IPF on Mesoscale Science and Technology of Materials and Metamaterials
Room: 210F - Session IPF+MS-MoM

Materials for Energy Generation and Storage (8:20-10:20) & Mesoscale Phenomena in the Biosciences I (10:40-12:00)

Moderator: Alain Diebold, SUNY College of Nanoscale Science and Engineering, Carolyn Larabell, University of California, San Francisco

8:20am **IPF+MS-MoM1 Synthesis and Behavior of Nanostructures in Mesoscale Architectures**, ***SangBok Lee***, *G.W. Rubloff, E. Gillette, C. Liu,* University of Maryland, College Park, *X. Chen,* Lam Research Corporation, *J. Hu, S. Wittenberg, L. Graham,* University of Maryland, College Park, *P. Banerjee*, Washington University, St. Louis **INVITED**

As advanced nanostructured electrodes continue to push boundaries for both high power and high energy, it will become increasingly important to understand how structure on the mesoscale impacts charge transport and electrochemical reactions. Understanding the influence of structure on ionic and electronic transport behavior, as well as its influence on degradation is highly essential to design and control improved electrodes. Here, we describe the fabrication of two types of electrodes; one with electrodes constructed in the most simple cylindrical nanopores - "all-in-one nanopore battery" - and the other with electrodes in controllable 3D interconnecting pore network to propose a strategy for bridging the gap between precision, self-aligned nanostructure electrodes and disordered, high density electrodes. These architectures highlight some of the challenges of characterizing tortuosity and porosity in nanostructures, but also provides an opportunity to work with a systematically variable mesoscale electrode structure.

9:00am **IPF+MS-MoM3 Ultralight Microlattices: Defining the Limits of Lightweight Materials**, ***William Carter***, HRL Laboratories, LLC **INVITED**

Design of “materials architecture” is emerging as a new and complimentary approach to classical materials selection in engineering design. By adjusting the geometric arrangement of solid phases and voids within a material, it is possible to extend the achievable property space for lightweight materials and functional coatings. Optimal microlattice materials that can be formed in a wide range of architectures and base materials, with properties spanning from unprecedented low density and surprisingly high mechanical recovery to structural alternatives to honeycomb and foams. The starting polymer microlattice templates are created using an array of interpenetrating self-forming photopolymer waveguides from a single exposure mask. Free-standing hollow micro-lattice materials can be formed based on a wide range of high performance thin films (metals, ceramics and polymers) by coating a micro-lattice template followed by subsequent removal of the template. The process enables precise and independent control over micro-lattice architecture at all levels of structural hierarchy (~100nm up to ~10cm). This technique is also inherently scalable to low-cost high-throughput manufacturing (~10-60 second exposure), highly scalable to large sizes (m2), enabling practical design and fabrication of a wide range of lattice materials including metals, polymers and ceramics.

9:40am **IPF+MS-MoM5 "Can Opto-Electronics Provide the Motive Power for Future Vehicles?"**, ***Eli Yablonovitch***, University of California, Berkeley **INVITED**

A new scientific principle[1] has produced record-breaking solar cells. The 28.8% single-junction solar efficiency record, by Alta Devices [2], was achieved by recognizing the importance of extracting luminescent emission. This is exemplified by the mantra: “A great solar cell also needs to be a great LED”. It was essential to remove the original semiconductor substrate, which absorbed luminescence, and to replace it with a high reflectivity mirror. The solar efficiency record crept up as the rear reflectivity behind the photovoltaic film was increased, 96% reflectivity -- 97% -- 98% luminescent reflectivity;-- each produced a new world efficiency record.

In thermo-photovoltaics, high energy photons from a thermal source are converted to electricity. The question is what to do about the majority of low energy infrared photons? It was recognized that the semiconductor band-edge itself can provide excellent spectral filtering for thermophotovoltaics, efficiently reflecting the unused infrared radiation back to the heat source. Exactly those low energy photons that fail to produce an electron-hole pair, are the photons that need to be recycled.

Thus the effort to reflect band-edge luminescence in solar cells has serendipitously created the technology to reflect all infrared wavelengths, which can revolutionize thermo-photovoltaics. We have never before had such high rear reflectivity for sub-bandgap radiation, permitting step-function spectral control of the unused infrared photons for the first time. This enables conversion from heat[3] to electricity with >50% efficiency. Such a lightweight “engine” can provide power to electric cars, aerial vehicles, spacecraft, homes, and stationary power plants.

1. O. D. Miller, Eli Yablonovitch, and S. R. Kurtz, “Strong Internal and External Luminescence as Solar Cells Approach the Shockley–Queisser Limit”, IEEE J. Photovoltaics, vol. 2, pp. 303-311 (2012). DOI: 10.1109/JPHOTOV.2012.2198434

2. Kayes, B.M.; Hui Nie; Twist, R.; Spruytte, S.G.; Reinhardt, F.; Kizilyalli, I.C.; Higashi, G.S. “27.6% Conversion Efficiency, A New Record For Single-Junction Solar Cells Under 1 Sun Illumination” Proceedings of 37th IEEE Photovoltaic Specialists Conference (PVSC 2011)Pages: 4-8, DOI: 10.1109/PVSC.2011.6185831

3. The heat source can be combustion, radio-activity, or solar thermal.

10:40am **IPF+MS-MoM8 The Convergence of Synthetic Biology and Biofabrication: Guiding Biological Function at the Mesoscale**, ***William Bentley***, Fischell Department of Bioengineering, University of Maryland **INVITED**

Synthetic biology provides a means for articulating concepts into new products and products. Its toolbox is extensive, including the ability to create synthetic genomes and tailor their regulation. Early successes augmented the cell’s biosynthetic capacity and rewired its regulation, transforming our ability to produce products ranging from small molecules to fully functional therapeutic proteins at high yield. Also, the theoretical formalisms of metabolic engineering provided a basis for optimally routing its biochemical flux. With pathway analysis and optimization, cells are now engineered to produce large quantities of economically important molecules. Indeed, many “green” routes to chemical synthesis have appeared and many more are emerging. There exists great enthusiasm and investment to revolutionize several industries. Importantly, these activities have focused largely on the cell’s intracellular biochemical network and relied less on molecular cues from the immediate surroundings. Largely untapped within synthetic biology are the signaling motifs that guide cell processes and interactions among communicating populations. That is, signal molecules guide many cellular processes and these can be exploited to endow cells with “executive” function, where decision events are programmed and cells carry out tasks in addition to making products. That is, the cells themselves can be the primary “products” of synthetic biology – putting them to work in complex “noisy” environments will require tailoring their exposure to chemical cues. For example, we may eventually use engineered bacteria to fight cancer, cure diabetes, or “tune” the microbiome in our GI tracts. Biofabrication, the use of biological components and biological processes for assembly, can provide a means for tailoring hierarchical order in biological systems. We exploit the principles of biofabrication to create 3D “test tracks” where chemical cues can be spatiotemporally controlled and task-accomplishing bacteria can be appropriately designed. We will discuss the link between synthetic biology and biofabrication and highlight the potential for new discovery as well as process and product innovation.

11:20am **IPF+MS-MoM10 Using Mesoscale Modeling to Design Materials that Compute: Coupling Self-Oscillating Gels and Piezoelectric Films**, *V.V. Yashin, S.P. Levitan,* ***Anna C. Balazs***, University of Pittsburgh **INVITED**

Lightweight, deformable materials that can sense and respond to human touch and motion can be the basis of future wearable computers, where the material itself will be capable of performing computations. To facilitate the creation of "materials that compute", we draw from two emerging modalities for computation: chemical computing, which relies on reaction-diffusion mechanisms to perform operations, and oscillatory computing, which performs pattern recognition through synchronization of coupled oscillators. Chemical computing systems, however, suffer from the fact that the reacting species are coupled only locally; the coupling is limited by diffusion as the chemical waves propagate throughout the system. Additionally, oscillatory computing systems have not utilized a potentially wearable material. To address both these limitations, we develop the first model for coupling self-oscillating polymer gels to a piezoelectric (PZ) micro-electro-mechanical system (MEMS). The resulting transduction between chemo-mechanical and electrical energy creates signals that can be

propagated quickly over long distances and thus, permits remote, non-diffusively coupled oscillators to communicate and synchronize. Moreover, the oscillators can be organized into arbitrary topologies because the electrical connections lift the limitations of diffusive coupling. Using our model, we predict the synchronization behavior that can be used for computational tasks, ultimately enabling "materials that compute."

Accelerating Materials Discovery for Global Competitiveness Focus Topic
Room: 114 - Session MG+BI+MS+NS+TF-MoM

Development of Novel Materials
Moderator: Talat Rahman, University of Central Florida

9:00am **MG+BI+MS+NS+TF-MoM3 Molecular Engineering of Dyes for Dye-Sensitized Solar Cells via Rational Design**, ***Jacqueline Cole***, University of Cambridge, UK **INVITED**

Dye-sensitized solar cells (DSCs) have unique attributes that afford them prospective applications as smart windows - windows in buildings that generate electricity from sunlight. This electricity will be fed into a local grid that will create sustainable buildings for future cities.

Materials discovery of new DSC dyes is one of the remaining bottlenecks to technological progress of smart windows. This talk shows we are attempting to overcome this materials bottleneck via two complementary routes to molecular design: (i) a 'top down' approach that uses large-scale data mining to identify brand new classes of DSC dyes [1]; (ii) a 'bottom up' approach that computationally transforms well-known non-DSC dyes into suitable DSC dyes [2,3].

The ‘top down’ approach involves large-scale data-mining to search for appropriate dye candidates [1]. Here, structure-property relationships for DSC dyes have been codified in the form of molecular dye design rules, which have been judiciously sequenced in an algorithm to enable large-scale data mining of dye structures with optimal DSC performance. This affords, for the first time, a DSC-specific dye-discovery strategy that predicts new classes of dyes from surveying a representative set of chemical space. A lead material from these predictions is experimentally validated, showing DSC efficiency that is comparable to many well-known organic dyes.

The ‘bottom up’ approach concerns case studies on families of well-known laser dyes that are transformed into functional DSC dyes using molecular engineering [2,3]. The underlying conceptual idea is to implement certain electronic structure changes in laser dyes, using molecular engineering, to make DSC-active dyes; while maintaining key property attributes of the laser dyes that are equally attractive to DSC applications. This requires a concerted experimental and computational approach; results predict new dye co-sensitizers for DSC applications.

References

[1] J. M. Cole, K. S. Low, H. Ozoe, P. Stathi, C. Kitamura, H. Kurata, P. Rudolf, T. Kawase, “Data Mining with Molecular Design Rules Identifies New Class of Dyes for Dye-Sensitised Solar Cells” *Phys. Chem. Chem. Phys*. 48 (2014) 26684-90

[2] S. L. Bayliss, J. M. Cole, P. G. Waddell, S. McKechnie, X. Liu, “Predicting solar-cell dyes for co-sensitization”, *J. Phys. Chem. C* 118 (2014) 14082–14090

[3] F. A. Y. N. Schroeder, J. M. Cole, P. G. Waddell, S. McKechnie, “Transforming benzophenoxazine laser dyes into chromophores for dye-sensitized solar cells: a molecular engineering approach”, *Advanced Energy Materials* (2015) DOI: 10.1002/aenm.201401728

10:40am **MG+BI+MS+NS+TF-MoM8 Controlled Spontaneous Nanoscale Patterning of Nonstoichiometric Reconstructions for Catalysis and Light Harvesting**, *J.M. Martirez, D. Saldana-Greco,* University of Pennsylvania*, W.A. Saidi,* University of Pittsburgh*, J.S. Lim,* ***Andrew Rappe***, University of Pennsylvania **INVITED**

The ability to manipulate the atomic and electronic structure and stoichiometry of surfaces is of utmost importance in optimizing heterogeneous catalysts. A critical requirement in this endeavor is a deep thermodynamic and kinetic understanding of surface reconstruction behavior, under various thermal and chemical constraints. We explore the reconstruction behaviors of Ti- and Mn-based perovskite type oxides: $BaTiO_3$, $PbTiO_3$, and $CaMnO_3$: the former two exhibit ferroelectricity, while the latter undergoes surface-induced magnetic ordering. Due to the characteristic properties of these oxides, we investigate the effect of their switchable polarization (for ferroelectric oxides) and near surface magnetic ordering ($CaMnO_3$) in their surface phase evolution, in addition to the effects of temperature and the chemical potentials of their constituent elements. We find that these oxides undergo surface reconstruction transformations that generally result in enrichment of their catalytically active components (Ti and Mn). These reconstructions show rich bonding and structural motifs that affect the active sites’ reactivity and accessibility. Furthermore, these surface transformations, as in $BaTiO_3$ and $PbTiO_3$, can be tuned with the help of an electric field. An applied electric field changes the material’s polarization, which then alters the surface electronic properties, and thereby also affects their sensitivity towards stoichiometric changes. In addition to the thermodynamic understanding of the surface reconstructions, we introduce the kinetic tunability of the surface reconstruction. We demonstrate this from a particular surface phase coexistence observed in $BaTiO_3$, namely the $c(2x2)$ and $c(4x4)$, where the diffusion behavior of the TiO units that compose both surfaces strongly dictate their degree of agglomeration. Finally, based on our interest in $CaMnO_3$ (001) surfaces, we have started to explore the more complex $CaMn_7O_{12}$. The electronic properties of this oxide yield interesting physical phenomena including charge ordering, non-collinear magnetism and improper ferroelectricity. We are currently investigating the ground state non-collinear magnetic configuration in this compound and its role on the stability of the charge-ordered state.

11:20am **MG+BI+MS+NS+TF-MoM10 Developing Evolutionary Algorithms for *a priori* Crystal Structure Prediction and Applications towards Novel Pressure-Stabilized Materials**, ***Eva Zurek***, University at Buffalo-SUNY **INVITED**

One way to accelerate the development of new materials is via *a priori* crystal structure prediction (CSP) of hitherto unknown systems, followed by the computation of their properties and determination of promising synthesis conditions. A number of algorithms designed to solve global optimization problems have recently been applied to CSP with much success, and evolutionary algorithms (EAs) have emerged as one of the most promising methods for systems where little or no experimental data is available. Therefore, we have developed the open-source XtalOpt EA for CSP as an extension to the widely used chemical builder and visualizer, Avogadro. In this talk we present new developments within XtalOpt that allow it to successfully predict the structures of crystals with larger and more complex unit cells. Furthermore, we summarize the application of XtalOpt towards the prediction of hydrogen-rich solids with unique stoichiometries that are computed to be stable at pressures that are attainable within diamond anvil cells. The influence of the structure of the hydrogenic lattice on the electronic structure and the propensity for high temperature superconductivity is discussed.

2D Materials Focus Topic
Room: 212C - Session 2D+EM+MC+MS+NS-MoA

2D Materials: Devices and Applications
Moderator: Joshua Goldberger, The Ohio State University, Arend van der Zande, University of Illinois at Urbana Champaign

2:20pm **2D+EM+MC+MS+NS-MoA1 Designer Materials from the Assembly of 2D Layered Heterostructures**, ***Cory Dean***, Columbia University **INVITED**
The capability to assemble two-dimensional (2D) materials into layered heterogeneous structures presents an exciting new opportunity in materials design. For example, encapsulating graphene with hexagonal BN yields enhanced transport properties with reduced environmental sensitivity, and allows for complex band structure engineering. This has enabled graphene to be exploited as a model experimental platform to study a wide range of fundamental physics arising both from conventional single-particle considerations, as well as more exotic emergent behaviour in the strongly interacting regime. Graphene however represents just one of a larger subset of layered materials, which are now receiving growing attention due to their diverse array of intrinsic properties. The opportunity to "mix and match" these disparate crystals to realize fundamentally new hybrid material properties provides an almost unbounded new direction as we look for quantum materials beyond graphene. In this talk I will outline some of the fundamental questions, and technical challenges facing these efforts and highlight some of our recent innovations in this direction. Implications for the development of new device geometries and scientific pursuits will be discussed.

3:00pm **2D+EM+MC+MS+NS-MoA3 Structural Semiconducting-to-Metallic Phase Transition in Monolayer Transition Metal Dichalcogenides Induced by Electrostatic Gating**, ***Yao Li***, *K.-A. Duerloo, E.J. Reed*, Stanford University
Dynamic electrical control of conductivity in two-dimensional (2D) materials is one of the most promising schemes for realizing energy-efficient electronic devices. Monolayer transition metal dichalcogenides (TMDs) are 2D materials that can exist in multiple crystal structures, each of different electrical conductivity. Using density functional approaches, we discover that a structural semiconducting-to-metallic phase transition in some monolayer TMDs can be driven by electrical stimuli, including change of charge density and bias voltage. We find that a bias voltage approximately 0.5~1 V can trigger the phase transition in $MoTe_2$, while a larger voltage is required for the transition in other monolayer TMDs. The threshold bias voltage is strongly influenced by the substrate on which the monolayer is placed. Carefully choosing the substrate could greatly reduce the threshold bias voltage for the phase transition, and therefore consume much less energy, suggesting potential applications in electronics with very high energy efficiency. The dynamic control of this semiconducting-to-metallic phase transition can be achieved utilizing standard electronic devices like the electrostatic gating employed in a field-effect transistor. We have also calculated the phase boundary of a reported metallic-to-metallic phase transition in $TaSe_2$ to compare with earlier STM experimental results and reasonable agreement is observed. Our findings open up the possibility of manufacturing ultrathin flexible two-dimensional phase change electronic devices with potential for higher energy efficiency than conventional electronic devices.

3:20pm **2D+EM+MC+MS+NS-MoA4 Use of Voltage-Contrast and Dynamical XPS for Characterization of Graphene-Based Devices in Operation**, ***Sefik Suzer***, Bilkent University, Turkey
A noncontact chemical and electrical technique of XPS is performed to investigate a number of deviecs under operation. The main objective of the technique is to trace chemical and location specified surface potential variations as shifts of the XPS peak positions under operating conditions. To implement the measurements we apply D.C. (Voltage-Contrast) and/or A.C. (Dynamical) voltage biases externally to the sample, while recording XPS data. Accordingly, we extract chemically resolved static and/or time-resolved information related with certain electrical properties of materials and devices made from them. Details of the technique and applications to a number of graphene-based devices, configured in a transistor geometry with and without gating, will be presented.

4:00pm **2D+EM+MC+MS+NS-MoA6 Avalanche Photodiodes based on MoS_2/Si Heterojunctions**, ***Oriol López Sánchez***, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *G. Fiori, G. Iannaccone,* Università di Pisa, Italy, *D. Dumenco,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *E. Charbon*, Delft University of Technology, Netherlands
Avalanche photodiodes (APDs) are the semiconducting analogue of photomultiplier tubes offering very high internal current gain and fast response. APDs are interesting for a wide range of applications in communications, laser ranging, biological imaging, and medical imaging where they offer speed and sensitivity superior to those of classical p-n junction-based photodetectors. The APD principle of operation is based on photocurrent multiplication through impact ionization in reverse-biased p-n junctions. Here, we demonstrate APDs based on vertically stacked monolayer MoS_2 and p-Si, forming an abrupt p-n heterojunction. With this device, we demonstrate carrier multiplication exceeding 1000 at 10 V reverse bias . Our devices show little degradation of SNR at high gains. These heterostructures allow the realization of simple and inexpensive high-performance and low-noise photon counters based on transition metal dichalcogenides.

4:20pm **2D+EM+MC+MS+NS-MoA7 From Black Phosphrus to Phosphorene**, ***Peide Ye***, Purdue University **INVITED**
Phosphorus is one of the most abundant elements preserved in earth, constructing with a fraction of ~0.1% of the earth crust. In general, phosphorus has several allotropes. The two most commonly seen allotropes, white and red phosphorus, are widely used in explosives and safety matches. In addition, black phosphorus, though rarely mentioned, is a layered semiconductor and has great potentials in optical and electronic applications. Remarkably, this layered material can be reduced to one single atomic layer in the vertical direction owing to the van der Waals structure, known as phosphorene, where the physical properties can be tremendously different from its bulk counterpart. In this talk, we trace back to the 100 years research history on black phosphorus from the synthesis to material properties, and extend the topic from black phosphorus to phosphorene. The physical and transport properties are highlighted, aiming at further applications in electronic and optoelectronics devices.

5:00pm **2D+EM+MC+MS+NS-MoA9 Ambient Oxidation and Alumina Passivation of Exfoliated Black Phosphorus Transistors**, ***Joshua Wood***, *S. Wells, D. Jariwala, K.-S. Chen, X. Liu, V. Sangwan, E. Cho, L. Lauhon, T.J. Marks, M.C. Hersam*, Northwestern University
Exfoliated black phosphorus (BP) is an elemental, two-dimensional (2D) nanomaterial with high carrier mobility (~100 $cm^2V^{-1}s^{-1}$), a layer-dependent band gap (~0.3 to 2.0 eV), and in-plane anisotropy. Further, 2D BP is air sensitive, culminating in undesirable surface reactions that degrade device performance. We find that unencapsulated, exfoliated BP flakes form oxidized derivatives following ambient exposure, as ascertained by X-ray photoelectron spectroscopy, atomic force microscopy, Fourier transform infrared spectroscopy, transmission electron microscopy, and electrostatic force microscopy measurements. BP ambient oxidation is driven by oxygen-saturated H_2O, as we observe two-fold faster degradation for BP on hydrophobic substrates versus hydrophilic ones. After 48 hours of ambient oxidation, unencapsulated BP field-effect transistors (FETs) decline in mobility and current on/off ratio by factors of over 1000. In contrast, alumina (i.e., AlO_x) passivated BP flakes and FETs are robust and unoxidized for over seven months in ambient conditions. Alumina-passivated BP FETs possess mobilities of ~100 $cm^2V^{-1}s^{-1}$, on/off ratios of 1000, and ambipolar transport, even following extensive ambient exposure [1]. This understanding of BP ambient oxidation—and how to prevent it—is also impacting ongoing work in solution-phase BP separation [2], BP chemical modification, and high-performance BP optoelectronic applications.

[1] J. D. Wood *et al.*, *Nano Lett.* **14**, 6964 (2014); [2] J. Kang *et al.*, *ACS Nano* **9**, 3596 (2015).

5:20pm **2D+EM+MC+MS+NS-MoA10 Electro-Acoustic Characterization of Transition Metal Dichalcogenide Films on $LiNbO_3$**, ***Edwin Preciado***, UC Riverside, *F.J.R. Schülein, A. Wixforth,* Universität Augsburg, Germany, *A. Nguyen, D. Barroso, M. Isarraraz, G. von Son, I. Lu, L. Bartels,* UC Riverside, *H. Krenner*, Universität Augsburg, Germany
We demonstrate mm-scale CVD growth of single layer molybdenum disulfide directly onto piezoelectric lithium niobate and present the fabrication of a hybrid FET – SAW (field effect transistor – surface acoustic

wave) device. Our experiments reveal close agreement between transport measurements utilizing conventional contacts and SAW spectroscopy. This approach will ultimately provide for a contact free transport characterization of 2D TMD films, avoiding concerns about the role of charge transfer at contacts as an artifact of such measurements.

IPF on Mesoscale Science and Technology of Materials and Metamaterials
Room: 210F - Session IPF+MS-MoA

Mesoscale Phenomena in the Biosciences II (2:20-3:40) & Metamaterials (3:40-5:40)
Moderator: Carolyn Larabell, University of California, San Francisco, Mark Brongersma, Stanford University

2:20pm **IPF+MS-MoA1 Mesoscale Imaging in Cell Biology**, ***Gerry McDermott***, *M. Do, J.-H. Chen, A. Walter, M.A. Le Gros, C.A. Larabell*, University of California, San Francisco **INVITED**

Soft X-ray tomography (SXT) is ideally suited to imaging the sub-cellular architecture of biological cells. In SXT, specimens are illuminated with 'water window' photons. X-rays within this energy range (284 – 543eV) are absorbed an order of magnitude more strongly by carbon- and nitrogen-containing organic materials than by water. Consequently, the variation in biomolecule composition and concentration within the specimen gives rise to quantitative, high-contrast images of intact, fully hydrated cells, without the need to use contrast-enhancing agents. The utility of SXT has recently been enhanced by the development of high numerical aperture cryogenic fluorescence tomography (CFT) for correlated imaging studies. This multi-modal approach allows labelled molecules to be localized in the context of a high-resolution 3-D tomographic reconstruction of the cell. This talk will describe correlated CFT-SXT and the application of this technique to long-standing questions in cell biology.

3:00pm **IPF+MS-MoA3 Biomimetic Material Approaches to Tissue Engineering, Regenerative Medicine, and Wound Healing**, ***Elizabeth Loboa***, UNC-Chapel Hill & NC State University **INVITED**

There is growing clinical need in wound healing, tissue engineering, and regenerative medicine for controlled release systems that encapsulate therapeutic compounds and provide sustained release in a site-specific manner. Biocompatible, biodegradable nanofibrous scaffolds with their morphological similarities to the natural extracellular matrix (ECM) in vivo, high surface area to volume ratio, and small interfibrous pore sizes hold great potential for this application. Loading dopants within an electrospun polymeric matrix allows for consistent entrapment throughout the nanofibers. Further, the high surface area to volume ratio of these matrices maximizes the interaction of the carrier with a surrounding medium. A critical parameter for achieving success in controlled release is controlled diffusion of molecules out of the electrospun scaffolds. The drug release characteristics of nanofibrous scaffolds rely on how well the drug is encapsulated inside the nanofibers. These characteristics are critically affected by fiber morphology.

In this presentation, Dr. Loboa will discuss approaches in her lab to elucidate and optimize biomimetic fibrous systems for wound healing, tissue engineering, and regenerative medicine applications. Focus will be placed on regeneration of skin and musculoskeletal tissues and approaches to wound care and tissue regeneration while combating multi-drug resistant bacteria.

3:40pm **IPF+MS-MoA5 Structured Light and Structured Surface Waves from Metasurfaces**, ***Federico Capasso***, Harvard University **INVITED**

Patterning surfaces with subwavelength spaced metallo-dielectric features (metasurfaces) allows one to locally control the amplitude, phase and polarization of the scattered light, allowing one to generate complex wavefronts such as optical vortices of different topological charge and dislocated wavefronts. 1,2 Recent results on achromatic metasurfaces will be presented including lenses and collimators. Metasurfaces have also become a powerful tool to shape surface plasmon polaritons (SPPs) and more generally surface waves. I will present new experiments on imaging SPP that have revealed the formation of Cherenkov SPP wakes and demonstrated polarization sensitive light couplers that control the directionality of SPP and lenses which demultiplex focused SPP beams depending on their wavelength and polarization.

1. N. Yu and F. Capasso Nature Materials 13, 139 (2014)

2. P. Genevet and F. Capasso Reports on Progress in Physics 78, 24401 (2015)

4:20pm **IPF+MS-MoA7 Quest for Extreme Photonics**, ***Nader Engheta***, University of Pennsylvania **INVITED**

Waves can be tailored, manipulated and sculpted by materials. Recent development in condensed matter physics, nanoscience, and materials science and technology has made it possible to construct materials and structures with unusual “extreme” characteristics. These “extreme” scenarios in light-matter interaction may come in several forms: It may be due to extreme in dimensionality such as metasurfaces and one-atom-thick materials, extreme near field such as subwavelength nonreciprocal vortexes in near zones of plasmonic structures, extreme anisotropy in design of superlattices with anisotropic effective mass of charged carriers, giant nonlinearity in phase-change dynamics, extreme information processing as in optical metatronics and "informatic" metastructures, and extreme material parameters such as epsilon- and/or mu-near-zero (ENZ, MNZ, and EMNZ) features leading to phenomena of “static optics”. Such “extreme photonics” may provide us with exciting functionalities in both wave physics and quantum optics and engineering. In this talk, some of our ongoing work in these areas will be discussed along with some of the opportunities and challenges in this area.

5:00pm **IPF+MS-MoA9 2D Materials: Graphene and Beyond**, ***Tony Heinz***, Stanford University **INVITED**

The past few years have witnessed a surge of activity in the study of graphene and, more recently, in other atomically thin two-dimensional materials. We will describe some the reasons for the intense interest in these new material systems, highlighting their unusual electronic properties. We will show how we can use light to probe the distinctive properties electrons in model 2-D materials such as graphene and transition metal dichalcogenides. We will discuss the basics of light-matter interactions in these 2-D materials, as well as signatures of electron-electron and electron-phonon interactions, describing both the fascinating physics of these material systems and emerging applications in photonics.

IPF on Mesoscale Science and Technology of Materials and Metamaterials
Room: 210F - Session IPF+MS-TuM

Degradation Science (8:00-10:00) & Electrochemistry from Nano to Meso Scale (11:00-12:20)
Moderator: Gary Rubloff, University of Maryland, College Park, Stacey Bent, Stanford University

8:00am **IPF+MS-TuM1 Mesoscale Evolution & Temporal Analytics of Photovoltaic Energy Materials: A Degradation Science Approach**, ***Roger French***, Case Western Reserve University **INVITED**

Degradation science1 combines physical and statistical approaches to examine degradation mechanisms and pathways of a material or system in order to improve materials and reduce system failures by incorporating modeling, monitoring, and prediction of lifetime performance. Degradation of PV modules evolves over long time-frames and length scales, which is a characteristic of mesoscale science. Degradation arises due to the distinct, complex, and interactive phenomena which lead to failure. Real-world studies under diverse environmental conditions must be combined and cross-correlated with accelerated in-lab studies, using data science and analytics methodologies, so as to span the time and length scales that control the system's behavior over lifetime. Semi-supervised generalized structural equation (semi-gSEM) modeling can be used to relate physical mechanistic submodels with data-driven statistical submodels as networks of mechanisms and modes with statistically significant pathway relationships. The relationships and coupling strengths (βij) amongst variables can be rank-ordered in their contributions to the system's degradation. Temporal evolution, damage accumulation and change points among mechanisms/modes (variables) are accounted for in the semi-gSEM models. Towards these goals, a statistical methodology has been developed and applied to investigate the response of full sized PV modules to accelerated stress conditions. The results of this initial study indicate that a correlation exists between system level power loss and the buildup of acetic acid resulting from the hydrolytic degradation of EVA polymer encapsulant. To further explore this proposed mechanistic pathway, studies are underway to characterize the degradation of minimodule samples under a broader range of similar multifactor accelerated stress conditions. Sample types feature frontside silver gridlines of two different widths and exposure conditions vary in irradiance level and temperature. Samples are measured non-destructively at many points along their lifespan, using confocal Raman microscopy to capture chemical signals and various techniques to gather electrical performance information, with the goal of observing the co-evolution of EVA degradation and gridline corrosion. This represents an important first step towards exploring the often misunderstood role of EVA degradation in PV module performance loss, and building a more integrated picture of PV module degradation as a whole. Initial data analytics of six months' real-world performance data of 60 c-Si PV modules on the SDLE SunFarm shows deviation of performance ratio among modules at the same geometric location. Grouping of samples with similar performance patterns was performed with hierarchical clustering, K-means clustering was used to confirm the optimum number of clusters. A brand dependent module performance model was developed based on a subgroup of 21 modules from 7 manufactures. Over 1.5 million I-V curves measured every 5 minutes for 500 days on 10 modules with/without mirror on dual-axis trackers were analyzed use an automated analytic functions we developed. Maximum power point, open circuit voltage, short circuit current, slope of the curve near open circuit voltage, and slope of the curve near short circuit current are either directly extracted or estimated from measured I-V curves. An algorithm based on moving local regression model was developed to detect the change points on I-V curves, which caused by bypass diode turning on when I-V curve was measured under non-uniform irradiance. These examples of the use of degradation science, with its physical and statistical foundation and data analytics approach, will hopefully enable the community to address the long-term reliability uncertainty of photovoltaics as they become a major component in the world's energy systems.

1. French, Roger H., Rudolf Podgornik, Timothy J. Peshek, Laura S. Bruckman, Yifan Xu, Nicholas R. Wheeler, Abdulkerim Gok, et al., 2015, "Degradation Science: Mesoscopic Evolution and Temporal Analytics of Photovoltaic Energy Materials," Current Opinion in Solid State and Materials Science, Doi: 10.1016/j.cossms.2014.12.008

8:40am **IPF+MS-TuM3 Why Structural Failure is Mesoscale: From Dislocations to Fatigue Cracks**, ***Anthony Rollett***, Carnegie Mellon University **INVITED**

Structural failure of materials is a mesoscale problem because, for example, we lack the tools to predict when and where fatigue cracks will appear in relation to materials microstructure. Dislocations are well understood as line defects but we do not how to compute the behavior of large numbers of dislocations in relation to microstructure. Enormous strides have been made in quantifying the growth of fatigue cracks over the years and improving predictions of component lifetime but all at the microstructural scale and above. Nevertheless, it is clear that the behavior of short cracks is less well quantified, where short is relative to the length scale(s) found in materials microstructure, e.g. grain size. Short fatigue cracks in nickel-based superalloys have been characterized using conventional SEM and orientation mapping. High Energy Diffraction Microscopy (HEDM) and computed tomography (CT) was used to map out the crack positions in 3D. The main finding is that cracks develop most readily along long twin boundaries with high resolved shear stress on the slip systems parallel to the twin plane. Also, both halves of a different superalloy, fully fractured sample have been fully characterized in 3D using the same tools. The HEDM and CT were performed with high energy x-rays on beamline 1ID at the Advanced Photon Source (APS). This talk will review current dislocation modeling, empirical understanding of fatigue cracks in engineering materials and what the experimental and theoretical roadmap might be to address the problem set.

9:20am **IPF+MS-TuM5 Engineered 3D Mesoscale Battery Electrodes: Opportunities and Issues**, ***Paul Braun***, University of Illinois at Urbana-Champaign **INVITED**

Over the past decade, three-dimensional structures have been widely proposed as a path for enhanced lithium-ion batteries. While the sophistication of self and directed-assembly approaches for functional structures has increased dramatically, application of these structures has remained elusive, in part because real structures almost always contain finite defect densities, cannot be produced from materials with the appropriate electrochemical properties, and cannot be produced in sufficient volume for application. We have now made considerable strides in integration of electrically conducting and energy storage material into lithium-ion battery electrodes. We accomplish this by applying template-based and post-synthetic materials transformations, and have focused on ultra-large volume processing strategies. As the technology has approached commercialization, understanding the mechanistics of capacity fade and other electrochemical degradation pathways has become increasingly important.

11:00am **IPF+MS-TuM10 A Materials Genome Approach to Design of Novel Materials and Liquids for Energy Conversion and Storage**, ***Kristin A. Persson***, Lawrence Berkeley National Laboratory **INVITED**

The Materials Genome Initiative (MGI) aims to develop an infrastructure to discover, develop, manufacture, and deploy advanced materials at least twice as fast as possible today, at a fraction of the cost. In this talk I will highlight the advances and development of the Materials Project (www.materialsproject.org), which is an MGI-funded effort to compute the properties of all known inorganic materials and beyond, design novel materials and offer data to the community together with online analysis and design algorithms.1 The current release contains data derived from density functional theory (DFT) calculations for over 60,000 materials, each with searchable associated properties such as relaxed structure, electronic state, energy storage capability, aqueous and solid stability, and more. The software infrastructure enables thousands of calculations per week – enabling screening and predictions - for both novel solid as well as molecular species with target properties. Current application areas include photocatalysis, thermoelectrics, beyond-Li energy storage, and alloy design.

To exemplify the approach of first-principles high-throughput materials design, we will make a deep dive into future energy storage technologies, showcasing the rapid iteration between ideas, computations, and insight as enabled by the Materials Project infrastructure and computing resources. To understand and design novel electrodes for multivalent energy storage requires efficient and robust evaluation of stability, voltage, capacity, volume change, and most importantly, active ion mobility, which is the foremost bottleneck in these systems. Understanding of the structural and chemical features – extracted from calculations and benchmarked against available experimental data - which correlate with facile, selective ion diffusion will be presented and discussed. We are also devoting a large effort to understanding, screening and designing organic liquid electrolyte systems for novel energy storage systems for which the bulk solvation

structure and its impact on electrolyte performance is largely uncharted. As an example, we find that contact ion-pair interaction is prevalent in multi-valent electrolytes, even at modest concentrations which influences charge transfer, conductivity and even the stability of the electrolyte.

11:40am **IPF+MS-TuM12 Electrical Double Layer Effects on Ion Transport in Thin-Layer Solid-State Electrolytes**, ***Henry White, J. Xiong, M. Edwards***, University of Utah **INVITED**

We present finite-element modeling of Li^+ transport in solid-state electrolytes, including the role of the double layer electric fields. We developed a 1-D model that describes the mass transport and electric potential, assuming that Li^+ is the predominant charge carrier. Mass transport is described by the Nernst-Planck equation and the electric potential is described by Poisson's equation. These equations were solved in a fully coupled manner, i.e., the electric field affects the mass transport through the electromigration term in the Nernst-Planck equation, while the excess charge due to unequal ion concentrations affects the electric field as the space charge term in Poisson's equation.

We present calculated potential and concentrations distributions, as well as the contributions of migration and diffusion to the flux of each species. We present investigations of the effect of the solid-state electrolyte thickness on mass transport, varying the thickness from 10 nm to 2000 nm. The current normalized to electrolyte thickness is shown to decreases as the thickness decreases.

Thin Film
Room: 111 - Session TF+EM+MI+MS-TuM

ALD for Alternative Devices
Moderator: Paul Poodt, Solliance/TNO, Richard Vanfleet, Brigham Young University

8:00am **TF+EM+MI+MS-TuM1 FAST-ALD™ with Close Proximity (CP) Plasma for Low Temperature Applications: Nano-Composite Layer (NCL) Stacks for Flexible Substrates**, ***SangIn Lee***, Veeco **INVITED**

The stress of the film is an important factor in mechanical stability and reliability of the devices, especially flexible electronic applications and microelectro-mechanical systems (MEMS), because it causes mechanical cracks, delamination and degradation in reliability of the device. Moreover, mechanical integrity of nano-scaled devices requires not only the physical properties of the individual films such as thermal expansion coefficient and elastic modulus, but also integral structural properties such as interface adhesion, and therefore residual stress of the film need to be managed.

Veeco's proprietary ALD technology, Fast Array Scanning Technology (FAST-ALD™) with Close-Proximity (CP) Plasma, has unique characteristics that are differentiated from other spatial ALD technologies. CP-plasma in FAST-ALD™ provides very uniform radical streams onto the substrate without plasma-induced damages and substrate heating enabling FAST-ALD™ to provide plasma-ALD films and stable polymeric MLD films from CP Plasma which cannot be obtained from conventional plasma process, for high-quality films at extremely low temperature for use in stress-sensitive device applications such as low-k films on Si wafers or flexible functional films on plastic substrates.

Stresses in inorganic ALD layers can be offset by either carbon-incorporated dielectric (CID) interlayers or polymeric MLD interlayers. The relative percentage of the inorganic ALD film to CID interlayer can be changed to tailor the stress of the stacked film to the device requirements. In this experiment, the combinations of an inorganic dielectric layer (Al_2O_3) with CID interlayers as part of nano-laminates, obviously in the same philosophy with polymeric MLD interlayers, nano-composite layer (NCL) stacks were deposited at 80°C to control the stress of the stacks from tensile to compressive state and vice versa, by changing the thickness and atomic content of Al_2O_3 layer and materials. By changing the ratio of the thickness in NCL stacks, 4:2 stacked film (4 Al_2O_3 layers and 2 CID layers as a sub-stack) and 1:1 stacked film (1 Al_2O_3 layer and 1 CID layer as a sub-stack) with total 30nm thickness show very low tensile stress and compressive stress of +58MPa and -89MPa, respectively, indicating the potential application of these free standing film stacks to nano-scaled devices and/or environmentally sensitive devices. NCL stack shows higher immunity to cracks and competitive barrier properties than that of the single ALD layer. NCL concept approaches can be applied to semiconductor in low-k pore sealing and oxidation barrier in the backend-of-line (BEOL) and cutting-edge devices with flexible substrates.

8:40am **TF+EM+MI+MS-TuM3 Atmospheric Roll-to-Roll Spatial Molecular Layer Deposition for flexible barriers**, ***Fieke van den Bruele, F. Grob, P. Poodt***, Holst Centre / TNO, Netherlands

Proper encapsulation of devices such as OLEDs and thin-film photovoltaics is critical, as exposure to moisture from the ambient will degrade these devices, reducing their efficiency, lifetime, or even lead to failure altogether. Especially for OLEDs, the barrier requirements are very challenging, with a Water Vapor Transmission Rate < 10^{-6} g/m^2/day. To achieve these very low WVRTs, very high quality barrier layers are required, being pinhole free over the entire device area. Encapsulation of flexible devices is even more challenging as the encapsulation should not affect the device flexibility too much.

The recent development of roll-to-roll and large-area Spatial ALD technology has spurred the interest in ALD for encapsulation and barriers. Thin layers of inorganic material (10-20 nm) made with (spatial) ALD have sufficiently low intrinsic WVTR but often do not meet the requirements for barriers because they are very sensitive to particles and roughness that lead to defects. Thick inorganic films are less sensitive to particles, but suffer from stress and can have a limited flexibility. Various flexible thin film encapsulation techniques have been recently developed, often combining one or more thin inorganic diffusion barrier layers (e.g. SiN_x, Al_2O_3) with an organic layer that acts as stress relief layer but has no additional barrier functionality. One of those proposed interlayers for stress relief and flexibility are organic materials deposited through Molecular Layer Deposition (MLD). A well-studied example are the Alucones, prepared by reacting trimethyl aluminum with an alcohol. There are several reports on the barrier properties of Al_2O_3 – Alucone multilayer stacks, but the results seem to be inconclusive.

Assessing the flexibility these MLD layers are is not straightforward as measuring the mechanical properties of these very thin layers is difficult. We use a simple, qualitative method to test the flexibility of these MLD layers, by combining bending test with a polymer etch test to visualize cracks and other defects in the MLD film caused by bending. Preliminary results show that the flexibility of MLD layers, like their organic counterparts, largely depend on film thickness and can suffer from instability.

The next step in making MLD barriers is upscaling towards large-area and roll-to-roll production. We will present the results of our atmospheric roll-to-roll spatial MLD of alucones on polymer foils. Furthermore, an outlook to full-industrial scale R2R ALD/MLD production of barriers will be discussed.

9:00am **TF+EM+MI+MS-TuM4 Low Temperature, Temporal and Spatial Atomic Layer Deposition of TiO_2 using Titanium Tetra-Isopropoxide as Precursor**, ***Morteza Aghaee,*** Eindhoven University of Technology, Netherlands, *P.S. Maydannik,* Lappeenranta University of Technology, Finland, *P. Johansson,* Tampere University of Technology, Finland, *M. Creatore,* Eindhoven University of Technology, Netherlands, *T. Homola, D.C. Cameron,* Masaryk University, Czech Republic, *J. Kuusipalo*, Tampere University of Technology, Finland

Spatial atomic layer deposition (S-ALD) is a technique which has been shown to lead to high quality moisture barrier films (e.g. Al_2O_3) in a roll-to-roll process[1]. However, TiO_2 is expected to outperform Al_2O_3 because of its higher stability against long-term degradation than Al_2O_3. For high throughput S-ALD at low temperature, highly reactive precursors with high vapour pressure are necessary. Titanium chloride is typically used but has the disadvantages of residual chlorine incorporation in the film and generation of corrosive by-products. Titanium tetra-isopropoxide (TTIP) is a valid alternative because of its high vapour pressure at room temperature compared to other titanium organometallic compounds[2]. TTIP has not previously been used as a precursor for S-ALD.

In this work, a preliminary investigation has been carried out on the temporal ALD approach consisting of alternating exposure of a polyethylene naphthalate (PEN) substrate to the precursors TTIP and water, ozone or oxygen-fed plasma. The deposition was carried out at a substrate temperature of 80-120ºC. The highest growth rate (0.056 nm/cycle) and refractive index (2.33) values have been obtained by using an O_2- fed plasma. The water vapour transmission rates have been found to be lower than 5×10^{-4} g.m^{-2}.day^{-1} at 38°C, 90% RH conditions for a film thickness of 20 nm. For the water process, WVTR values were found to be in the range of 10^{-3} for a 40 nm film.

Based on these results, a low pressure S-ALD process was developed using a Beneq TFS200R system. Titanium dioxide films were successfully deposited by TTIP and water as S-ALD precursors in the same temperature range as temporal, and their properties were characterised in terms of growth per cycle, refractive index and chemical composition. The growth rate saturated at precursor exposure time of 230 ms at every deposition temperature, which was slightly higher than the growth rate in temporal ALD mode at the same temperature range. Similar properties (refractive

index and chemical composition) to temporal ALD have been obtained by adopting S-ALD.

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[1] P. S. Maydannik, T. O. Kääriäinen, K. Lahtinen, D. C. Cameron, M. Soderlund, P. Soininen, P. Johansson, J. Kuusipalo, L. Moro, and X. Zeng, J. Vac. Sci. Technol. A **32**, 051603 (2014).

[2] M. Aghaee, P. S. Maydannik, P. Johansson, J. Kuusipalo, T. Homola, M. Creatore, D. C. Cameron, Submitted to J. Vac. Sci. Technol. (2015)

9:20am **TF+EM+MI+MS-TuM5 Spatial Atomic Layer Deposition into Flexible Porous Substrates**, ***Kashish Sharma,*** University of Colorado at Boulder, *D. Routkevitic, N. Varaksa,* In Redox, *S.M. George*, University of Colorado at Boulder

Spatial atomic layer deposition (S-ALD) is important for ALD commercialization. S-ALD has been successfully demonstrated on flat substrates. In this work, S-ALD was examined on flexible porous substrates using anodic aluminum oxide (AAO) membranes and Li ion battery electrodes. The AAO membranes were coated with ZnO ALD using diethylzinc and ozone as the reactants. The Li ion battery electrodes were coated with Al O ALD using trimethylaluminum and ozone as the reactants. These experiments utilized a rotating cylinder reactor for S-ALD that is scalable to roll-to-roll operation [K. Sharma et al., , 01A132 (2015)].

ZnO S-ALD into the pores of AAO membranes depends on gas transport that is determined by the pore diameter, pore aspect ratio and reactant pulse duration. The reactant pulse duration is defined by the substrate speed in S-ALD. Different reaction conditions and AAO membrane characteristics were explored using energy dispersive spectroscopy (EDS) to measure the Zn coverage profiles. Substrate speeds were defined by rotating cylinder rates of 10, 100 and 200 revolutions per minute (RPM). The AAO pore diameters were 50, 100 and 150 nm.

For AAO pore lengths of 10 microns, the EDS analysis revealed that uniform Zn coverage profiles were obtained at 10 RPM. The Zn coverage profiles were less uniform at higher RPM values and smaller pore diameters. These results indicate that S-ALD into porous substrates is feasible. However, the uniformity of the ALD coverage will depend on reaction parameters and the characteristics of the porous substrate. In addition, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ Li ion battery electrodes on flexible metal foil were coated with Al_2O_3 ALD using the S-ALD reactor at 10-100 RPM. Initial coin-cell testing has demonstrated that enhanced capacity stability of these cathode electrodes is obtained after 2-5 Al_2O_3 ALD cycles.

9:40am **TF+EM+MI+MS-TuM6 Accurate Precursor and Reactant Delivery for Quantitative Atomic Layer Deposition**, ***Masafumi Kitano,*** Stanford University, *M. Nagase, N. Ikeda,* Fujikin Incorporated, Japan, *P.C. McIntyre*, Stanford University

Atomic layer deposition (ALD) has been widely discussed in the literature from various points of view. Typically, the amount of the precursor and reactant supplied into the ALD chamber is dictated only by controlling valve operation time, and is not quantitatively defined. To achieve a more quantitative ALD process, we have developed new flow rate control system (FCS) which can accurately dose precursor and reactant into an ALD reactor. This FCS consists of an orifice plate, pressure sensor, thermal sensor, and piezo control valve. It can be heated to 250˚C to achieve sufficient vapor pressure for most precursors used in ALD of various inorganic compounds and elements. The FCS controls the flow rate under critical expansion conditions (or choked flow conditions); the flow rate through the orifice is proportional only to the upstream pressure of the orifice.[1,2] The piezo control valve accurately controls the upstream pressure and, thus, the flow rate. This mode of operation makes it possible to control the dosing of precursor and reactant by simply operating an endpoint valve placed close to the ALD reactor, because the upstream pressure is controllable whether the gas flow is running or not.

We have demonstrated an ALD process with trimethylaluminum (TMA) and water vapor (H_2O) reaction for Al_2O_3 deposition using the FCS to accurately control dosing into the ALD reactor. Excellent uniformity and reproducibility of deposition, and high quality dielectric properties of the resulting Al_2O_3 films have been achieved. The critical doses of TMA and H_2O into the chamber have been found to achieve surface saturating ALD of Al_2O_3 on a silicon substrate.

[1] A. Guthrie, R. K. Wakerling, "Vacuum Equipment and Techniques" McGraw-Hill book company, Inc., pp17, (1949)

[2] R. H. Perry, D. Green, "Perry's Chemical Engineers' Handbook, Sixth Edition" McGraw-Hill Co., pp5-14, (1984)

11:00am **TF+EM+MI+MS-TuM10 ALD for Capacitor Technologies**, ***Ramakrishnan Rajagopalan,*** *C. Randall*, The Pennsylvania State University **INVITED**

Atomic layer deposition (ALD) is a powerful processing technique that can be used to modify interfacial processes occuring in electrochemical capacitors. Charge storage mechanism in electrochemical capacitors is either due to electrostatic double layer formation or pseudocapacitive faradaic interactions at electrode/electrolyte interfaces. The talk will present an overview of our efforts in developing pseudocapacitive vanadium oxide thin films using ALD approach on high surface area carbon electrodes. The deposition process is dependent upon the carbon properties such as surface functionalization and porosity. We will report our investigation of deposition of ALD films on nanostructured carbon electrodes with controlled porosity in mesopores (<20 nm) to ultramicropore (0.8 nm to 2 nm) ranges. ALD also facilitates the possibility of combining electrochemical effects with dielectric effects. ALD of dielectrics such as Al_2O_3 on electrodes used in aqueous, organic and lithium based electrolytes can mitigate the issues relating to electrochemical stability due to solvent decomposition reactions and leakage performance with limited effect on the ESR performance of the capacitor. There is also possibility of designing novel solid state capacitor structures that synergistically integrates the electrical double layer interactions due to ions with dielectric energy storage.

11:40am **TF+EM+MI+MS-TuM12 Compositionally and Functionally Graded Hybrid Layer for High-Performance Adhesion**, ***Yichuan Ding,*** *R.H. Dauskardt*, Stanford University

Reliable bonding of organic/inorganic interfaces continues to be one of the most important challenges in multilayer devices including microelectronic, photovoltaic and display technologies. Hybrid molecular materials which contains both organic and inorganic components has been shown to be well suited for bonding organic/inorganic (metals, metal-oxides, nitrides, …) interface, mitigating moisture degradation and even stress migration. The hybrid films (less than 100nm) made of two primary precursors, an epoxysilane and a zirconium alkoxide, have been deposited via solution based synthesis, with low cost and high throughput. By optimizing sol-gel chemistry and processing conditions, we achieved an impressive tenfold improvement in interfacial adhesion at the epoxy/Si substrate interface, and have proven the suppression of moisture degradation at the interface.

In this work, we emphasized on our newly developed spray deposition technique with more versatility and better suited to large-scale manufacturing. We utilized both bilayer coating and dual-sources spray strategies to create highly compositionally and functionally graded hybrid film compared with films achieved via traditional dip-coating. XPS depth profiling shows highly graded hybrid films with independent compositional control within 80nm can be achieved via spray coating in the dry regime. We took advantage of the compositional control brought by spray coating to unravel the structure-property relationships in the multi-functional hybrid films by varying components/parameters to fine tune the molecular structure of the resulting film and relate that to its properties obtained from our advanced thin-film mechanical testing techniques together with other chemical characterization techniques (XPS, FTIR, NMR and GCMS). The evolution of the hybrid molecular network during film process and how molecular level details of the hybrid film has a large effect on its mechanical properties were better understood.

IPF on Mesoscale Science and Technology of Materials and Metamaterials
Room: 210F - Session IPF+MS-TuA

Frontiers in Physics
Moderator: Jim Hollenhorst, Agilent, Cathy O'Riordan, AIP

2:20pm **IPF+MS-TuA1 Giving New Life to Materials for Energy, the Environment and Medicine**, ***Angela Belcher***, MIT Koch Institute for Integrative Cancer Research **INVITED**

Organisms have been making exquisite inorganic materials for over 500 million years. Although these materials have many desired physical properties such as strength, regularity, and environmental benign processing, the types of materials that organisms have evolved to work with are limited. However, there are many properties of living systems that could be potentially harnessed by researchers to make advanced technologies that are smarter, more adaptable, and that are synthesized to be compatible with the environment. One approach to designing future technologies which have some of the properties that living organisms use so well, is to evolve organisms to work with a more diverse set of building blocks. The goal is to have a DNA sequence that codes for the synthesis and assembly of any inorganic material or device. We have been successful in using evolutionarily selected peptides to control physical properties of nanocrystals and subsequently use molecular recognition and self-assembly to design biological hybrid multidimensional materials. These materials could be designed to address many scientific and technological problems in electronics, military, medicine, and energy applications. Currently we are using this technology to design new methods for building batteries, fuel cells, solar cells, carbon sequestration and storage, enhanced oil recovery, catalysis, and medical diagnostics and imaging. This talk will address conditions under which organisms first evolved to make materials and scientific approaches to move beyond naturally evolved materials to genetically imprint advanced technologies with examples in lithium ion batteries, lithium-air batteries, dye-sensitized solar cells, and ovarian cancer imaging.

3:00pm **IPF+MS-TuA3 XFEL Movies of Molecular Machines at Work**, ***John Spence***, Arizona State University **INVITED**

With about 1E12 coherent hard X-ray photons per shot of 10 fs duration at 120 Hz, the invention of the X-ray laser (XFEL) has provided many new research opportunities for stuctural biology, which I will review. Our first discovery, that these pulse are so brief that they outrun radiation damage, so that damage-free diffraction patterns at atomic resolution and femtosecond time resolution can be recorded to make movies of protein function, has proved immensely fruitful. Other advances in solution scattering, analysis of protein nano crystals, and imaging of single particles which cannot easily be crystallized, such as viruses, wll be also be reviewed. This work forms part of the activity of the NSF's BioXFEL STC, a consortium of seven US campuses devoted to the use of XFELs for Biology. (http://www.bioxfel.org).

4:20pm **IPF+MS-TuA7 Frontiers of Ocean Sensing**, ***Susan K. Avery***, Woods Hole Oceanographic Institution **INVITED**

The ocean accounts for more than two-thirds of Earth's surface and is our planet's largest biome, yet remains largely unexplored. Because seawater is opaque to most wavelengths of electromagnetic radiation, all but a few centimeters of the upper ocean are invisible to satellites. As a result, only about 5 to 15 percent of the seafloor is mapped in any detail and much of the water column has not been explored. Many of the transient phenomena that occur on, in, or above the ocean—and across a wide range of spatial and temporal scales—have been extremely difficult to capture, and even more difficult to monitor over long periods. New technologies and new adaptations of existing technologies, however, are opening the ocean in all its complexity to researchers at sea and on shore. Our challenge now is to take advantage of these innovations in sensing and observing, not only to fully grasp the role that the ocean plays in making Earth habitable, but also how it fits into planetary and societal changes that are taking place before our very eyes.

5:00pm **IPF+MS-TuA9 New States of Electronic Matter and their Potential for Science and Computation**, ***Joel Moore***, University California, Berkeley **INVITED**

A major development in solid-state physics over the past decade is the discovery of several new classes of electronic materials that combine features of metals and semiconductors in novel and potentially useful ways. "Topological insulators" are materials that insulate in bulk but have atomically thin conducting layers at their surfaces as a subtle consequence of spin-orbit coupling. "Weyl" and "Dirac" semimetals are three-dimensional materials that realize two different 3D generalizations of the massless electronic structure of graphene, a single layer of carbon atoms, whose discovery was recognized by the 2010 Nobel Prize. We explain the origin of these materials and how they might enable dissipationless electrical conduction and superconducting states with fractional "Majorana" particles.

5:40pm **IPF+MS-TuA11 The Universe in Motion: Listening to Gravitational Waves with LIGO**, ***Michael Zucker***, Massachusetts Institute of Technology **INVITED**

Almost 100 years ago, Einstein showed that traces of matter and energy's gyrations are continuously broadcast throughout the universe, in the form of *gravitational waves:* ripples in the underlying geometry of space. Fresh from a major upgrade, the Laser Interferometer Gravitational-wave Observatory (LIGO) is now poised to detect and decode these broadcasts, opening a new era of physics and astronomy. I will talk about why LIGO is so different from other observatories, and describe some of the daunting technological challenges we've overcome to help us realize Einstein's vision.

Manufacturing Science and Technology
Room: 114 - Session MS-TuA

Working with National Labs and User Facilities
Moderator: Charles Eddy, Jr., U.S. Naval Research Laboratory, Bridget Rogers, Vanderbilt University

2:40pm **MS-TuA2 Research Opportunities at the Cornell Nanoscale Science and Technology Facility, a member of the National Nanotechnology Coordinated Infrastructure.**, ***Michael Skvarla***, *D. Ralph*, Cornell NanoScale Science and Technology Facility

The Cornell Nanoscale Science and Technology Facility (CNF) is one of a network of open-access shared facilities partially subsidized by the US National Science Foundation to provide researchers with rapid, affordable, shared access to advanced nanofabrication tools and associated expertise. Projects can be accomplished either hands-on or remotely. Hundreds of engineers and scientists nationwide, from academia, industry, and government, utilize CNF to make structures and systems from the nanometer to the centimeter scale. CNF offers unique capabilities in world-leading electron-beam lithography, advanced stepper photolithography, soft lithography, and rapid prototype development, along with the ability to deposit, grow, and etch a very wide variety of materials. CNF's technical staff are dedicated full-time to user support, providing one-on-one help with process development, training, and troubleshooting. They can offer expertise for a wide range of fabrication projects, including not just electronics but also nanophotonics, magnetics, MEMS, thermal and energy systems, electrochemical devices, fluidics, and the life sciences. More than 30% of CNF's users come from biology/bioengineering fields. All users are welcome; no experience in nanofabrication is necessary and a central part of CNF's mission is to assist users from "non-traditional" fields seeking nanofabrication techniques for the first time. CNF's user program is designed to provide the most rapid possible access (typically 2 weeks from first contact) with the lowest possible barriers to entry (users retain full control of their IP, with no entanglement by CNF or Cornell University). More than 85% of CNF's external academic users come from institutions with their own local cleanroom facilities, but still they utilize CNF for advanced capabilities, staff expertise, or tool reliability not available locally.

This talk will explore the tools, services and advice available to CNF users, and show examples of ongoing work. We will also provide the latest details on the National Nanotechnology Coordinated Infrastructure (NNCI) program, a new NSF-sponsored network of shared facilities similar to CNF that is in the process of being organized at abstract submission.

We invite you to explore the CNF and NNCI and discuss ways we can help bring your research visions to fruition. CNF's User Program Managers will at no cost provide detailed processing advice and cost estimates for potential new projects. The CNF technical staff also meets every Wednesday afternoon for conference calls where we welcome questions about any topic related to nanofabrication. Visit cnf.cornell.edu to contact us and get started.

3:00pm **MS-TuA3 The CNST NanoFab at NIST is Open for Business**, ***Vincent Luciani***, NIST Center for Nanoscale Science and Technology

The NIST Center for Nanoscale Science and Technology (CNST) supports the U.S. nanotechnology enterprise from discovery to production. As part of the CNST, the shared-use NanoFab provides its users rapid access to a comprehensive suite of tools and processes for nanoscale fabrication and measurement. The CNST NanoFab at NIST is part of the Department of Commerce and therefore puts a high priority on operating a business friendly, easily accessible facility. The same rates are applied to all users, whether from industry, academia or a CNST colleague down the hall. Applications are accepted at any time and are reviewed and processed every week. Also, NIST does not claim any inherent rights to inventions made in the course of a NanoFab project. The NanoFab features a large, dedicated facility, with tools operated within a class 100, 8,000 square foot (750 m^2) cleanroom or in adjacent laboratories that have superior air quality along with temperature humidity, and vibration control. Over 80 major process tools are available, including but not limited to e-beam lithography, 5x reduction stepper photolithography, nano-imprint lithography, laser writing for mask generation, scanning and transmission electron microscopy, metal deposition, plasma etching, chemical vapor deposition, atomic layer deposition, deep silicon etching and ion beam etching. The NanoFab staff consists of scientists, engineers and technicians that specialize in all areas of nanofabrication and provide training and ongoing technical assistance to users. Our goal is to be a catalyst to our user's success and to help nurture nanotechnology commerce in the Unites States. Project applications and instructions are easily available on the web. Users inside NIST and from all around the country are provided on-line access to tool schedules and the tool reservation system. From physicists, engineers and biologists to medical researchers, users find common ground at the nanoscale in the CNST NanoFab.

3:20pm **MS-TuA4 The Molecular Foundry: A Knowledge-Based User Facility for Nanoscale Science**, ***Branden Brough***, The Molecular Foundry, Berkeley Lab

The Molecular Foundry, a nanoscience research center at Lawrence Berkeley National Laboratory provides communities of users with access to expert staff and leading-edge instrumentation to enable research on the nanoscale in a multidisciplinary, collaborative environment. Selected through an external peer-reviewed proposal process, users come from academic, industrial or national laboratories, both domestic and international, free of charge. Located in the Bay Area's active academic environment and near Silicon Valley, research is organized into seven closely coupled facilities: Inorganic, Organic, and Biological facilities for synthesis, preparation, and assembly; Nanofabrication, for processing and integration; the National Center for Electron Microscopy and Imaging and Manipulation, for characterization; and Theory, for understanding and predicting material properties. In summarizing the Foundry program, a selection of recent results will be highlighted such as those using automated high-throughput synthesis of nanocrystals, 2d materials, metal-organic frameworks, and sequence-specific polymers; aberration-corrected electron microscopy and electron tomography of individual proteins; 20 nm resolution optical spectroscopy; synthesis and simulations of nano-hybrid thermoelectrics and electrode-electrolyte interfaces; and interfaces between inorganic nanoscale building blocks with living cells.

The Molecular Foundry is supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

4:40pm **MS-TuA8 User Opportunities at the Center for Nanoscale Materials: From Hybrid Nanomaterials to Tailoring Nanoscale Interactions**, ***Kathleen Carrado Gregar***, Center for Nanoscale Materials at Argonne National Laboratory

The mission of the Center for Nanoscale Materials (CNM) user facility at Argonne National Laboratory is to provide expertise, instrumentation, and infrastructure for interdisciplinary nanoscience and nanotechnology research by scientists and engineers from academia, industry, and government agencies. The Center's goal is to support and explore ways to create functional hybrid nanomaterials and to tailor nanoscale interactions for energy-related research and development programs. The CNM addresses grand challenges in energy and information conversion and transport, while furthering the Department of Energy (DOE) missions in energy generation, storage, and efficiency. Unique capabilities at CNM include a large clean room, expansive synthesis and nanofabrication resources, a hard x-ray nanoprobe at the Advanced Photon Source synchrotron, myriad scanning probes including low temperature, ultrahigh vacuum STMs, TEMs with in situ holders and chromatic aberration-correction, a 30 TFlop supercomputer, oxide MBE, and ultrafast optical probes. Another CNM asset includes outstanding staff with expertise in nanocrystal and nanoparticle synthesis, complex metal oxides, nanophotonics, plasmonics, scanning probe microscopy, nanofabrication, functional bio-inorganic hybrid nanomaterials, and theory, simulation and modeling. Core technological materials range from photocatalysts to graphene to nanocrystalline diamond. All of these capabilities and expertise are available to the international research community through peer-reviewed user proposals; access is free of charge for allocated non-proprietary research in the public domain. CNM is one of DOE's premier Nanoscale Science Research Centers serving as the basis for a national program encompassing new science, new tools, and new computing capabilities for research at the nanoscale (https://nsrcportal.sandia.gov). Recent staff and user research highlights will be presented, painting a picture of present and future nanoscience and nanotechnology at the CNM (www.anl.gov/cnm).

The Center for Nanoscale Materials, an Office of Science user facility, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract no. DE-AC-02-06CH11357.

5:00pm **MS-TuA9 Using EMSL Capabilities to Advance Your Research**, ***Donald Baer***, *M. Engelhard*, Pacific Northwest National Laboratory

EMSL, the Environmental Molecular Sciences Laboratory, is a Department of Energy user facility. EMSL's vision is to pioneer discoveries and effectively mobilize the scientific community to provide the molecular science foundation for the DOE Office of Biological and Environmental Research research priorities and our nation's critical biological, environmental and energy challenges. To accomplish this vision, EMSL science is focused in four areas: biosystem dynamics and design, atmospheric aerosol systems, terrestrial and subsurface ecosystems and energy materials and processes. Processes that occur at surfaces and interfaces are critical in each of these areas and EMSL provides a wide range of unique and state-of-the-art spectroscopy, microscopy, magnetic resonance and computational capabilities to advance the relevant sciences (www.emsl.pnnl.gov).

Scientific discovery and technological innovation in environmental molecular sciences are facilitate by EMSL's integrated set of experimental and computational resources. Researchers are invited to apply for the opportunity to collaborate with recognized experts and use state-of-the-art instruments and facilities. Researchers use resources at EMSL for little or not cost if results are shared in open literature. The primary mode for obtaining access to EMSL is through an annual call for proposals oriented around specific topics identified with each science theme. This call appears in late December, Four-page proposals are due in March. As a multi-capability facility, we seek proposal that combine scientific innovation through instrument integration combining computational and experimental approaches for discovery. Increasingly we are developing and using capabilities that enable real-time *in situ* measurements in a variety of environments.

5:20pm **MS-TuA10 From Neutron Nanoscience to Direct-write Nanofabrication at the Center for Nanophase Materials Sciences**, ***Olga Ovchinnikova***, Oak Ridge National Laboratory

The Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL) is a multidisciplinary user facility that provides the research community with access to expertise and equipment to address the most challenging issues in nanoscience. Industrial, government and academic researchers from around the world may access capabilities in functional imaging, atom-precise synthesis, and nanofabrication. The CNMS is a leader in a range of advanced nanofabrication techniques including electron beam assisted deposition on the sub-10 nm level using both gas and liquid precursors as feedstock material, 3D fabrication and atomically precise material sculpting, as well as direct matter manipulation on the atomic level by electron beams to induce material functionality. Spatially resolved quantitative measurements of physical and chemical properties of materials are available to users through unique measurement capabilities of band excitation scanning probe microscopy, scanning transmission electron microscopy, helium ion microscopy, and atom probe tomography. Furthermore, theoretical and computational approaches are available to CNMS users, as frameworks for deep-data analytics methods for imaging, and computational prediction of functional and physical properties in nanostructures, benefiting from the broad ORNL computational capabilities. Located adjacent to the Spallation Neutron Source at ORNL, CNMS acts as a gateway for the nanoscience community to ORNL's world-class neutron science facilities, by providing diverse

complementary capabilities such as selective deuteration, sample environments for multi-modal measurements, fabrication of templates for neutron reflectivity experiments, and many other materials science capabilities to complement neutron results. As one of the five Department of Energy Nanoscale Science Research Centers (see nsrcportal.sandia.gov), CNMS makes all of these capabilities, and the staff expertise to fully benefit from them, available free of charge to users who intend to publish the results, or at-cost for proprietary research, as described at cnms.ornl.gov. [The CNMS at Oak Ridge National Laboratory is a DOE Office of Science User Facility.]

Manufacturing Science and Technology
Room: Hall 3 - Session MS-TuP

Aspects of Manufacturing Science and Technology
Poster Session

MS-TuP1 Development of Graphene/Al Composite Materials with High Strength, ***Yusuke Oguro***, *A. Matsumuro*, Aichi Institute of Technology, Japan

Graphene shows many extraordinary properties. It is conducts heat and electricity with great efficiency and is nearly transparent. Furthermore it has the surprisingly mechanical properties with tensile strength of 100 times stronger than steel by weight and Young's modulus with 1 TPa. Now the field of the electronic device is studied energetically. But, studies are hardly investigated in the field of the application to new composite materials. The properties show superior high specific strength. We are convinced that they greatly contribute to develop the innovative materials and overcome environmental problem.

In this study, we focused on graphene/Al composite bulk materials. As graphene materials, we used nanographene with a several layers due to large quantity production and very cheap. Firstly we investigated the method of synthesis of monolayer nanographene sheet by our original ultrasonic vibration method in order to utilize original high strength characteristics of monolayer graphene sheet. We must also prevent from aggregation of graphene sheets in composite materials because the aggregation parts would surely cause a loss of strength of the materials. In order to disperse graphene around Al powders with average diameter of Al about 100 nm, the same ultrasonic vibration method was applied with isopropyl alcohol as a solvent before sintering composite materials . The powder before press sintering was prepared to dry in a furnace at about 340 K for 40 minutes. The composite materials with uniform dispersion of graphene were fabricated by with piston-cylinder type press apparatus under the condition of the applied pressure of 1 GPa and the temperature of 723 K for 4 hours in Ar gas atmosphere. We investigated the optimal condition of the composite materials as changing dispersion time by ultrasonic vibration from 1 to 6 hours. And we also investigated the optimal condition of the composite materials as changing composition rates from 0 to 3.0 wt.%graphene.

In our results, all composite materials sintered showed uniform bulk materials without aggregation of graphene. X-ray diffraction showed no metallic compounds between Al and nanographene. The densities of composite materials decreased down to 2.43 g/cm^3 of 3.0 wt.%graphene. Vickers hardness of the composite material at 1.0 wt.%graphene showed the maximum value of 308 Hv, and the density was 2.46 g/cm^3. So, the specific strength increased up to 396 kN・m/kg. It is about 1.4 times bigger than that of Al material. Therefore, graphene/Al composite materials give us dreams of development for innovative materials.

Additive Manufacturing/3D Printing Focus Topic
Room: 211B - Session AM+EM+MS+TF-WeM

Materials, Designs, and Applications of Additive Manufacturing

Moderator: Erik B. Svedberg, The National Academies

8:00am **AM+EM+MS+TF-WeM1 An Overview of Additive Manufacturing**, ***Ed Morris***, *R. Gorham*, NCDMM **INVITED**

"An Overview of Additive Manufacturing" - Additive manufacturing, also called 3D printing, has captured worldwide attention. Many believe that it is introducing the next industrial revolution because of its impact on product innovation and its unique manufacturing capabilities. America Makes – National Additive Manufacturing Innovation Institute is the first Manufacturing Innovation Institute established as part of a National Network for Manufacturing Innovation. Mr. Ed Morris, Director of America Makes and Vice President, National Center for Defense Manufacturing and Machining, will give an overview of additive manufacturing, and will discuss America Makes' actions to accelerate the use of additive manufacturing technologies in the United States and increase our nation's global manufacturing competitiveness.

8:40am **AM+EM+MS+TF-WeM3 Material Considerations and Opportunities for Laser Powder Bed Additive Manufacturing**, ***Michael W. Peretti***, *D.H. Abbott*, General Electric Aviation **INVITED**

Additive Manufacturing (AM) has the potential to be a significant supply chain disruptor over traditional means for manufacturing a broad range of components for aerospace and other demanding applications. The ability to unlock complex, high-performance designs while reducing part count and number of manufacturing steps is beginning to revolutionize the way we think about making things. One of the key areas of development to further expansion of opportunities for AM is the production and supply of high-quality raw materials. This presentation discusses the critical issues for AM input raw materials, with particular emphasis on metal powder input stock for laser powder bed AM processes. Some background and experience from GE Aviation's development of the LEAP fuel nozzle will be shared, along with comments on the direction that the AM industry could take and the role of and potential for AM-specific metal powder alloys.

9:20am **AM+EM+MS+TF-WeM5 High Quality and High Speed EBM 3D Printing by the Integration of High Performance Electron Sources**, ***Colin Ribton***, TWI Ltd., UK, *S. del Pozo*, TWI Ltd. and Brunel University, UK

Production of high integrity components must use smart manufacturing methods to be efficient in use of scarce materials and other resources, and must ensure its environmental impact is minimized. Advanced manufacturing techniques, such as metal powder bed 3D printing , can be carried out by selective laser melting (SLM) or electron beam melting (EBM). In both cases the component is built layer by layer, with a beam as an intense energy source drawing each layer by melting powder. EBM is significantly faster than SLM and has been used to create metal parts in large quantities over the past 5 years. EBM machines have produced many tens of thousands of orthopedic implants. There are a number of key benefits in employing this manufacturing technology – including 'complexity for free', efficient use of material and flexibility of design. Increasingly, the aerospace industry is investigating the use of EBM for the manufacture of aircraft components and aero engine parts. However, the size of many of these components presents challenges to the EBM process in production rate and quality consistency over long build times (i.e. 150 hours).

The aim of this work is to overcome key obstacles concerning future requirements for EBM 3D printing for production of aerospace parts through the integration of two enabling technologies. The work will develop and integrate a novel plasma cathode electron source with an EBM machine focusing on realizing the enhanced capabilities of low maintenance, consistent manufacturing performance and higher productivity. Also, development and integration of an array probe device will provide quantified quality assurance of machine manufacturing readiness. The key research challenges will be the design of the electron source and optics and the development of new build procedures making best use of the new source.

The equipment will enable the wider adoption of EBM leading to efficient use of materials – particularly strategic titanium alloys and nickel based super alloys at first.

9:40am **AM+EM+MS+TF-WeM6 Laser Induced Forward Transfer of High-Viscosity, Polymer-Based VO_2 Inks**, ***Eric Breckenfeld***, *H. Kim, T. Sutto, N. Charipar, A. Piqué*, Naval Research Laboratory

Additive manufacturing direct-write processes such as direct-write assembly, micropen, inkjet, and laser-induced forward transfer (LIFT) have become increasingly popular as interest in printable electronics and maskless patterning has grown. Compared to conventional lithography, these additive manufacturing processes are inexpensive, environmentally friendly, and well suited for rapid prototyping and large-area applications. At the same time, researchers have pursued various chemical solution deposition processes for combining additive manufacturing technology with functional electronic materials. Among a multitude of transition-metal oxides, vanadium dioxide (VO_2) has emerged as a material of particular interest due to its sharp semiconductor-to-metal phase transition near room temperature. A set of distinct optical and electronic properties which arise as a result of this transition have made VO_2 popular for thermochromic coatings, resistive switching, optical storage, light modulators, and other applications. Here, we demonstrate the development of a polymer-based solution for the deposition of VO_2 thin films. By exploring a variety of sintering and annealing conditions as well as exploring different polar solvents, we have optimized the growth of these films on glass and crystalline substrates. We go on to explore printing of VO_2 devices via the LIFT technique, which is notable for its ability to print high-viscosity inks and pastes. Finally, we will discuss our efforts toward the development of low temperature laser sintering in order to realize VO_2 films on substrates incompatible with high furnace temperatures.

11:40am **AM+EM+MS+TF-WeM12 Printing Multi-Functionality using Additive Manufacturing**, ***Ryan Wicker***, University of Texas at El Paso **INVITED**

Since the commercial introduction of Additive Manufacturing (AM) technologies more than two decades ago, considerable advancements in processing speed, accuracy, resolution and capacity have been achieved and the available AM materials have expanded considerably, enabling customized end-use products to be directly manufactured for a wide range of applications. Many AM technologies have been released that use different processes for fabricating the individual layers from a variety of liquid, solid, and powder-based materials ranging from photoreactive polymers to metals. In 2000, the University of Texas at El Paso identified AM as an emerging technology and invested strategically in establishing the W.M. Keck Center for 3D Innovation (Keck Center). The Keck Center has grown to occupy over 13,000 sq. feet with more than 50 commercial and experimental AM machines, representing 10 system manufacturers, nine distinct layer processing methods, and several custom AM-based patented and patent-pending systems. One particular focus of Keck Center research is on developing the methods and systems required to have automated control over material placement and structure creation, leading to, for example, the realization of complex 3D devices that integrate electronics and thus intelligence within mechanical structures as well as 3D spatially complex bioactive, implantable, tissue engineered constructs. There are myriad issues associated with combining multiple materials to create functional products – from the deposition and processing of different materials to the combined performance of the materials in the resulting product. Despite these issues, the opportunities for AM in aerospace, defense, biomedical, energy and enumerable other applications continue to expand as the achievable length scales in AM decrease, the number of materials available for use in AM increases, the performance of these materials are characterized and controlled in the final product, and new strategies for integrating AM with other manufacturing technologies are successfully demonstrated.

Electronic Materials and Processing
Room: 211C - Session EM+AS+MS+SS-WeA

Surface and Interface Challenges in Wide Bandgap Materials

Moderator: Aubrey Hanbicki, U.S. Naval Research Laboratory, Rachael Myers-Ward, U.S. Naval Research Laboratory

2:20pm **EM+AS+MS+SS-WeA1 Effects of Nitrogen and Antimony Impurities at SiO_2/SiC Interfaces**, ***Patricia Mooney***, Simon Fraser University, Canada **INVITED**

4H-SiC is an attractive material for devices operating at high power and high temperatures because of the large bandgap energy, 3.23 eV, the high critical breakdown field, 2.0 $MVcm^{-1}$, and high electron mobility,

850 $cm^2V^{-1}s^{-1}$. Commercialization of 4H-SiC MOSFET technology was long delayed due to the high density of defects near the SiO_2/SiC interface. Post oxidation annealing in NO ambient, the process that enabled the commercialization of SiC Power ICs in 2011, significantly reduces the density of near-interface traps and results in typical effective MOSFET channel electron mobility (μ_{FE}) values of ~20 $cm^2V^{-1}s^{-1}$ [1]. The relatively high density of near-interface traps having energy levels within 0.5 eV of the SiC conduction band was investigated using constant capacitance transient spectroscopy (CCDLTS). These measurements showed that NO annealing reduced the density of the two near-interface oxide trap distributions, attributed to Si interstitials and substitutional C pairs in SiO_2, by as much as a factor of 10 [1,2].

It has also been shown that introducing impurities such as Na, P, or Sb near the SiO_2/SiC interface further increases μ_{FE}, to peak values of 104 $cm^2V^{-1}s^{-1}$ and to 50 $cm^2V^{-1}s^{-1}$ at high electric field for Sb [3]. The much higher value of μ_{FE} in Sb-implanted MOSFETs was attributed to counter-doping by Sb in SiC near the interface. To investigate the effects of Sb at SiO_2/SiC interfaces, Sb ions were implanted near the surface of the 4H-SiC epitaxial layer and the wafer was annealed at 1550℃ in Ar to activate the Sb donors. Dry thermal oxidation was done at 1150℃ and the sample was then NO-annealed at 1175℃ for 30 or 120 min. CCDLTS results of Sb-implanted MOS capacitors were compared with those having no Sb implant but with similar dry oxidation and NO-annealing processes. The density of near-interface oxide traps was similar in samples with and without Sb, indicating that Sb has little effect on those defects. However, CCDLTS spectra taken at bias and filling pulse conditions that reveal defects in the SiC depletion region, show both the deeper of the two N donor levels at E_C - (0.10±0.01) eV and a second energy level only in Sb-implanted samples at E_C - (0.12±0.01) eV. To our knowledge this is the first measurement of Sb donors in SiC and it confirms counter doping of SiC by Sb near the SiO_2/SiC interface.

[1] P.M. Mooney and A.F. Basile, in *Micro and Nano-Electronics: Emerging Device Challenges and Solutions*, Ed. T. Brozek (CRC Press, Taylor and Francis, 2014) p. 51.

[2] A.F. Basile, et al., J. Appl. Phys. **109**, 064514 (2011).

[3] A. Modic, et al., IEEE Electron Device Lett. **35**, 894 (2014).

3:00pm **EM+AS+MS+SS-WeA3 Hydrogen Desorption from 6H-SiC (0001) Surfaces**, ***Sean King***, Intel Corporation, *R. Nemanich, R. Davis*, North Carolina State University

Due to the extreme chemical inertness of silicon carbide (SiC), *in-situ* thermal desorption is commonly utilized as a means to remove surface contamination prior to initiating critical semiconductor processing steps such as epitaxy, gate dielectric formation, and contact metallization. *In-situ* thermal desorption and silicon sublimation has also recently become a popular method for epitaxial growth of mono and few layer graphene. Accordingly, numerous thermal desorption experiments of various processed silicon carbide surfaces have been performed, but have ignored the presence of hydrogen which is ubiquitous throughout semiconductor processing. In this regard, we have performed a combined temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS) investigation of the desorption of molecular hydrogen (H_2) and various other oxygen, carbon, and fluorine related species from *ex-situ* aqueous hydrogen fluoride (HF) and *in-situ* thermal and remote hydrogen plasma cleaned 6H-SiC (0001) surfaces. Using XPS, we observed that temperatures on the order of 700 - 1000°C are needed to fully desorb C-H, C-O and Si-O species from these surfaces. However, using TPD, we observed H_2 desorption at both lower temperatures (200 – 550°C) as well as higher temperatures (> 700°C). The low temperature H_2 desorption was deconvoluted into multiple desorption states that, based on similarities to H_2 desorption from Si (111), were attributed to silicon mono, di, and trihydride surface species as well as hydrogen trapped by sub-surface defects, steps or dopants. The higher temperature H_2 desorption was similarly attributed to H_2 evolved from surface O-H groups at ~ 750°C as well as the liberation of H_2 during Si-O desorption at temperatures > 800°C. These results indicate that while *ex-situ* aqueous HF processed 6H-SiC (0001) surfaces annealed at < 700°C remain terminated by some surface C-O and Si-O bonding, they may still exhibit significant chemical reactivity due to the creation of surface dangling bonds resulting from H_2 desorption due from previously undetected silicon hydride and surface hydroxide species.

3:20pm **EM+AS+MS+SS-WeA4 Chemical and Microstructural Characterization of Interfaces between Metal Contacts and β-Ga_2O_3**, ***Lisa M. Porter***, *Y. Yao, J.A. Rokholt, R.F. Davis,* Carnegie Mellon University, *G.S. Tompa, N.M. Sbrockey, T. Salagaj*, Structured Materials Industries, Inc.

β-Ga_2O_3 is a promising alternative to traditional wide bandgap semiconductors, as it has a wider bandgap (~4.9 eV) and a superior figure-of-merit for power electronics and other devices; moreover, β-Ga_2O_3 bulk single crystals have recently been grown commercially using melt-growth methods. While several groups have demonstrated Ga_2O_3-based devices such as Schottky diodes and MOSFETs, understanding of contacts to this material is limited. In this study, we investigated a variety of metal contacts (Ti, In, Mo, W, Ag, Au, and Sn) to both (-201) β-Ga_2O_3 single crystal substrates (from Tamura Corp.) and β-Ga_2O_3 epitaxial layers grown by MOCVD on various substrates (sapphire and single crystal β-Ga_2O_3) by co-authors at Structured Materials Industries. We have characterized these substrates and epilayers using techniques such as X-ray diffraction and transmission electron microscopy (TEM), which show that the epitaxial layers are oriented (-201) with respect to the substrates. We found that the electrical characteristics of the metal contacts to the Ga_2O_3 epilayers and substrates are highly dependent on the nature of the starting surface and the resulting interface, and less dependent on the work function of the metal than expected. For example, both Ti and bulk In readily form ohmic contacts to Ga_2O_3, whereas other low-workfunction metals, such as Sn, did not form ohmic contacts even after annealing to 800 °C. For Ti ohmic contacts on Sn-doped Ga_2O_3 substrates the optimal annealing temperature was ~400 °C: the electrical characteristics continually degraded for annealing temperatures above ~500 °C. Thermodynamics predicts that Ti will reduce Ga_2O_3 to produce Ti oxide, therefore indicating that the Ti/Ga_2O_3 interface is unstable. In correspondence with this prediction, high-resolution cross-sectional TEM images of 400 °C-annealed samples show the formation of an ultra-thin (~2 nm) interfacial amorphous layer. TEM samples at higher annealing temperature have also been prepared for analysis; electron energy loss spectroscopy will be used to characterize the interfacial composition profiles in these samples to determine the relationship between composition and thickness of the interfacial layer and the electrical degradation of the contacts. Schottky diodes with Au, Mo, W and Sn as the Schottky metal were also fabricated. The Schottky barrier heights (SBHs) showed a weak dependence on the metal workfunction. An overview of the electrical behavior of different metals as ohmic or Schottky contacts to Ga_2O_3 and the interfacial chemistry and microstructure will be presented.

4:20pm **EM+AS+MS+SS-WeA7 Regrown InN Ohmic Contacts by Atomic Layer Epitaxy**, ***Charles Eddy, Jr.***, U.S. Naval Research Laboratory, *N. Nepal,* Sotera Defense Solutions, *M.J. Tadjer, T.J. Anderson, A.D. Koehler, J.K. Hite, K.D. Hobart*, U.S. Naval Research Laboratory

For the past 25 years, compound semiconductors comprised of elements from group III-B of the periodic table and nitrogen have attracted a sustained, high-level of research focus. More recently they have found growing application to rf and power electronics in the form of advanced transistor structures such as the high electron mobility transistor (HEMT) with and without insulated gates. Key performance parameters for such devices (cut-off frequency for rf transistors and on-resistance for power transistors) are often dominated by the contact resistance. The current best approach to contact resistance minimization involves aggressive processing requirements that challenge device fabrication, especially when insulated gates are required. A potential solution is the regrowth of highly conducting semiconductor contact layers where ohmic contacts are needed.

Here we report on initial efforts to employ regrown indium nitride (InN) contact layers by atomic layer epitaxy (ALE) as a low temperature solution to the ohmic contact challenge for III-N transistors. Recently, we have reported that good crystalline quality InN can be grown at less than 250°C

by ALE [1]. Here we employ such conditions to grow very thin layers and assess them morphologically and electrically.

InN regrown contact layers of 5nm thickness grown on sapphire are very smooth (rms roughness < 0.17nm) and possess sheet resistances as low at 3.6 kΩ/sq, corresponding to electron sheet carrier densities of 2-3 x10^{13} cm^{-2} and mobilities of 50 cm^2/V-s. These electron mobilities are higher than previously reported (30 cm^2/V-s) for much thicker films (1.3 μm) [2]. Similarly grown 22.5 nm thick InN layers on highly resistive silicon were processed with mesa isolation regions and 20/200 nm thick titanium/gold contact metals. Without any contact annealing, an ohmic contact resistance of 9.7x10^{-7} Ω-cm^2 (1.2 Ω-mm) was measured, comparable to the best high temperature alloyed contact to an AlGaN/GaN HEMT.

In our initial non-alloyed ohmic contact process, contact regions were recessed down to the GaN buffer layer to establish physical contact between the highly-conductive InN layer and electrons in the HEMT channel. A 25 nm thick InN layer was then grown by ALE, and the InN-filled ohmic regions were then capped with a Ti/Al/Ti/Au layers. Using the metals as an etch mask, the InN outside of the ohmic regions was etched away. We will report on initial results of application of ALE InN regrown contact layers and the modified fabrication approaches to AlGaN/GaN HEMTs.

1. N. Nepal, et al., *J Cryst. Growth and Design*, **13**, 1485-1490 (2013).

2. Kuo et al., *Diamond & Related Materials***20**, 1188 (2011).

4:40pm **EM+AS+MS+SS-WeA8 High-Temperature Characteristics of Ti/Al/Pt/Au Contacts to GaN at 600°C in Air**, ***Minmin Hou***, *D.G. Senesky*, Stanford University

The high-temperature characteristics (at 600°C) of Ti/Al/Pt/Au contacts to gallium nitride (GaN) in air are reported. GaN is a wide bandgap semiconductor material being developed for high-temperature electronics and micro-scale sensors. Ti/Al/Pt/Au metallization is frequently used for forming ohmic contacts to GaN. However, few studies have been devoted to studying the electrical characteristics of the Ti/Al/Pt/Au metallization at elevated temperatures and even fewer in oxidizing environments. It is not practical to obtain a hermetic sealing at elevated temperatures and a number of sensing applications may require non-hermetic packages. Therefore, the electrical characteristics of Ti/Al/Pt/Au contacts in a hot oxidizing ambient instead of an inert ambient or vacuum can provide new insights. In this work, the electrical and microstructural properties of Ti/Al/Pt/Au contacts to GaN upon exposure to 600°C in air are presented.

In this work, microfabricated circular-transfer-line-method (CTLM) patterns were used as the primary test structure. Ti/Al/Pt/Au were patterned through a standard lift-off process on unintentionally-doped GaN epitaxial layer grown by metal organic chemical vapor deposition (MOCVD) on sapphire. After lift-off, the samples were subject to a rapid thermal annealing (RTA) process at 850°C for 35 seconds in a nitrogen ambient.

To observe the impact of thermal exposure on the electrical and microstructural properties, the test structures were subject to a 10-hour thermal storage test in a furnace (air ambient), during which time the test structures were taken out of the furnace every two hours and their I-V characteristics were measured at room temperature. After the initial 2-hour "burn-in" period, the contact resistance remained stable over the entire reminder thermal storage test, with the variance within less than 3% and the specific contact resistivity remained on the order of 10^-5 Ω-cm^2.

In addition, the samples were subject to in-situ high-temperature I-V tests at 600°C in air both before and after the thermal storage using a high-temperature probe station. The linear I-V response confirms that the contacts remained ohmic after the thermal storage. The contact resistance at 600°C showed minimal change (approximately 9%) for a 20-μm-wide gap CTLM test structure, before and after thermal storage.

The microstructural analysis with atomic force microscopy (AFM) showed minimal changes (less than 0.1%) in surface roughness after thermal storage. The results support the use of Ti/Al/Pt/Au metallization for GaN-based sensors and electronic devices that will operate within a high-temperature and oxidizing ambient.

5:00pm **EM+AS+MS+SS-WeA9 Schottky Contacts and Dielectrics in GaN HEMTs for Millimeter-Wavelength Power Amplifiers**, ***Brian Downey***, Naval Research Laboratory **INVITED**

Although GaN RF transistor technology has begun to enter commercial markets, there are still several active research efforts aimed at extending the operating frequency of GaN devices to the millimeter-wavelength (MMW) frequency range of 30 – 300 GHz. In order to facilitate power gain at MMW frequencies, both geometric device scaling and novel heterostructure/device design are required, which present interesting materials and processing challenges. In this talk, an overview of NRL's approaches to MMW GaN high-electron-mobility transistor (HEMT) technology will be presented. In one approach, N-polar GaN inverted HEMT structures are employed, which places the GaN channel at the surface of the device. In this case, Schottky gate contacts are made directly to the N-polar GaN channel. The effect of GaN crystal polarity on Schottky barrier height will discussed along with strategies to increase the Schottky barrier height of metals to N-polar GaN. In a second approach, Ga-polar GaN HEMTs with vertically-scaled barrier layers are utilized to reduce the surface-to-channel distance in order to maintain electrostatic control of the channel in short gate length devices. The high electric fields in these vertically-scaled barrier devices can create large tunneling-related gate leakage currents, leading to high off-state power dissipation and soft breakdown characteristics. The use of gate dielectrics in these scaled structures will be discussed including their effect on device electrical performance.

5:40pm **EM+AS+MS+SS-WeA11 Nitrogen as a Source of Negative Fixed Charge for Enhancement Mode Al2O3/GaN Device Operation**, ***MuhammadAdi Negara***, *R. Long, D. Zhernokletov, P.C. McIntyre*, Stanford University

In recent years, significant research efforts have focused on developing enhancement mode (E-mode) GaN-based devices fueled by many potential applications. Simpler power amplifier circuits using a single polarity voltage supply and increased safety using a normally-off device can be achieved using E-mode devices leading to lower cost and an improvement of system reliability. Using the combination of E-mode and depletion mode (D-mode) devices in direct coupled logic open up also new applications for nitride semiconductors. To realize normally-off operation of GaN transistors, several approaches have been reported in the past including recessed gate structures [1], p-type gate injection [2], fluorine plasma treatment [3], surface channel GaN [4], thermally oxidized gate insulator [5] and oxide charge engineering [6]. In this report, nitrogen impurities introduced during atomic layer deposition of an Al_2O_3 gate dielectric are investigated as a means of modifying the threshold voltage (V_{th})/flat band voltage (V_{fb}) of GaN MOS devices. As reported in reference [7], nitrogen may incorporate on either cation or anion substitutional sites or on interstitial sites in Al_2O_3 and become a source of negative fixed charge within Al_2O_3. The effectiveness of this approach for fixed charge modification of ALD-grown Al_2O_3 compared to several alternative approaches will be presented.

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6:00pm **EM+AS+MS+SS-WeA12 Activation of Mg-Implanted GaN Facilitated by an Optimized Capping Structure**, ***Jordan Greenlee***, *B.N. Feigelson, T.J. Anderson, K.D. Hobart, F.J. Kub*, Naval Research Laboratory

For a broad range of devices, the activation of p and n-type implanted dopants in GaN is needed. The activation of implanted ions by annealing requires post-implantation damage removal and the arrangement of implanted ions in their proper lattice sites. Post-implantation activation of Mg via annealing requires high temperatures (>1300 ˚C). At these high annealing temperatures, GaN decomposes, leaving behind a roughened surface morphology and a defective crystalline lattice, both of which are detrimental for GaN device applications. To combat decomposition, either a high pressure environment, which is prohibitively expensive and not easily scalable, or a capping structure combined with short exposure to T >1300˚C is required to preserve the GaN. In this work, we explore the effects of different capping structures and their ability to protect the GaN surface during a high temperature pulse, similar to those used in the Multicycle Rapid Thermal Annealing (MRTA) process.

It was determined that the sputtered cap provides sufficient protection for the underlying GaN during a rapid heat pulse. The in situ MOCVD-grown AlN cap, although it should have a better interface and thus provide more protection for the GaN layer, is inferior to the sputtered cap as determined by Nomarski images. After etching the surface with AZ400k developer, it was determined that the GaN underneath the MOCVD-grown cap has pits as-grown. Since both GaN layers were grown with the same recipe, we attribute these pits to the HT MOCVD AlN growth process. Atomic force microscopy was used to determine the as-grown and post annealing surface morphologies of the samples. The as-grown sample covered with MOCVD AlN does not exhibit the same smooth step flow growth as the as-grown sample without the MOCVD AlN cap. After annealing and etching off the

AlN caps, the surface that was capped with MOCVD AlN shows evidence of pitting while the sample that was protected with only sputtered AlN no longer exhibits step flow growth like the as-grown sample. Since we are above 2/3 of the melting point of GaN, we expect that bulk diffusion is occurring and causing this rearrangement at the surface. This implies that sputtered AlN can provide sufficient protection of the underlying GaN surface, which will facilitate mid-process implantation and activation of Mg in GaN.

Additive Manufacturing/3D Printing Focus Topic
Room: 211A - Session AM+EM+MS+TF-ThM

Technologies Enabled by Additive Manufacturing/Future of Additive Manufacturing
Moderator: Vincent Smentkowski, General Electric Global Research Center

8:40am **AM+EM+MS+TF-ThM3 Additive Manufacturing Enabling Advanced Technologies**, ***Teresa Clement***, Raytheon Company **INVITED**
The aerospace and defense industry for the last decade has taken note and contributed to significant advances in materials and process capabilities enabled by the field of additive manufacturing (AM) to fabricate beyond state-of-the-art advanced technologies. Conventional and non-conventional industry partners continue to push the boundaries of next-generation materials and multi-materials for additive manufacturing in order to further extend product capabilities. As these material developments continue evolving, our industrial base begins to realize the many benefits of AM: reducing lifecycle costs, engineering resilience and capability surprise by rapidly reconfigurable responses to adaptive adversarial threats, and the enabling of truly agile manufacturing via AM integration with the model based enterprise (aka marrying AM to the 'digital thread'). Some specific examples of advanced technologies are discussed herein, with examples of design iteration cycle-time reduction and use of material/process controls to verify by inspection and full characterization demonstrations of improved or unprecedented material performance and multi-functionality (electrical, thermal, structural, etc) made possible by additive manufacturing.

9:20am **AM+EM+MS+TF-ThM5 4D Printing: Three Dimensional Printing with Material Composition as the Fourth Dimension**, ***Douglas C. Hofmann***, NASA Jet Propulsion Laboratory, California Institute of Technology **INVITED**
Much of the current research in additive manufacturing in the aerospace community is focused on qualifying materials for service, which is a critical requirement for using additive materials. However, additive manufacturing is a powerful tool for creating materials and applications that cannot be replicated using traditional means. In the past, this has meant 3D printing complex geometries that cannot be easily machined. In the current talk, we will discuss what we call 4D printing; 3D printing where the fourth dimension is the material composition. By using multiple materials strategically in additive manufacturing, a whole new frontier of materials science becomes possible. The science behind these alloys and their applications will be discussed.

11:00am **AM+EM+MS+TF-ThM10 The Future of Additive Manufacturing and Multifunctional Parts**, ***Phill Dickens***, University of Nottingham, UK, United Kingdom of Great Britain and Northern Ireland **INVITED**
Additive Manufacturing has many advantages for producing complex components and systems and this has already started to be exploited for parts made of a single material. There is now much interest in the possibility of building parts with multiple materials so that electrical circuits and electronic items can be included within the structure. This paper will highlight some of the research that is taking place at the University of Nottingham and some recent examples of simple products that could exploit this technology.

Some of the issues will be covered where the layer manufacturing process provides some limitations.

Electronic Materials and Processing
Room: 210E - Session EM+MS-ThM

III-N Nitrides for Optoelectronic Applications
Moderator: Rachael Myers-Ward, U.S. Naval Research Laboratory, Aubrey Hanbicki, U.S. Naval Research Laboratory

8:00am **EM+MS-ThM1 Hollow Cathode Plasma-Assisted Atomic Layer Deposition of Wurtzite InN and $In_xGa_{1-x}N$ Thin Films with Low Impurity Content**, ***Ali Haider***, *S. Kizir, C. Ozgit-Akgun, E. Goldenberg, M. Alevli, A. Kemal Okyay, N. Biyikli*, Bilkent University, Turkey
Among the III-nitride compound semiconductor family, InN is known with its unique properties which are crucial for both electronic and optoelectronic applications such as narrow band gap, small effective mass, and high electron mobility. Since InN and its alloys are currently the backbone of LED industry for bandgap tuning and are mostly grown using high-temperature epitaxy, experimental efforts on enabling low-temperature growth are critical to widen its perspective for applications like flexible (opto)electronics. In addition, a growth method in which indium composition can be precisely controlled for $In_xGa_{1-x}N$ alloys is highly imperative for band gap engineering.

In this work, we summarize our recent progress on the development of crystalline InN and $In_xGa_{1-x}N$ thin films with low impurity content at a substrate temperature as low as 200 °C by hollow cathode plasma-assisted ALD (HCPA-ALD). Deposition of polycrystalline wurtzite InN thin films was achieved using trimethylindium ($InMe_3$) and N_2 plasma sources. Process parameters including $InMe_3$ pulse time, N_2 flow rate and duration, purge time, deposition temperature, and plasma power were investigated. Detailed structural and optical characterizations of InN and $In_xGa_{1-x}N$ were performed. N_2 plasma exposure time had a profound effect on the impurity content of the InN films. After saturating the surface of substrate with $InMe_3$ molecules, the ligands of $InMe_3$ were removed completely only after sufficient exposure dose of N_2 plasma. Insufficient exposure times of N_2 plasma resulted in InN films with higher carbon impurity contents as determined from XPS measurements, which were arising from methyl ligands of $InMe_3$. After optimizing the precursor dosages, XPS survey scan obtained from the bulk part of the InN film showed that *h*-InN films were carbon and oxygen free. On the other hand, indium composition in different $In_xGa_{1-x}N$ thin films was determined by energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and X- ray diffraction. GIXRD measurements revealed the hexagonal wurtzite crystalline structure of the grown InN and $In_xGa_{1-x}N$ thin films. Refractive index of the InN film at 750 nm was estimated to be 2.67 while refractive indices of $In_xGa_{1-x}N$ thin films increased from 2.28 to 2.42 at wavelength of 650 nm with increase in indium composition. Optical band edge studies of the $In_xGa_{1-x}N$ films confirmed the successful tunability of the optical band-edge with alloy composition. Our results show that HCPA-ALD is an alternative technique to grow crystalline InN and $In_xGa_{1-x}N$ films at low substrate temperatures.

8:20am **EM+MS-ThM2 Infrared Nanoscopy of Indium-rich InGaN Epilayers**, ***Yohannes Abate***, *D. Seidlitz, N. Dietz,* Georgia State University, *I. Ferguson*, Missouri University of Science and Technology
The unique optical and electrical properties of ternary $In_{1-x}Ga_xN$ epilayers and heterostructures therewith makes this material system attractive for various optoelectronic device applications, including but not limited to high-speed electronics, frequency agile photovoltaic solar cells, or light emitting devices. However, the presently utilized growth methods enable the indium incorporation in $In_{1-x}Ga_xN$ heterostructures to a narrow composition range, before phase instabilities are encountered. As a potential pathway to extend the stable composition range and the control of point defects in the alloys, we explored in recent years the reactor pressure dependency under superatmospheric MOCVD - also denoted high-pressure chemical vapor deposition (HPCVD) - conditions. In this contribution we will report and discuss on the growth of indium-rich ternary $In_{1-x}Ga_xN$ epilayers and the influence of the pulse separations on the phase purity and stability of indium-rich $In_{1-x}Ga_xN$ epilayer and resulting structural and optical properties. The InGaN epilayers have been characterized by x-ray diffraction, Raman spectroscopy, atomic force microscopy, and by several optical techniques such as infrared (IR) reflectance and optical absorption spectroscopy. The free carrier concentrations have been estimated by analyzing the IR-reflectance spectra and by Raman A1(LO) mode line shape analysis.

8:40am **EM+MS-ThM3 Surface Treatment and Characterization of InN (0001)**, *S.P. Park, T. Kaufman-Osborn, K. Sardashti,* University of California San Diego, *S.M. Islam, D. Jena,* University of Notre Dame, ***Hyunwoong Kim***, *A.C. Kummel*, University of California San Diego

Indium nitride (InN) is a promising material due to the its band offset to GaN. However, employing InN in practical devices is still challenging because it has an electron accumulation at the surface which is hypothesized to be due to an In-In double layer at the surface. For practical InN devices, it is critical to remove this In-In double layer and form a non-metallic surface. This work describes the transformation of the atomic order, elemental composition, and electric structure of InN (0001) surface during the removal of the metallic layer and its replacement with gate oxide using scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), and scanning tunneling spectroscopy (STS). Three cleaning methods were studied. (1) Ex -situ wet cleaning was performed by using HCl, NH OH, and (NH) S solution to remove native oxide. STM showed the surface is smooth and uniform and STS showed n-type conductivity with a band gap of 0.7 eV consistent with strong intrinsic accumulation of electrons on the surface. (2) In-situ atomic hydrogen cleaning on wet cleaned InN surface was performed. However, due to the preferential nitrogen depletion in atomic hydrogen cleaning, the ratio of indium to nitrogen was increased. STM images showed rows of indium dimers, and STS showed that there was a metallic zero band gap surface, consistent with an In-In double layer surface termination. (3) As an alternative method to eliminate the accumulation of electron at InN surface, an O passivation was performed on wet cleaned InN. The O exposed surface was atomically flat and uniform. STM line traces showed islands were formed with step height of 3.5 angstrom consistent with formation of an O-In-O layer. The band gap of the O passivated InN surface was 0.8 eV and the Fermi level was midgap consistent with absence of In-In double layer.ALD nucleation was studied using TMA pre-dosing and an additional 10 cycles of TMA and H_2O doses on an O_2 passivated InN substrate. After the 10 cycles of ALD, the ratio of Al to O ratio was 2:3 consistent with the stoichiometric ratio of Al_2O_3, The ALD process broadened the band gap from 0.8 eV to 1 eV due to the formation of Al-O-Al bonding, In sum, an unpinned non-metallic surface without the formation of In-In layer was achieved on InN using an oxidant and cyclic dose of TMA and water.

9:00am **EM+MS-ThM4 State-Of-The-Art High Efficiency Thermoelectric Material: III-Nitrides as a Wide Bandgap Semiconductor**, *B. Kucukgok, N. Lu,* University of North Carolina at Charlotte, ***Nikolaus Dietz***, Georgia State University, *I. Ferguson*, Missouri University of Science and Technology

Thermoelectric (TE) devices have gained widespread interest as a renewable energy source in the field of energy conservation and emission reduction due to their direct conversion of heat into electricity by Seebeck effect of TE materials. Additionally, TE devices have been used in wide variety of applications, due to their reliability, stability, and low-cost, such as automotive industry, spacecraft radioisotope power supply, and photovoltaic solar cells. Since TE device performance is directly related to material efficiency, material selection becomes essential. Recently, the interest of potential applications of III-nitride semiconductors in the TE field has been initiated due to their distinguished features including high-temperature operation, high mechanical strength, and large-band gap range and their promising TE figures of merit (*ZT*), mostly for materials based on AlGaN and InGaN alloys. Here, we demonstrate the room temperature thermoelectric properties of III-nitrides such as GaN and its alloys, grown by metalorganic chemical vapor deposition (MOCVD). The structural, optical, electrical, and thermal properties of the samples were examined by X-ray diffraction, photoluminescence, van der Pauw hall-effect, and thermal gradient methods, respectively. The objectives of this paper are to understand the role of defects, carrier density n, and composition x on the TE properties of III-nitrides.

9:20am **EM+MS-ThM5 Nanofabrication of Advanced Nanophotonic Structures by Nanoimprinting**, ***Stefano Cabrini***, Lawrence Berkeley National Laboratory (LBNL) **INVITED**

To exploit the potentialities of Nanophotonics, it is important to control the properties of the material at the nanometer scale, obtaining a good agreement between the experiments and the theory. Nanofabrication can open the way for new concept of devices. In this presentation we will present the fabrication and characterization of simple photonic crystals directly pattern by nanoimprinting using a special functional resist with high refractive index.

11:00am **EM+MS-ThM10 Advanced III-Nitride Device for RF Switch Applications: A Record 2THz Fco Super-Lattice Castellated Field Effect Transistor (SLCFET) for Low Loss RF Switching**, ***Shalini Gupta***, *R. Howell, E. Stewart, J. Parke, B. Nechay, M. King, H. Cramer, J. Hartman, R. Freitag, M. Snook, I. Wathuthanthri, G. Henry, K. Renaldo*, Northrop Grumman ES **INVITED**

Northrop Grumman Electronic Systems (NGES) reports on the development of a novel field effect transistor structure, based on a super-lattice epitaxial layer combined with a three dimensional castellated gate structure to achieve a 3x improvement in RF switch figure of merit compared to current state of the art transistor technologies. RF switch components are vital for the successful implementation of a variety of system architectures, spanning applications from phased array radars to the wireless components of mobile phones and consumer electronics.

NGES used MOCVD growth techniques to grow a GaN/AlGaN based super-lattice on a 100 mm diameter semi-insulating SiC substrate which is used as the SLCFET conductive channel. This super-lattice creates multiple 2DEGs producing parallel current channels between the source and drain of the device resulting in currents several times higher than conventional FETs and a record low GaN epi sheet resistance of 60 ohm/sq. The low epi sheet resistance in turn reduces the on resistance of the FET which results in a low insertion loss RF switch. Although super-lattice structures have been employed to make optoelectronic semiconductor devices, their use in FETs have been limited due to difficulty in pinching-off the stacked paralleled current channels. This is because the top channels screen the bottom channels from the electric field of the gate thereby increasing the voltage needed to pinch off the channel and turn off the device to a value beyond the breakdown field of the semiconductor. The SLCFET overcomes this challenge by employing a side-pinching gate. This is realized by etching features in the semiconductor prior to a 0.25 um gate deposition which allows the gate metal to surround the channels on the top and sides. This feature resembles the crenellations of a castle and hence is called a castellated gate.

Electrical measurements of the SLCFET transistor reveal a high I_{MAX} of 2.7 A/mm and a pinch off voltage of -8V. The SLCFET has a low on resistance (R_{ON}) of 0.4 Ohm-mm and an off capacitance (C_{OFF}) of 0.2 pF/mm, resulting in an RF switch figure of merit (Fco = $1/2\pi R_{ON}C_{OFF}$) of 2 THz, 3x higher than the current state of the art FET based RF switches. SLCFET MMICs have been designed and tested including Single Pole Double Throw (SPDT) switches, tunable filters, and true time delay units. State of the art electrical results have been obtained, such as a series-shunt broadband (1-18 GHz) SLCFET SPDT with a measured insertion loss of 0.25 dB at 10 GHz, with -35 dB of isolation and -23 dB of return loss. These state-of-the-art results demonstrate that SLCFET is an enabling technology for next generation RF systems.

11:40am **EM+MS-ThM12 Developing Periodically Oriented Gallium Nitride for Frequency Conversion**, ***Jennifer Hite***, *R. Goswami, J.A. Freitas, M.A. Mastro, I. Vurgaftman, J.R. Meyer,* U.S. Naval Research Laboratory, *C.G. Brown,* University Research Foundation, *F.J. Kub, S.R. Bowman, C.R. Eddy, Jr.*, U.S. Naval Research Laboratory

Gallium nitride is a semiconductor widely used in both optical and electronic devices. The polarity of GaN (+/- c-direction) influences many properties of the resultant material, including chemical reactivity and electric field in these 'spontaneously polarized' materials. By engineering inversion layers, we have demonstrated control of GaN polarity on both polar faces of GaN. By employing a selective growth method to deposit the IL, the lateral polarity of the GaN can be alternated, thus enabling structures referred to as periodically oriented (PO) GaN.

On N-polar substrates, we demonstrated that optimization of the MOCVD growth rates resulted in sharp, vertical interfaces and smooth surfaces. This work has moved the technology substantially closer to practical non-linear optic emitters by using HVPE to extend the PO GaN templates on N-polar substrates to total thicknesses of up to 500 mm, while faithfully maintaining the pattern of alternating polarity. Additionally, cross-sectional cathode-luminescence (CL) imaging of such an extension shows that the large initial dislocation densities occurring in the original inversion layers greatly decreased after about 25 μm of regrowth.

For growth on Ga-polar substrates, we have demonstrated that inversion layers can be created using atomic layer deposition (ALD) of Al_2O_3. This new capability is especially relevant because Ga-polar films are more prominent in devices, as they result in lower impurities, higher quality and smoother films. In this case, GaN grown over the inversion layer is N-polar. This inversion layer was used to form laterally-patterned stripes of alternating Ga- and N-polar films. We find that annealing the ALD films crystallizes the Al_2O_3, thereby allowing N-polar GaN to be grown over the new sapphire-like surface. Transmission electron microscopy shows that the inversion layer in a PO GaN structure is crystalline, a-plane oriented, and a-phase. TEM characterization further indicates that the GaN layers, both

above and below the Al_2O_3 inversion layer, are c-oriented without any rotation between them. The optimization of this process has enhanced the surface smoothness. The latest results in demonstrating secondary harmonic generation will be presented.

These methods of GaN polarity inversion offer the promise of engineered materials with custom lateral and vertical polarity variations for applications in novel electronic and optoelectronic devices, a subset of which are expected to be suitable for non-linear optics.

12:00pm **EM+MS-ThM13 Electronic and Optical Device Applications based on III-Nitride Films Grown by Plasma-Assisted ALD**, *B. Tekcan, **Sami Bolat**, C. Ozgit-Akgun, N. Biyikli, A.K. Okyay*, Bilkent University, Turkey

For many electronic and optical applications, III-nitride materials are much sought after due to their direct and high optical band-gap, high electron saturation velocity and band-gap tunability [1]. These important features enable many possible device applications, which are generally used in high power and high frequency applications [2]. However, these films are generally grown using high temperature and high vacuum processes namely, MOCVD [3], MBE [4] which limit substrate selection along with CMOS compatibility. In our work, we offer an alternative way of growth to fabricate thin film transistors (TFTs) and UV metal-semiconductor-metal (MSM) photodetectors. Hollow cathode plasma assisted Atomic Layer Deposition (HC-PA-ALD) technique make low temperature device applications possible. We have grown GaN and InGaN films and analyzed TFT and photodetector properties in detail. Electrical and optical characteristics of these devices are inspected.

The results can pave the way for ALD to be used for III-Nitride based electronic and optical devices. Thin film transistor exhibit $2x10^3$ ON/OFF ratio with threshold voltage of 11.8 V. Metal-semiconductor-metal (MSM) photodetectors, on the other hand, showed 20 pA under -20 V voltage bias with a UV responsivity of 680 m A/W under 290 nm incident light with only a 20 nm thick film. Effect of annealing on the device performance is also studied. TFTs ON/OFF ratio increased to $2x10^4$ with a lower threshold voltage and contact resistance decreased 4000 times when annealed at 800 °C for 30 seconds. Moreover, MSM devices performance also enhanced after annealing 600 °C. The photoresponsivity as high as 950 m A/W at 290 nm incident light is recorded. The dark current reduced significantly, a current value of 50 fA is recorded under -20 V voltage bias.

Along with GaN devices, InGaN based photodetectors are fabricated and characterized. MSM devices based on InGaN devices showed responsivity and dark current levels controlled by In concentration. The resistivity of the films decreased with concentration of In in the semiconductor. Changing the In concentration, bandgap tunability is possible.

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Thursday Afternoon, October 22, 2015

Additive Manufacturing/3D Printing Focus Topic
Room: 211A - Session AM+EM+MS+TF-ThA

Additive Fabrication for Electronic Devices and Systems
Moderator: Jim Fitz-Gerald, University of Virginia, Gregory Whiting, Palo Alto Research Center

2:20pm **AM+EM+MS+TF-ThA1 Additive Printing for Flexible Electronic Devices**, *A.C. Pierre, **Ana Claudia Arias***, University of California at Berkeley **INVITED**

The area of printed electronics has been focused on the use of new classes of semiconducting and conducting materials in two main applications, displays and photovoltaics. Both applications require materials long-term stability, long shelf life as well the need for patterning and deposition over large areas. Over the past 10 years significant progress in the performance of printable materials has been reported including highly efficient solar cells, light emitting diodes and thin film transistors with mobilities as high as 10 cm^2/Vs. The work is highly motivated by the potential for high through put, high volume, low cost manufacturing. While large area electronics continues to be a good application for printed flexible devices, wearable medical devices, which benefit from new form factors, represent a good shift in direction of research in the field. Wearable medical sensors have the potential to play an essential role in the reduction of health care costs as they encourage healthy living by providing individuals feedback on personal vital signs and enable the facile implementation of both in-hospital and in-home professional health monitoring. In printed flexible electronics however, there are no standards for materials set, device models and fabrication methods. This lack of standards slows down design of new systems and the success of the technology as a whole. In this talk, I will review the state of the art of devices produced by printing and introduce a blade coating method that yields highly homogeneous flexible thin films that are applied to LEDS, photodiodes and TFTs. The application of these devices as building blocks for flexible electronics systems will also be discussed.

3:00pm **AM+EM+MS+TF-ThA3 Digital Microassembly for High-performance Printed Electronics**, ***Eugene Chow**, J.P. Lu, G.L. Whiting, D.K. Biegelsen, S. Raychaudhuri, A.R. Völkel, J. Veres, P. Maeda, I. Matei, S. Nelaturi, L.S. Crawford*, Palo Alto Research Center (PARC) **INVITED**

Digitally printing micro-scale pre-fabricated building blocks instead of simpler materials enables an alternative route to printed electronics and opens up fundamentally new manufacturing capabilities. However, existing printing technologies do not provide the required accuracy and orientation control to print such micro objects. We will describe a demonstration of the fundamental process steps of such an electronic chip printer based on electrographic manipulation and xerographic concepts.

4:00pm **AM+EM+MS+TF-ThA6 3D Printed Bionic Nanomaterials**, ***Michael McAlpine***, University of Minnesota **INVITED**

The ability to three-dimensionally interweave biology with nanomaterials could enable the creation of bionic devices possessing unique geometries, properties, and functionalities. The development of methods for interfacing high performance devices with biology could yield breakthroughs in regenerative medicine, smart prosthetics, and human-machine interfaces. Yet, most high quality inorganic materials: 1) are two dimensional, 2) are hard and brittle, and 3) require high crystallization temperatures for maximally efficient performance. These properties render the corresponding devices incompatible with biology, which is: 1) three dimensional, 2) soft, flexible, and stretchable, and 3) temperature sensitive. These dichotomies are solved by: 1) using 3D scanning and printing for hierarchical, interwoven, multiscale material and device architectures, 2) using nanotechnology as an enabling route for overcoming mechanical discrepancies while revealing new effects due to size scaling, and 3) separating the materials synthesis and 3D printed assembly steps to enable conformal integration of high quality materials with biology. The coupling of 3D printing, novel nanomaterial properties, and 'living' platforms may enable next-generation nano-bio interfaces and 3D printed bionic nanodevices.

Electronic Materials and Processing
Room: 210E - Session EM+MS-ThA

III-N Nitrides II
Moderator: Nikolaus Dietz, Georgia State University

2:20pm **EM+MS-ThA1 Accelerating Adoption of Wide Band Gap Semiconductors though Manufacturing Innovation**, ***John Muth***, North Carolina State University **INVITED**

As part of the national strategy for the United States to compete in the increasingly competitive global marketplace, a National Network for Manufacturing Innovation (NNMI) is being implemented to create a competitive and sustainable research-to-manufacturing infrastructure for U.S. Industry, academia and government to solve industry relevant problems.

PowerAmerica a $146 million dollar investment by the Department of Energy, Industry and the State of North Carolina is the second NMNI to be announced and with its industry and academic partners has initiated 20 projects focused on manufacturing wide band gap semiconductor devices and demonstrating their advantages in power electronic applications.

The mission of PowerAmerica is to develop advanced manufacturing processes to enable cost competitive, large-scale production of wide bandgap semiconductor-based power electronics, which allow electronic systems to be smaller, faster and more efficient than power electronics made from silicon. Innovations in manufacturing, improvements in reliability and demonstrations of system level advantages are important aspects of PowerAmerica's strategy to accelerate the adoption of wide band gap semiconductors into power electronics.

The number of systems that use power electronics between generation and use is about 20% today and is expected to grow to about 80% by 2030 a wide variety of technologies will be disrupted by the system advantages offered by wide band gap semiconductors. These include electric vehicles, motor drives, data centers, smart grid, photovoltaic and other renewable energy systems as well as niche applications in consumer electronics. In addition to the technical work performed in PowerAmerica a significant effort is being put towards workforce development and education. These efforts will prepare industry to compete in and the next generation of engineers and workers to lead the world into a brighter, more energy efficient world.

3:00pm **EM+MS-ThA3 InGaN/GaN Nanostructures for Efficient Light Emission and White Light Emitting Diodes**, *Y. Nakajima, **P. Daniel Dapkus**, Y. Lin*, University of Southern California **INVITED**

InGaN/GaN quantum well LEDs that form the basis for efficient solid state lighting exhibit properties that limit the ultimate efficiency that can be achieved for this application. Among these deleterious properties are a high current efficiency decrease not related to heating – efficiency droop – and reduced efficiency in the green and yellow regions of the spectrum. It has been speculated that one of the causes for the droop and the reduced efficiency of green and yellow emitting diodes is the presence of piezoelectric fields that result from the growth of these structures on the polar (0001) plane of GaN.

In this work we report investigations of the formation of GaN nanostructures that are defined by non-polar and semi-polar planes that act as templates upon which quantum well active regions are formed. Nanorods, nanosheets, and nanostripe pyramids are described that are predominantly defined by {1-100}, {11-20}, and semi-polar planes and act as templates for the growth of InGaN/GaN multiple quantum well active regions. We describe the properties of blue LEDs formed on these templates and compare them to devices made on planar (0001) substrates.

Efficient green emitting LEDs and monolithic white light emitting LEDs require the extension of the range of efficient light emission in the InGaN / GaN materials system. We demonstrate high efficiency green and yellow light emitting multiple quantum well (MQW) structures grown on GaN nanostripe templates. The nanostripe dimensions range from 100 nm to 300 nm and have separations that range from 300 nm to 1 micron. Such small lateral dimensions are chosen to promote the elimination of threading dislocations from the structures. Nanostripes with various nonpolar and semi polar surfaces are grown with selective area growth on patterned c-plane GaN where the mask openings are oriented between the [10-10] and [11-20] directions. With stripes are aligned along the [10-10] and [11-20] directions, the sidewalls can be controlled to be nearly vertical or inclined

and intersecting. Both shapes were examined and MQWs were grown on these different stripes. Photoluminescence (PL) measurement shows that MQWs grown on stripes with (10-11) surfaces and triangular shape emit the longest peak wavelength and have the best surface stability. Efficient PL emission peak wavelengths as long as 570 nm are realized on the triangular stripes with (10-11) surfaces by optimizing the MQW growth conditions for long wavelength emission. LED structures that utilize MQWs grown on nanostripes with (10-11) surfaces were fabricated to further demonstrate the viability of the approach.

4:00pm **EM+MS-ThA6 Tuning Bandgap Through Cation Ordering in New PV Materials**, ***Steve Durbin***, *R.A. Makin, N. Feldberg,* Western Michigan University, *J.P. Mathis, N. Senabulya, R. Clarke*, University of Michigan

There continues to be considerable interest in so-called earth abundant element compound semiconductors, of which we have multiple candidates at present. One material worth considering, $ZnSnN_2$, is properly termed a ternary heterovalent compound and is a member of the more general family of II-IV-V_2 semiconductors. It is analogous to InN, whereby pairs of indium atoms are replaced by a periodic arrangement of a Zn and Sn atom, and in that way is related to ClGS as that material corresponds to II-VI semiconductors. Although $ZnSnN_2$ is predicted to crystallize in an orthorhombic lattice with a bandgap of approximately 2.0 eV (calculations reported in the literature vary somewhat), we have observed that single crystal thin films grown by plasma-assisted molecular beam epitaxy are more likely to form in a wurtzitic lattice, with a lower electronic bandgap energy. In fact, we have recently observed both optical absorption and x-ray emission spectroscopy results on a series of films which agree with density functional theory calculations predicting a bandgap as small as 1 eV - the direct consequence of disorder in the cation sublattice. Careful tuning of the growth parameters enables the degree of order to be varied, and consequently the bandgap energy as well. This provides the intriguing possibility of tuning the bandgap through the growth process, as opposed to the traditional approach of alloying. The optimal bandgap energy of approximately 1.5 eV would therefore be an intermediate state between the two extremes.

4:20pm **EM+MS-ThA7 Comparison Studies of GaN Grown with Trimethylgallium and Triethylgallium for Optoelectronic Applications**, ***Mustafa Alevli***, Marmara University, Turkey, *A. Haider,* Bilkent University, Turkey, *N. Gungor,* Marmara University, Turkey, *S. Kizir, S. Alkis, A.K. Okyay, N. Biyikli*, Bilkent University, Turkey

Si is famous for the well-developed mature CMOS technology and a promising substrate for GaN due to its wafer size, low material cost, and possible integration with the CMOS. However, it is very difficult to deposit high-quality GaN films on Si due to its high deposition temperature which results in inter-diffusion at the GaN/Si interface and the relatively large lattice mismatch. Atomic layer deposition is a low temperature technique that can provide an alternative path for the deposition of GaN on Si.

In this study, GaN materials were grown at 200°C by two different kinds of metalorganic precursors, one by using trimethylgallium (TMG) and another by using triethylgallium (TEG) as gallium sources. It is reported that the carbon concentration was fifty times higher in the GaN films grown by TMG precursor than in that grown by TEG precursor. As it is going to be shown in this contribution, optical and electrical properties of Hollow cathode plasma-assisted atomic layer deposition of crystalline GaN films will be presented. When TMG pyrolyzes, it introduces more reactive CH_3 radicals in to the CVD reactor when it is compared to TEG precursor. It means that TMG enhances carbon incorporation in epitaxial film structure.

Spectroscopic ellipsometry studies on GaN films shows that refractive indices of GaN films increase when TMG was used as metalorganic precursor. The increase in the refractive index values indicates that the crystalline quality of GaN films improved with the use TMG. The change in the metalorganic precursor did not affect either the Bragg peak positions or crystalline phase of deposited GaN films. The grazing-incidence XRD patterns of both GaN films revealed that the films are polycrystalline with hexagonal wurtzite structure and are referring to (100), (101), (002), (102), (110), and (103) planes. The increase in the intensity and improvement in the FWHM value of the (002) peak also showed that the crystallinity improved for TMG grown GaN films. Further More,. The effect of alkyl precursors is also studied by a variety of characterization techniques Fourier Transform infrared reflectance, optical transmission, X-ray photoelectron spectroscopy, current-voltage characteristics of which the results will be discussed in detail.

This work is supported by TÜBİTAK project #114F002.

4:40pm **EM+MS-ThA8 Growth Control of InGaN Alloys and Nanostructures by Migration-Enhanced, Plasma-Assisted MOCVD**, ***Daniel Seidlitz,*** *I. Senevirathna, Y. Abate, N. Dietz,* Georgia State University, *A. Hoffmann*, Technical University Berlin, Germany

This contribution will present results of the structural and optoelectronic properties of InN and InGaN alloys and nanostructures as a function of temperature, reactor pressure and the temporal injection of metalorganic precursors and plasma activated nitrogen species (e.g. N*/NH*/NH_x*).

Migration-enhanced plasma-assisted metal organic chemical vapor deposition (MEPA-MOCVD) is utilized for the growth of InN and InGaN layers and nanocomposites at growth temperatures in the range of 450°C and 700°C. The custom-built MEPA-MOCVD system consists of a showerhead reactor combined with a hollow cathode (HC) plasma source (Meaglow) powered by a high-frequency (13.56 MHz) RF generator with a output power up to 600W. The HC plasma source creates reactive nitrogen fragments, which afterglow region approaches the growth surface. Plasma emission spectroscopy (PES) is utilized for real-time information about the formation and concentration of plasma generated active species. Added provisions allow a spatial and temporal injection of both, nitrogen and metalorganic precursors and enable the control of the epitaxial layers and their composition during the growth process.

Ex-situ investigations by Atomic Force Spectroscopy (AFM) as well as Fourier Transform Infrared Reflectance (FTIR) and Raman spectroscopy assess structural and optoelectronic properties (e.g. surface roughness, high-frequency dielectric constant e_∞, film thickness, etc.) of the deposited InN and InGaN nanostructures.

Correlation of the in-situ obtained plasma characteristics with the ex-situ results of the structural and optical properties of the InN and InGaN nanostructures are provided, as well as correlations between plasma afterglow regime position above the growth surface and the epitaxial layer properties. The aim of these studies is to access the phase stability regime of indium-rich ternary group III-nitrides as a function of growth temperature, kinetic energy of plasma species, reactor pressure, and temporal and spatial precursor supply.

5:00pm **EM+MS-ThA9 GaN on Rare-earth Oxide Buffer –A New Player in GaN-on-Si Technology**, ***Rytis Dargis***, *A. Clark*, Translucent Inc.

We present the results of process development for GaN MOCVD epitaxial growth on Si using single crystal rare-earth oxide buffer layers. Advantage of this technological approach over traditional GaN-on-Si that uses a AlN nucleation buffer is the chemical isolation of the Si substrate from the group-III metals thereby preventing Si diffusion into the III-N layer. This removes one of the main breakdown failure modes being the silicon doped interface. Additionally, the relatively high breakdown electric field of rare-earth oxides (e.g. 4MV/cm for erbium oxide) can be used as part of the overall vertical breakdown thereby reducing the thickness of the III-N layer structure without impairment of electrical breakdown properties of a power device. This is important to the overall process since thinner GaN not only reduces MOCVD cycle time but results in lower stress in the structure. Additionally, thermal and chemical stability of the oxides opens up opportunity for implementation of a more flexible process for GaN-on-silicon including solutions used in GaN-on-sapphire.

Two types of the oxide buffers with thickness of 300 nm were grown of Si (111): single Er_2O_3 and double layer Er_2O_3-Sc_2O_3 structure were employed. Robustness and scalability of the oxide process make it suitable for manufacturing.

To validate the technology, the standard AlN-first process was used. GaN with thickness of 2 µm was grown in a state of the art 200mm manufacturing tool. It demonstrated excellent management of the stress in the structure with 25µm convex curvature, superior surface morphology (RMS = 0.56 nm, Z-range = 4.1 nm) and good crystal structure (GaN (002) FWHM = 561 arcsec, GaN (102) FWHM = 907 arcsec).

Our newly developed GaN-first MOCVD process, which is based on a typical GaN-on-sapphire process, uses nitridation and low temperature GaN buffer. During the growth, the upper part of the oxides is transformed into rare-earth nitride with lattice constant smaller than that of the oxide and consequently lower lattice mismatch to GaN (e.g. lattice constant mismatch between GaN and ScN is approximately -0.2%). The GaN layers with total thickness of 2.5 µm grown on the both types of the buffers exhibit smooth surface with RMS < 1 nm and Z-range <10 nm. The wafers exhibit good structural quality with X-ray diffraction GaN (002) peak FWHM of 540 arcsec and 684 arcsec for GaN on Er_2O_3 layer and Er_2O_3/Sc_2O_3 stack respectively. SIMS data shows no oxygen or rare-earth metal diffusion into the GaN.

5:20pm **EM+MS-ThA10 Plasma Enhanced Atomic Layer Deposition of Al_2O_3 on AlGaN/GaN High Electron Mobility Transistors**, ***Xiaoye Qin***, *R.M. Wallace*, University of Texas at Dallas

Metal insulator semiconductor AlGaN/GaN high electron mobility transistors (MISHEMTs) are promising for power device applications due to a lower leakage current than the conventional Schottky AlGaN/GaN HEMTs. Among a large number of insulator materials, Al_2O_3 dielectric layer, deposited by atomic layer deposition (ALD), is often employed as the gate insulator because of a large band gap (and the resultant high conduction band offset on AlGaN)[1], high breakdown field, conformal growth, and a relatively high dielectric constant. However, the thermal ALD Al_2O_3 does not passivate the surface effectively according to our previous work.[1–4] In this work, the half cycle study of plasma enhanced atomic layer deposited (PEALD) Al_2O_3 on AlGaN is investigated using *in situ* X-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS) and *ex situ* electrical characterizations. A faster nucleation or growth is detected in PEALD than thermal ALD using an H_2O precursor. The PEALD Al_2O_3 layer decreases the gate leakage current as the ALD Al_2O_3. Importantly, the remote O_2 plasma oxidizes the AlGaN surface slightly at the initial stage, which passivates the surface and reduces the OFF-state leakage. This work demonstrates that PEALD is a useful strategy for Al_2O_3 growth on AlGaN/GaN devices.

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