thin-Film Heaters Based on Atomic Layer Deposited Oxides onto Copper Nanowire Networks Dogancan Tigan, Sevim Polat Genlik, Bilge Inner and Husnu E. Uslan; Middle East Technical University, Ankara, Turkey.

Transparent heaters utilizing random metallic nanowire networks received great attention in recent years due to their significant performance. Commonly, silver and copper nanowires are used to make transparent heaters because of their high electrical conductivity as well as high optical transmittance in the visible spectrum. However, due to their high thermal conductivity, their efficiency is often limited. In this work, we report the fabrication of high-performance transparent thin film heaters utilizing copper nanowires with oxide shells through simple means. Reducing Fresnel Reflection Losses in Chalcogenide Based Infrared Optical Fibers via Direct Nanoimprinting Mikkel Lotz2, Christian R. Petersen1, Christos Markos1, Ole Bang1, Mogens Jakobsen1 and Rafael Taboryski1; 1DTU Fotonik, Technical University of Denmark, Kongens Lyngby, Denmark; 2DTU Nanotech, Technical University of Denmark, Kongens Lyngby, Denmark.

Fresnel reflection at the glass-air interface in chalcogenide glass based optical components generally constitutes a significant portion of the overall losses due to the relative high refractive index (2-3) of the glass. In arsenic triselenide (As2Se3) based mid-infrared optical fibers the Fresnel reflection losses surmount to about a 40% reduction in transmitted power. Traditionally, mid-infrared optical systems have relied on antireflective dielectric coatings to solve this problem, but only a limited number of materials are chemically and thermo-mechanically compatible with chalcogenide glass. Nevertheless, we recently reported on the progress towards fabricating broadband mid-infrared antireflective moth-eye nanostructures on the surfaces of commercially available As2Se3 optical windows by thermal nanoimprinting. We now present a study into a more cost-effective method of reducing the Fresnel reflection losses in As2Se3-based optical fibers by nanoimprinting antireflective nanostructures directly onto the end-facets.

Based on a simulation approach using rigorous coupled-wave analysis we first design a hexagonal array of moth-eye nanostructures optimized for the mid-infrared. A silicon master containing the moth-eye nanostructures is then fabricated using DUV lithography to create an etching mask and dry-etching to fabricate the structures in the silicon substrate. A nickel mold is then made by depositing a nickel-vanadium seed layer to the silicon master and
subsequently electroforming it with nickel. The nickel mold is released by dissolving the silicon master in a potassium hydroxide solution. The negative relief mold of nickel (Ni shim) is then coated with Perfluorodecytrichlorosilane (FDTS), which acts as an anti-stiction coating using Molecular Vapour Deposition (MVD).

Using a mid-infrared supercontinuum laser source with a radiation spectrum from 2-4.2 μm, we observe >30% improvement to the transmitted optical power (from 56% to almost 90% of incident power) as a result of nanoimprinting the input and output facets of a As$_2$Se$_3$-multi-mode fiber and a single-mode fiber, using the fabricated Ni shim.

**PM03.07.15**

**Damage Induced Surface Texturing of PDMS Composites, a Single Fiber Insertion Study**

Navid Namdari and Reza Rizivi; Mechanical Engineering, The University of Toledo, Toledo, Ohio, United States.

Damage and mechanical failure are detrimental for materials in engineering applications. However, recent studies have shown that properly designed debonding and pullout phenomena in composite fractures can be implemented to introduce added functionalities by damage induced surface texturing (DIST). In this approach, randomly oriented or aligned fibers are incorporated in a polymeric matrix, followed by transversal shearing of the surface. As a result, the shear-fractured surface will have protruded fibers on it because of the debonding followed by subsequent pullout. The protruded fibers play a key role in imparting new functionalities to the cut surface. To date, two important applications have been affected by the introduction of DIST. The first application is in enhancing the ice friction coefficient by as much as 900% in carbon-based styrene butadiene styrene (SBS) composites. Furthermore, DIST has also shown a significant potential in hydrophobic surfaces where the water droplet contact angle increased by 30% in SBS reinforced with carbon fiber (CF) composites. DIST is a simple, economical, and a scalable method compared to lithography, hot embossing, and laser ablation. In addition, there is no need to use costly and time-consuming post-processing stages to introduce anisotropic properties into the material. Tailoring the pullout length can directly affect the functionality of the surface. Thus, selecting appropriate process parameters plays a key role in designing an optimized surface. The aim of this study is to investigate the effect of fiber type, polydimethylsiloxane (PDMS) modulus of elasticity, fiber stiffness, and fiber/matrix interface on the pullout length of the fiber. A PDMS with varying hardness of 10, 20, 30, and 50 was selected as the compliant material that will incorporate carbon and poly(p-phenylene-2,6-benzobisoxazole (PBO) fibers. A single fiber insertion method was carried out with a sequential alignment of eight single fibers on a frame placed in a cubic mold before casting the PDMS. The samples were cut transversely to the direction of alignment with a custom-built cutter once the PDMS was cured. The protrusion lengths were measured with an image processing software (ImageJ) from the scanning electron microscopy (SEM) micrographs of the cut surface. Smaller protrusion lengths were observed by increasing the matrix modulus, according to the predictions of the model proposed by Wells and Beaumont [1]. Moreover, using regular and high-modulus PBO fibers brought to light the fact that increasing the fiber stiffness can enhance the pullout length. Finally, we evaluate the effect of epoxy sizing, plasma treatment, and no sizing on the pullout length of the carbon fiber.


**PM03.07.16**

**Anodization Patterning for Organic Electronic Circuits with Low Operation Voltage**

Tomovski Yokota, Hiroaki Jinno and Takao Someya; The University of Tokyo, Tokyo, Japan.

Organic circuits are much attracted in realizing the flexible and bendable electronics such as flexible display and flexible sensor systems. The important technology for realizing the high yield and high performance organic circuits with low operation voltage is anodized oxide gate dielectrics. Recently, many groups report the low operation voltage organic transistor with anodized oxide gate dielectric layer [1, 2]. Compare with a plasma-formed aluminum oxide layer, an anodized alumina oxide layer shows higher mechanical durability [1]. One of the biggest problems of anodization process is patterning. Normally, anodization process needs to connect the all electrodes to form the oxide layer. For this reason, it is very difficult to make the complicated circuit with anodized oxide gate dielectrics. Although some novel method of anodization patterning were developed [3], it is still difficult to apply these methods to organic integrated circuits.

In this study, we succeed to pattern the anodized aluminum oxide layer by the photolithography technique. The minimum resolution of the patterning is less than 10 μm. To pattern the anodization oxide layer, first we patterned the photo resist on the connection wires. By covering the connection wire with photo resist, it is possible to selectively anodize only the other electrodes. After forming the anodization oxide layer, we removed the photo resist and etched the connection wire by wet etching process. The thickness of anodized aluminum oxide layer is only 20 nm. To improve the device performance, we modified the surface of aluminum oxide layer by the octadecyl phosphoric acid (C18-SAM). By using anodized aluminum oxide and C18-SAM gate dielectrics, we succeed to fabricate the organic pseudo-CMOS circuits and amplifier circuits. This inverter circuits show the high inverter gain of 2000. And pseudo-CMOS inverter based self-feedback amplifier system was operated only 3 V with a signal gain exceeding 1000.


**PM03.07.17**

Roll-To-Roll Manufacturing of Hybrid Thermoelectric Devices

Zimeng Zhang and Shiren Wang; Texas A&M University, College Station, Texas, United States.

Hybrid thermoelectric devices have gained the spotlight for its potential in future portable electronic systems for harvesting energy from waste heat and storing electric energy. Flexible thermoelectric generator plays an essential role in these devices by capturing body heat and generates electricity. However, it is challenging to integrate mechanical flexibility, scalable processibility and cost efficiency together in the production of a flexible thermoelectric generator. Especially, high power generating flexible thermoelectric generators without high temperature and high-pressure annealing treatment are highly sought after. Here, we designed a roll-to-roll production system for vertical-type flexible thermoelectric fabrication in a large-scale, continuous and energy efficient manner. The roll-to-roll process provides an attractive approach for high-rate production and cost-efficiency while allowing devices to be fabricated automatically in mass quantities. Organic thermoelectric materials which are highly flexible, cost-effective and ease-of-process were used for both p- and n-type thermoelectric composite inks. The thermoelectric pellets are formed within preformed cavity molds via extrusion. The printed thermoelectric generator with 10 p- and n-type pairs exhibited exceptional performance of ~0.65 uW output power at a temperature gradient of 25 °C. The hybrid system of both energy generation and energy storage is incorporated in the fabricated device. The hybrid device can be further used for powering small electronics such as medical sensors and smartwatch. The results demonstrated the possibility of continuous production of the vertical-type flexible thermoelectric generator with excellent performance and show the great promise of self-powered wearable electronics.

**PM03.07.18**

**Anodization Patterning for Organic Electronic Circuits with Low Operation Voltage**

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Automated Fabrication of Uniaxially Aligned Nanofibers via Beltspinning

This study proposes a continuous and straightforward method for fabricating suspended micro- and nano-diameter polymer fibers by using an automated single step drawing system. Termed beltspinning, fiber alignment, diameter, and morphology can be controlled by varying draw ratio, rotational belt speed, and polymer solution properties. The belt spinning device is inexpensive and simple to operate as it does not require an electric field. The device can draw single or multi-filament arrays of nanofibers from any kinds of polymer and solvent. Fibers are continuously spun by the direct contact and mechanical drawing between the two rotating belts. The automated track can produce continuously aligned fibers along a single linear axis, which is advantageous for building uniaxially aligned scaffolds for tissue engineering. To demonstrate, fibers were manually pulled from polymer solutions containing 10, 20, and 30% w/v PVAc and 7, 10, and 13% w/v PU. As the system rotates and cycles, the viscous liquid polymer solution applied to the belt begins to evaporate and form semi-solid fiber bridges. The polymer bridges then proceed down the angled track where the fiber is farther stretched and elongated over a wide range of fiber diameters. Polymer nanofibers with diameters as small as 400 nm with a length of 30 cm were produced using this technique. Controlling the drawing parameters, all kinds of polymeric materials (polymer melts and solutions), and biopolymers (protein materials), and polymer composite materials. The setup is inexpensive to implement, nozzles-less, easy to scale up, and the tracks can be patterned/textured for aligned fiber arrays. The ability to draw various materials into uniaxially aligned nanofibers opens the door to applications associated with 1D nanostructures and development of new nanodevice configurations, while also providing opportunities in a wide variety of 3D substrate geometries that have been difficult or impossible to obtain, such as tissue engineering scaffolds. The preferential alignment of nanofibers can also lead to the formation of nanostructured materials with highly anisotropic behavior and new features, such as electrical, magnetic, ferroelectric, ferromagnetic, and structural mechanical. For example, drawing polymeric fibers can increase chain alignment and crystallinity, it is a conventional method to improve the thermal conductivity of the polymer along the axial direction of the nanofibers. While electrospinning has been successfully used in preparing many kinds of polymer fibers with high thermal conductivity, it has some disadvantages, such as the need for polar solvent carriers that are relatively high in electrical conductivity to spin highly resistive polymer materials, such as PE. Since studies have shown that the thermal conductivity of the mechanical drawn PE nanofiber is comparable to the electrospun PE nanofiber, the automated drawing process can be implemented via beltspinning.

SESSION PM03.08: Processing with High Temperature and Light
Session Chairs: Gyoujin Cho and Nikos Kehagias
Thursday Morning, November 29, 2018
Hynes, Level 1, Room 108

8:00 AM PM03.08.01
Rapid Processing of Metal Oxide Thin-Film Transistors Enabled by Photonic Curing
Trey Daunis, Weijie Xu, James M. Tran, Kurt Schroeder and Julia W. Hsu; The University of Texas at Dallas, Richardson, Texas, United States; NovaCentrix, Austin, Texas, United States.

Traditional thermal annealing using a hot plate or an oven to process or transform materials is time consuming and inherently incompatible with roll-to-roll processing. In this work, we will demonstrate the use of photonic curing to transform sol-gel precursors to metal oxide films on a time scale compatible with high-throughput manufacturing. Solution deposited metal oxides have potential for realizing high-performance electronic components, such as thin film transistors (TFTs), on flexible large-area substrates. Transformation from sol-gel precursors to metal oxides typically requires annealing temperatures above 400 °C, which presents a problem for most flexible plastic substrates. Recently, solution combustion synthesis and UV-assisted annealing have demonstrated metal oxide formation at temperatures compatible with polymer substrates (< 250 °C). However, these techniques still require tens of minutes of thermal annealing time per device layer, adding up to hours of processing time. Here, we apply photonic curing to transform sol-gel precursors to oxide films for both the semiconductor and the dielectric layers in TFTs. Photonic curing uses short pulses (<1 ms) of broad spectrum light (200 – 1500 nm) from a Xe lamp at high intensity to selectively raise the temperature of the thin films while minimizing heating of the substrate. This can complete the conversion of sol-gel precursors to oxides on a time scale two orders of magnitude shorter than traditional annealing methods. In this work, TFTs are first fabricated on Si substrates using a ZrO2 gate dielectric and In2O3 semiconductor that are converted with a total annealing time of just 2 minutes. The devices exhibit a higher channel mobility (µ = 9 cm²V⁻¹s⁻¹) and on/off ratio (Ion/off > 10⁶) than the same TFT device structure made using a UV-ozone assisted metal oxide conversion plus thermal annealing at 250 °C with a total processing time of 3 hours (µ = 1.4 cm²V⁻¹s⁻¹, Ion/off = 10³). The sol-gel to metal oxide transformation process is characterized by XPS, FTIR, and ellipsometry. Photonic curing is further explored to convert sol-gel oxide films on polyethylene naphthalate (PEN) substrates. The increase in processing speed will be crucial to enabling high-throughput roll-to-roll manufacturing of metal oxide electronic devices.

8:15 AM PM03.08.02
Roll-to-Roll Ion Beam Assisted Deposition of Single-Crystalline-Like Conductive TiN Buffer Layer Directly on Metal Substrate for Thin-Film Optoelectronic and Electrical Applications
Sicong Sun, Ying Gao, Yongkuan Li and Venkat Selvamanickam; Department of Mechanical Engineering & Texas Center for Superconductivity and Advanced Manufacturing Institute, University of Houston, Houston, Texas, United States.

Single-crystalline-like buffer layers made by ion beam assisted deposition (IBAD) have been used to grow highly epitaxial functional layers on inexpensive metal and flexible glass substrates. Most commonly-used single-crystalline-like buffer structures consist of oxide materials such as LaMnO3/MgO. While such oxide layers have led to high-performance epitaxial superconductor tapes, GaAs photovoltaics and Si and Ge-based flexible electronics, they isolate the active layers from the substrate. This architecture has a few drawbacks including possibility of thermal destruction in the event of an overcurrent situation and the need to fabricate lateral back contacts by etching and photolithography. Single-crystalline-like buffer structure of a conductive material is a very desirable design since they allow electrical and thermal contact between the active layers and the substrate which allows high thermal dissipation ability and the ability to fabricate back contacts on the substrate without the need to etch the active layers. TiN has been reported as a promising material for developing conductive buffer layer to replace oxides because of its good electrical conductivity and high thermal stability. Here we report a new method to grown biaxial-textured single-crystalline-like TiN thin film on polished metal tape by continuous roll-to-roll ion beam assisted deposition. Single-crystalline-like TiN has been directly realized on low-roughness metal tape surface (RAM, 0.35nm, 1µm scale) without any seed layer at room temperature. In-plane texture Αρ of 5.6° and out-plane texture Αα of 1.8° are achieved in the homoepitaxy TiN on IBAD TiN. Such electrically- and thermally-conductive single-crystalline-like TiN have been used for epitaxial growth of active layers for photovoltaics, flexible electronics and superconductor applications by roll-to-roll manufacturing.

8:30 AM PM03.08.03
Ultra-Rapid Transformation of Materials Characteristics via Photonic Processing
Demosthenes Koutsogeorgis; School of Science and Technology,
In this contribution we investigate the well-studied P3HT/ZnO systems to develop the growth of oxide layers directly onto polymer thin films in TFTs. The observed effects of polymer variation is investigated by examining the crystallographic and morphological characteristics, and their potential ambipolar behaviour. These solution processed devices exhibit lower saturated mobilities compared to their single component counterparts, however well-balanced integration and purging of precursors and inert gases prevent their application for mass production under atmospheric conditions. Atomic layer deposition (ALD) is a thin film deposition technique which produces thin, conformal films due to the precise control over the thickness and growth rate of ~1 Å/cycle at a carefully optimized web velocity of 7 mm/second. The deposited Al2O3 thin films showed good morphological, chemical, and optical properties. The films demonstrated very low root mean square roughnesses (Rq) of ~1.73 nm. The fabrication of Al2O3 thin films was confirmed through X-ray photoelectron spectroscopy (XPS) analysis and its characteristic peaks of Al 2p, Al 2s and O 1s were appeared at the binding energies of 74 eV, 119 eV and 531 eV, respectively. The compositional study was also supported by conducting fourier transform infrared spectroscopy (FTIR) analysis. The optical transmittance of more than 85 % in the visible region was observed for the films. The electrical characterization of memristor devices showed that the Al2O3 encapsulation has a prominent influence on their performance, and life time. The results reveal that the R2R-AALD technology has a great potential for mass production of thin films and has a promising future in the field of flexible electronics.

Roll-to-Roll Atmospheric Atomic Layer Deposition Technology for Thin Films and Flexible Electronic Applications

Since the inception of Atomic Layer Deposition (ALD) Technology in 1974 by Dr. Tuomo Suntola, it has been adopted by numerous industries for variety of applications. ALD has earned a reputable status in electronic industry especially in the sectors of solar cells, displays, and energy storage devices etc. Although, the conventional ALD technologies are quite capable to produce good quality thin films of wide variety of materials, yet the sequential introduction and purging of precursors and inert gases prevent their application for mass production under atmospheric conditions. In this research work, a novel technology of roll-to-roll atmospheric atomic layer deposition (R2R-AALD) has been implemented for the increased production of Al2O3 thin films on movable web of polyethylene terephthalate (PET) substrates at low temperatures (< 100 °C), and the films were also implemented for the encapsulation of organic Poly (4-vinylphenol) (PVP) flexible memristor devices as for their life time enhancement. Trimethylaluminum (TMA) and water has been used as precursors. A compact multiple slit gas source head has been used to transport the precursors and the inert gas to the surface of the substrate and to efficiently remove the bye products and the unreacted gases from the reaction zone. The films deposition has been carried out under the working pressure of 740 Torr, which is very near to the atmospheric pressure. Thin films were developed under a promising growth rate of ~1 Å/cycle at a carefully optimized web velocity of 7 mm/second. The deposited Al2O3 thin films showed good morphological, chemical, and optical properties. The films demonstrated very low root mean square roughnesses (Rq) of ~1.73 nm. The fabrication of Al2O3 thin films was confirmed through X-ray photoelectron spectroscopy (XPS) analysis and its characteristic peaks of Al 2p, Al 2s and O 1s were appeared at the binding energies of 74 eV, 119 eV and 531 eV, respectively. The compositional study was also supported by conducting fourier transform infrared spectroscopy (FTIR) analysis. The optical transmittance of more than 85 % in the visible region was observed for the films. The electrical characterization of memristor devices showed that the Al2O3 encapsulation has a prominent influence on their performance, and life time. The results reveal that the R2R-AALD technology has a great potential for mass production of thin films and has a promising future in the field of flexible electronics.

9:15 AM PM03.09.01
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9:15 AM PM03.09.02
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Hybrid active layers comprising of both inorganic and organic semiconducting materials are becoming more promising due to the ability to produce inexpensive, versatile and tailored electronic devices such as thin film transistors (TFT) or photovoltaic (PV) devices. By combining the advantages of the single components, it becomes possible to produce devices with the high stability of inorganic and the mechanical flexibility of organic materials. TFTs generally exhibit unipolar behaviour where the dominant charge carrier in the channel is either electrons or holes. However, recent work has demonstrated the use of a hybrid layer consisting of poly(3-hexylthiophene-2,5-diyl) (P3HT) on top of ZnO in TFTs which exhibits ambipolar behaviour. These solution processed devices exhibit lower saturated mobilities compared to their single component counterparts, however well-balanced electron and hole mobilities are achieved in their hybrid devices. There is scope for further optimisation of these devices, including reversing the active layer order and exploring alternative deposition techniques.

Atomic layer deposition (ALD) is a thin film deposition technique which produces thin, conformal films due to the precise control over the thickness and composition of films on the atomic scale. The ability to grow ZnO films with such precision and at low temperatures results in ALD having good compatibility with organic materials. The growth of ZnO relies heavily on the surface chemistry therefore varies with the type of substrate. As a result, the nucleation and growth of ZnO on different polymers result in variations in morphology and electrical properties. Previous studies have explored the growth mechanism of ZnO onto P3HT via ALD, showing that the precursors are able to vapour diffuse into amorphous regions of the polymer thin film resulting in incorporation of ZnO within the polymer nanostructure. Such hybrid structures have also been successfully incorporated into PV devices. In this contribution we investigate the well-studied P3HT/ZnO systems to develop the growth of oxide layers directly onto polymer thin films in TFT devices, comparing their performance with their single component counterparts. Our methodology is simple, first depositing P3HT from solution and subsequently ZnO by ALD. We demonstrate an ambipolar charge transport for these hybrid TFTs. Following this, the growth behaviour of ZnO onto alternative p-type semiconductor polymers, such as poly(9,9-diocetylfluorene-alt-benzothiadiazole), are explored. The observed effects of polymer variation is investigated by examining the crystallographic and morphological characteristics, and their potential ambipolar properties are studied by investigating their electronic properties.

Hierarchically structured solid scaffolds are often used to improve light absorption and carrier collection in thin-film photoelectrodes. The structure can simultaneously optimize the rates of light absorption, carrier collection at the semiconductor-liquid junction, and mass transport of reactants to improve the effective energy conversion properties of the material. However, the scaffolds require a continuous transparent, conductive coating to function as an electrode and maintain electrical contact to the entire, tortuous surface. The electrochemically robust transparent conducting oxide (TCO) fluorine-doped tin oxide (FTO) can only be grown by line-of-sight physical deposition methods such as RF sputtering or spray pyrolysis, which in general prevents the deposition of uniform thin coatings of FTO on the interior of a hierarchically structured scaffold. Other TCOs (tin-doped indium oxide (ITO), aluminum-doped zinc oxide (AZO)) can be grown conformally by surface specific methods such as atomic layer deposition (ALD). ITO and AZO films are only stable at near-neutral pH, limiting their use in photoelectrochemical energy conversion. Here, we describe a strategy for improving the stability of ALD-deposited AZO films for anodic operation in alkaline electrolytes. The addition of a conformal, nanoscale TiO$_2$ coating preserves a conductive AZO film for more than 24 hours at pH > 13. This is an improvement of several orders of magnitude compared to the lifetime of pure AZO films. Although the TiO$_2$ coating is not significantly conductive alone, we observed an improvement in the conductivity of the layered AZO/TiO$_2$ film. The TiO$_2$-coated AZO film can be used as an electron collector on hierarchically porous scaffold formed from close-packed inorganic silica spheres. The improved electrochemical stability suggests that this approach will greatly benefit the fabrication of ultra-thin film photoanodes based on alkaline-stable semiconductors, such as the ternary metal oxide systems NiMn$_2$O$_4$ and Bi$_2$VO$_6$.

Plasma enhanced atomic layer deposition (PE-ALD) affords excellent-quality thin-films for various applications [1]. However, conventional ALD is vacuum based and imposes limits toward high-throughput and low cost manufacturing. To overcome these limits, spatial PE-ALD at atmospheric pressure has been introduced [2]. We have shown outstanding gas diffusion barriers and semiconductor thin-films grown by spatial PE-ALD, recently [3,4]. For the PE-ALD of metals, reducing plasmas are needed. As of yet, work on spatial PE-ALD of metals at atmospheric pressure is very limited, as is the choice of suitable Ag precursors. In this work, we report on the growth of Ag by spatial PE-ALD at atmospheric pressure from a novel halogen-free, monomeric and volatile carbene-based Ag precursor at substrate temperatures as low as 80°C. The results are compared to those obtained from the more established precursor [Ag(fodd)(Pent)$_3$] (FOD), which contains fluorine, phosphorous and oxygen. An atmospheric pressure dielectric barrier discharge with Ar/H$_2$ as working gas is used as reducing agent for both compounds. Using Rutherford backscattering spectrometry, a growth rate of $2.1*10^{15}$atoms cm$^{-2}$cycle$^{-1}$ (corresponding to an equivalent of 0.36 Å cycle$^{-1}$) was obtained for the new precursor, as opposed to 0.3 Å cycle$^{-1}$ for the FOD precursor.[5] The slightly enhanced growth rate could probably be attributed to the higher reactivity of the carbene based Ag precursor. X-ray photoelectron spectroscopy confirmed that Ag films from the FOD precursor deposited at atmospheric pressure spatial PE-ALD contained a high level of fluorine residues. These residues could be efficiently avoided by using the new carbene-based precursor. Furthermore, growth characteristics in dependence of process parameters like deposition speed and substrate temperature, as well as saturation of the precursor were investigated. The substrate temperature was reduced to temperatures as low as 80°C to reduce the mobility of the silver atoms on the substrate surface and thus the percolation threshold. The prospects to use these ALD grown Ag layers to create semi-transparent electrodes for thin-film optoelectronic devices are discussed.


10:00 AM BREAK

10:30 AM PM03.09.03
Protection Schemes for Transparent Conducting Oxide Layers Grown by Atomic Layer Deposition on Hierarchically Structured Electrodes Peter J. Reed, Mya Norman and Robert H. Coridan; Chemistry, University of Arkansas, Fayetteville, Arkansas, United States.

10:45 AM PM03.09.04
Atmospheric Pressure Plasma Enhanced Spatial ALD of Silver from a New Halogen-Free Precursor Tim Hasselmann$^1$, Nils Boysen$^2$, Detlef Theirich$^1$, Selina Ottho$^1$, Anjana Devi$^2$, Klaus Meerholz$^2$ and Thomas Kied$^1$; $^1$Institute of Electronic Devices, University of Wuppertal, Wuppertal, Germany; $^2$Inorganic Materials Chemistry, Ruhr-University Bochum, Bochum, Germany; $^3$Institute for Physical Chemistry, University of Cologne, Cologne, Germany.

Enhanced Within-Wafer and Wafer-to-Wafer Uniformities of Batch-Type ALD Reactor by Using Dynamic Purging Process Ho Min Son$^1$, Woong Seon Choi$^1$, Haneul Jung$^2$, Seiwhung Choo$^3$, Byanghwan Kong$^3$, Jinjoo Kim$^4$, Jung Soo An$^5$ and Hong Joo Baek$^2$; $^1$Samsung Electronics Co., Ltd., Pyeongtaek-Si, Korea (the Republic of); $^2$Samsung Electronics Co., Ltd., Hwasong-Si, Korea (the Republic of).

During the last few years, atomic layer deposition (ALD) has been highlighted in the semiconductor industry. As device performances have been enhanced, the topography of the device structures have become more complex, and consequently, the requirements on the step coverage have become much more important. ALD is one of the best techniques to deposit conformal films on topographically complex structures. Also, the dimensions of the features have become smaller and narrower. Consequently, the required thickness of the films becomes less, thus low growth rate, one of the main drawbacks of ALD, is becoming less important. When the ALD technique was in the research phase for semiconductor applications, almost all studies were executed with single-wafer processing type reactors. However, as ALD is finding their way into high volume semiconductor manufacturing, the processing cost becomes an important factor to be taken into account. This has resulted in an introduction of batch-type ALD systems, particularly in dynamic random-access memory and flash memory fabs that are cost-sensitive.

As increasing the volume of the batch-type ALD reactor to enhance throughput, it became more difficult to deposit uniform films over the whole wafers, i.e., decreased within-wafer (WIW) uniformity and wafer-to-wafer (WTW) uniformity. We observed that the WIW and WTW uniformities are affected by the purge step in ALD process. In this study, we developed a dynamic purging process and achieved excellent WIW and WTW uniformities at more than 80-wafer batch size. The dynamic purging process is composed of cyclic steps with purging and vacuum pumping. As comparison studies, we also checked the WIW and WTW uniformities with normal purging processes. We deposited Al$_2$O$_3$ films using tri-methyl aluminum (TMA) and ozone as Al and O sources, respectively, with N$_2$ as a purge gas. With the dynamic purging process, we obtained enhanced WIW and WTW uniformities more than 50%. The dynamic purging process can be applied to all types of ALD reactors to increase uniformity, resulting in enhanced throughput.

10:45 AM PM03.09.06
Assembly of microscale objects with ever-decreasing sizes is essential for automated production of integrated electronic devices such as micro-LED displays. Here, we introduce a new engineered surface, comprising carbon nanotube (CNTs) forests coated with nanometer-scale ceramic layers, for dexterous pick-and-place manipulation solid objects using electrically switchable adhesion. We describe the electromechanical contact behavior of the nanocomposite surfaces, which are mechanically soft, have low intrinsic adhesion, and can be rapidly switched using with 100x greater adhesion by application of an electric potential to the CNTs. The large range of tunable adhesive strength accompanied by the low intrinsic adhesion allows manipulation of objects whose small sizes dictate surface forces dominate over gravity. We demonstrate pick-and-place manipulation of a variety of objects including colloidal particles (metal, ceramic, polymer) with diameters from 0.5-30 μm, silver nanowires (~12 μm long), and unpackaged light emitting diode (LED) chiplets (~170 μm). These manipulations do not require chemical/thermal surface modification or additional adhesives, demonstrating the versatility of this new approach.

11:00 AM PM03.09.07

Liquid Transfer in Nanoporous Printing Stamps

Dhanushkodi Mariappan1, Sanha Kim1, Michael S. Boutilier1, Junjie Zhao2, Hangbo Zhao1, Justin Hero2, Ulrich Muecke1, Hossein Sojoudi1, Karen Gleason2, Pierre-Thomas Brun2 and A. John Hart1; 1Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 4Mechanical, University of Colorado Boulder, Boulder, Colorado, United States; 5Chemical and Biological Engineering, Princeton University, Princeton, New Jersey, United States.

There is a growing industrial need for manufacturing technologies that can print devices with high resolution (~1 microns) and at high throughput. Conventional flexography is limited in resolution due to the instabilities in the ink loading and transfer mechanisms. A recent invention from our research group, engineered nanoporous stamps composed of polymer coated carbon nanotube (CNT) forests, are highly porous (~90%) and can retain the ink within their volume rather than on their surface only and has been used to print micron-scale features with highly uniform ink layer thickness.

In this talk, we explore the liquid transfer behavior from engineered nanoporous printing stamps using a high-speed visualization system and discuss the governing physics enabling the high-resolution high-speed printing. We conducted experiments using a custom-built printing apparatus which enables printing on flat and curved substrates by precisely controlling the force and printing speeds while observing the printing process in the time scales of milliseconds using a high magnification high speed imaging system. We observe all the steps in printing and describe the details of liquid meniscus evolution that lead to the ink transfer. Then we theoretically and experimentally study the dynamics of liquid spreading and reeding, emphasizing the effects of approaching and retraction speeds. Finally, we discuss how our understanding of ink transfer physics can be applied to the process control of contact printing for the precision electronics manufacturing.

11:15 AM PM03.09.08

Size Effects in Plasma-Enhanced Nano-Transfer Adhesion

Michael Deagen1, Edwin P. Chan2, Linda S. Schadler1 and Chatatnaya K. Ullal1; 1Rensselaer Polytechnic Institute, Troy, New York, United States; 2National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Large-area, layer-by-layer transfer molding requires an adhesion strategy that facilitates transfer to the substrate by maximizing interlayer bond strength while minimizing stamp demolding force. A size dependence on transfer rate was observed for plasma bonding at the nano-scale in both batch and continuous processes using a conventional plasma cleaner and corona treatment, respectively. We study the possible contributions to this size dependence by transferring poly(dimethylsiloxane) (PDMS) lines with periods down to 140 nm into woodpile structures from perfluoropolyether (PFPE) stamps at different plasma/corona exposures, as well as quantifying stamp demolding forces and interlayer bond strength through peel tests. Brief plasma exposure times of 1-3 seconds showed successful bonding, while brittle delamination occurred at the more conventional longer exposure times of 30-60 seconds. In addition, demolding force displayed significant anisotropy depending on peel orientation with respect to the line direction. The results presented here offer insights into plasma bonding at the nanoscale and offer a pathway to rapid, scalable bonding strategies for printing and microfluidics applications.

11:30 AM PM03.09.09

Technologies for Multi-Material Additive Manufacturing of Embedded Heating Devices for Printable Sorbent in Life-Support Systems in Space Travel Applications

Jamie Thompson1,2,3, Charlotte Bellerjeau4, Camille Petit4 and Gregory Whiting3; 1NASA Ames Research Ctr, Moffett Field, California, United States; 2Materials, Imperial College London, London, United Kingdom; 3EMDL, Xerox PARC, Palo Alto, California, United States; 4Mechanical, University of Colorado Boulder, Boulder, Colorado, United States; 5Chemical Engineering, Imperial College London, London, United Kingdom.

Life support is the most essential process in human space flight. Currently, on board the International Space Station (ISS), carbon dioxide is removed via a four-bed molecular sieve system. The involved processes are heavily dependent on heating large containers of sorbent material during sorbent regeneration at a large energy cost. Therefore, any technologies that minimize the power requirements or turnover time of life support processes are invaluable for human space exploration.

Printed sorbent heater composites produced via additive manufacturing can be used for in-space CO2 capture and conversion processes. Through the development of multi-material printing technologies for ceramics and conductors, a heating element was successfully embedded within a printed sorbent device, allowing for more efficient and quicker localized heating from within the sorbent material. Embedded heaters will significantly minimize energy consumption during sorbent regeneration. Devices are manufacturable with a single print process and only require a post-printing heat treatment before being ready for use in a sorbent bed system. The processes are compatible with both terrestrial and space manufacturing techniques. The evolution of these technologies explored the use of both metallic and nonmetallic conductor inks, as well as ceramic-conductor composite inks. Binders were also explored as part of the ink development to assess their role in both extrusion and drying/curing post processes. Pre-printing ink preparation methods capable of producing foams directly from homogenous solid phase solutions were developed to allow tunable porosity with minimal effects on printability. Changes to the nano, micro, and macrostructure of the sorbent materials were characterized to assess the extent of activation/deactivation caused by preparation, printing, and heat treatment steps.

11:45 AM PM03.09.10

Development of a Conductive Biodegradable Ink for Multi-Process Additive Manufacturing

Madhur Atreya1, Gabrielle Marinick2 and Gregory Whiting1; 1Mechanical Engineering, University of Colorado Boulder, Boulder, Colorado, United States; 2Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, United States.

Widely distributed electronic systems for environmental monitoring can enable the collection of large data sets useful for resource optimization in areas such as agriculture. However, the use of such sensor systems is limited by a number of factors including unit cost and the potential for creating significant amounts of persistent electronic waste in the environment. Continued research into transient electronic materials and devices has led to a number of available options for biodegradable conductive materials. However, development of biodegradable high-conductivity materials suitable for digital additive manufacturing under ambient conditions remains a challenge.
Building on previous work, we have created solution-based, conductive direct-write inks consisting of various metal particles (such as tungsten) and biodegradable polymeric binders (such as poly(lactic acid)). These printed conductors degrade under a combination of microbial action and water solubility in a predictable manner. Combining the direct-ink writing (DIW) process of these conductors with other digital additive processes, such as fused-deposition modelling (FDM), allows for the fabrication of three-dimensional electronic structures and complex geometries that enable the control of degradation time and mechanical properties.

Based on these materials and processes, a degradable sensor package for examining soil moisture was evaluated, with electronic properties, degradation characteristics and ecotoxicity of resulting by-products systematically analyzed.

SESSION PM03.10: Composites

Session Chairs: Shelby Nelson and James Watkins
Thursday Afternoon, November 29, 2018
Hynes, Level 1, Room 108

1:30 PM PM03.10.01

Processing and Characterization of Reinforced Polymer Matrix Nanocomposites with Graphene and h-BN Nanoflakes
Arab H. Hussein, Assimina Pelegri, Stephen D. Tse, Bernard Kear and Zhizhong Dong; Rutgers University, Piscataway, New Jersey, United States.

In this study, graphene (G) and hexagonal boron nitride (h-BN) microscale powders are exfoliated to nanoscale flakes in a liquid phase of poly-methyl methacrylate (PMMA) solution by an in-situ high shear process. G and h-BN are separately investigated for exfoliation and improvement of performance properties with/of the polymer. With pure PMMA as a reference, mechanical characterizations, including nanoindentation test (strength and stiffness) and dynamic mechanical analysis (DMA), were conducted on the reinforced polymer matrix nanocomposite systems. The surface morphology and nanoflake interface within the polymer matrix are investigated by scanning electron microscopy (SEM) and transmission electron microscope (TEM). Raman spectroscopy is used to determine the number of layers and the dispersion of the 2D flakes in the matrix, via the distribution of peak positions and intensities as a function of wavelength. The results demonstrate improvement in the final mechanical properties. During processing, changes in the viscoelastic behavior during exfoliation of graphene in the polymer is noted, along with G being more ‘reactive’ than exfoliated h-BN within the polymer matrix.

1:45 PM PM03.10.02

Characterization of Hierarchical Composites with Glass Fiber/Carbon Nanotube using Alternating Current Electrophoretic Deposition
Dae Han Sung1, Sagar Doshi1, Andrew Rider2 and Erik Thostenson1; 1Department of Mechanical Engineering and Center for Composite Materials, University of Delaware, Newark, Delaware, United States; 2Defence Science and Technology Group, Melbourne, Victoria, Australia.

The introduction of nanomaterials like carbon nanotubes (CNT) to conventional fiber-reinforced composites creates hierarchical structures where reinforcing fibers, which usually have diameters in the micrometer scale, are surrounded by nanoscale materials. In this research, we used an alternating current electrophoretic deposition (AC-EPD) technique to deposit CNTs directly onto the glass fibers. We expected that AC-EPD would reduce the influence of water electrolysis by which trapped hydrogen or oxygen bubbles made the gap between substrate fibers and electrodes, thereby facilitating a denser CNT network within fiber bundles and filaments as compared to direct current EPD. We compare two different aqueous CNT dispersions, anodic and cathodic, using a novel ozonolysis and ultrasonication technique that results in dispersion and functionalization in a single step. In the anodic solution system, ozone oxidation makes CNTs negatively charged (anions) with functional groups such as hydroxyl and carboxyl groups. On the other hand, in the cathodic system CNTs were functionalized with a polyethyleneimine (PEI) dendrimer where the amine groups protonate under acidic conditions and, in turn, became cations. Anions and cations moved to positively charged electrode (anode) and cathode, respectively, when electric potential was applied in each system. Characterization of the coated fiber surfaces and composites revealed a uniform coating of carbon nanotubes and penetration between the bundles. AC-EPD is novel and simple approach to modify interface / interphase properties of CNT hierarchical composites and has great potential to scale up hybridizing process of nanomaterials which can be utilized as multifunctional applications.

2:00 PM PM03.10.03

Continuous Production of Carbon Nanotube-Grafted Carbon Fibres—A Route to Manufacture Hierarchical Composites
Hugo De Luca1, David B. Anthony2, Chengyin Liu3, Suresh Kumar Raman Pillar4, Emile Greenhalgh4, Alexander Bismarck4, M. B. Chan-Park4 and Milo Shaffer1; 1Materials, Imperial College London, London, United Kingdom; 2Chemical Engineering, Imperial College London, London, United Kingdom; 3Aeronautics, Imperial College London, London, United Kingdom; 4School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore, Singapore.

The mechanical properties of fiber-reinforced composites depend on the properties of the fiber/matrix interface where stress concentrations prevail. Grafting of carbon nanotubes to produce a “hairy” or “fuzzy” carbon fiber creates hierarchical reinforcements, combining two different reinforcement length scales, in this instance micrometer and nanometer. This approach improves the interaction between fibers and polymer matrices, and can enhance thermal and electrical functionality of the final composite. Generally, hairy fiber production is limited to batch processes due to harsh synthesis conditions (e.g. high temperature, inert environment) inherent to chemical vapor deposition, and have only recently been scaled-up to continuous production. Carbon nanotube-grafting finally meets industry prerequisites for its implementation in carbon fiber production lines.

In this work, the continuous production of carbon nanotube-grafted carbon fibers was performed in an open chemical vapor deposition reactor with continuous in-line catalyst deposition. This patented technology can be adapted to different fibre types, including as whole tows, while ensuring that the substrate's initial mechanical properties are retained. At the single fiber level, the presence of a uniform 200 nm long carbon nanotubes coverage on the surface of carbon fibers led to an increase in interfacial shear strength of up to 7.5% (96.7 MPa) when compared to the baseline unsized material (89.4 MPa). In the anodic solution system, ozone oxidization makes CNTs negatively charged (anions) with functional groups such as hydroxyl and carboxyl groups. On the other hand, in the cathodic system CNTs were functionalized with a polyethyleneimine (PEI) dendrimer where the amine groups protonate under acidic conditions and, in turn, became cations. Anions and cations moved to positively charged electrode (anode) and cathode, respectively, when electric potential was applied in each system. Characterization of the coated fiber surfaces and composites revealed a uniform coating of carbon nanotubes and penetration between the bundles. AC-EPD is novel and simple approach to modify interface / interphase properties of CNT hierarchical composites and has great potential to scale up hybridizing process of nanomaterials which can be utilized as multifunctional applications.

2:15 PM PM03.10.04

Multifunctional Structural Energy Storage and Stiffening of Fibre-Reinforced Polymer Composites Through Aerogel Addition
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The desire to reduce overall weight in devices is a key driver for development; the ability to combine composites with energy storage which provide, simultaneously, structural integrity has the potential to replace single function components. To achieve this ambition, the multifunctional component must perform both functionalities sufficiently, but often there is a trade-off in performance which is a significant challenge to overcome.

The performance and application of polymer-matrix fibre composites is often limited by matrix-dominated failures, both mechanical and functional. There is, therefore, considerable interest in the use of nanocomposite matrices, for example using resins filled with carbon nanotubes or graphene, to introduce both intralamellar and interlamellar reinforcement of the resulting hierarchical composites. The objective is to improve delamination resistance, through-thickness properties, and compression performance, without compromising the in-plane tensile response. The potential to improve thermal, fire retardance, as well as solvent and electrical conductivity, offers additional opportunities especially for multifunctional materials. However, due to processing constraints, the nanoreinforcements are typically present only at low loading fractions and in discontinuous form, limiting the level of enhancement.

Here, we present an alternative strategy, to form a rigid bicontinuous reinforcing network throughout the matrix volume. A suitable precursor is first infused into a structural fibre weave or other preform, then converted to form a porous monolithic aerogel/xerogel matrix, with characteristic length scales around a few tens of nanometres. The presence of the reinforcing fibres allows the aerogel/xerogel to form a stable, handleable, structure. Both the rigid network and the porosity are bicontinuous, allowing a second matrix resin phase to be infused. This second phase may be a soft multifunctional phase; for example, one that can support ion conductivity for use in structural supercapacitors.

Purely mechanical properties can be investigated when the second phase is a conventional structural epoxy resin. We have studied two analogous systems, one combining carbon aerogel with carbon fibres, and one combining silica aerogel/xerogel with glass fibres, in both cases adding a secondary epoxy resin. In the carbon system, there are increases in compressive and tensile stiffness respectively, but drops in interlaminar and compression properties are all maintained or improved. In the glass system, the interface quality is retained, such that interlaminar and compression properties are all maintained or improved. These initial studies highlight a family of bicontinuous nanostructured matrix systems for hierarchical composites, which have great potential and are worthy of further study.

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Ultralight Xylem-Like Conductive 3D Porous Composite with Cellulose Nanofiber and Ag Nanowire
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Ultra-light porous structures demonstrating high strength-to-weight ratio and large surface area and porosity has been of recent interest especially due to their potential application as structural material such as the framework of airplane or vehicle (high strength to weight ratio), catalyst supports (large surface area), thermal insulation, and shock damping or acoustic absorption (high porosity). In order to fabricate such a structure, direct foaming of the melt or powder metallurgical (PM) technique was commonly used by blowing a gas in the liquid alloy or by admixing of foaming agents with reactive sintering. However, Metallic foam made by PM techniques represent only 65 - 90% of the porosity that showed limitation of lightweight in the structure. Recently, freeze casting method was suggested to solve the limitations of conventional fabrication methods, which uses ice crystal as a template instead of light-induced polymer templates. Pore orientation of the structure can easily be controlled by directional freeze casting method to yield geometrically patterned structures. Therefore, in this study, we propose a xylem-like structure using a composite of cellulose nanofiber and Ag nanowire that satisfies both the high strength enhancement of metal and ultra-light weight of organic with small relative density.

To fabricate the xylem-like 3D porous structure, a mixture of cellulose nanofiber (CNF) and Ag nanowire solution was used in the one-step freeze casting process. CNF (diameter: ~20 nm, length: a few microns) is a fibrous material that demonstrates significantly higher modulus compared to conventional polymer or organic materials that makes CNF more suitable as a structural support for free standing structure. In addition, CNFs can form continuous 2D wall via strong hydrogen bonds and van der Walls forces as they fill in the empty remaining space in between the ice crystals, and thus CNF is chosen as a backbone in the 3D composite, which is further strengthened by the addition of Ag nanowires.

This study successfully fabricated a CNF + Ag nanowire porous structure in the bulk form with controlled pore orientation through a low cost process of directional freeze casting. The strengthening effect of the amount of the Ag nanowire addition was achieved 14.3 times higher compressive strength (from 7 kPa to 100 kPa) below 1% of total relative density for xylem-like CNF + Ag nanowire structure. Especially, addition of 0.29% of relative density for Ag nanowires in xylem-like CNF structure showed same order of compressive strength with higher scalability compared to Ni metallic microlattice in micro scale. In addition, more than 5mg/cm³ of Ag nanowire embedded 2D CNF wall is also able to offer sufficient conductivity that maybe suitable for a variety of electronics applications such as battery or supercapacitor electrode.