

# Monday Morning, October 21, 2019

## 2D Materials

### Room A216 - Session 2D+EM+MI+NS-MoM

#### Properties of 2D Materials including Electronic, Magnetic, Mechanical, Optical, and Thermal Properties I

Moderator: Sanghoon Bae, Massachusetts Institute of Technology

8:20am **2D+EM+MI+NS-MoM1 Extreme Fatigue Life of Graphene**, *Teng Cui, S. Mukherjee, P.M. Sudeep, G. Colas, J. Tam*, University of Toronto, Canada; *P.M. Ajayan*, Rice University; *C.V. Singh, Y. Sun, T. Filleter*, University of Toronto, Canada

Materials can fail when subjected to cyclic loading at stress levels much lower than the ultimate tensile strength or yielding limit, which is known as mechanical fatigue. Understanding the fatigue behavior is critical for any emerging material in order to evaluate its long-term dynamic reliability. Two-dimensional (2D) materials have been widely applied to mechanical and electronic applications, where they are commonly subjected to cyclic stress. However, the fatigue life and underlying damage mechanisms of these atomically thin, nearly defect-free, materials are unknown. Here we show the first fatigue study of freestanding 2D materials, in particular graphene and graphene oxide (GO). Monolayer and few layer graphene and GO were found to all exhibit ultrahigh fatigue life of more than one billion cycles at large stress level in the GPa range. Such a remarkable fatigue life is higher than that of any material reported to date at similar stress levels. Graphene exhibits global and catastrophic fatigue failure preceded by bond reconfiguration near the defective site due to inhomogeneous charge distribution and higher potential energy. Graphene can fracture under cyclic loading but without progressive damage, which is distinct from the fatigue failure mechanism of any other materials. The presence of functional groups on GO imparts a local and progressive fatigue damage mechanism, which fits the macroscopic fatigue convention. The extraordinary fatigue life was found to diminish significantly when the material is scaled up in thickness (10s of layers). This work not only provides new fundamental insights into the widely observed fatigue enhancement behavior of graphene-embedded nanocomposites, but also serves as a starting point for the mechanical dynamic reliability evaluation of other 2D materials.

8:40am **2D+EM+MI+NS-MoM2 Epitaxial Growth and Thermal Degradation of Monolayer MoS<sub>2</sub> on SrTiO<sub>3</sub> Single Crystal Substrates**, *Peiyu Chen, W. Xu, Y. Gao, P. Holdway, J.H. Warner, M.R. Castell*, University of Oxford, UK

Monolayer MoS<sub>2</sub> crystals grown on amorphous substrates such as SiO<sub>2</sub> are randomly oriented. However, when MoS<sub>2</sub> is grown on crystalline substrates, the crystal shapes and orientations are also influenced by their epitaxial interaction with the substrate. In the first part of this talk, we present the results from chemical vapor deposition growth of MoS<sub>2</sub> on three different terminations of single crystal strontium titanate (SrTiO<sub>3</sub>) substrates: (111), (110), and (001). On all three terminations of SrTiO<sub>3</sub>, the monolayer MoS<sub>2</sub> crystals try to align their <2 -1 0>-type directions (i.e., the sulfur-terminated edge directions) with the <-1 -1 0>-type directions on SrTiO<sub>3</sub>. This arrangement allows near-perfect coincidence epitaxy between seven MoS<sub>2</sub> unit cells and four SrTiO<sub>3</sub> unit cells. On SrTiO<sub>3</sub>(110), this even distorts the crystal shapes and introduces an additional strain detectable by photoluminescence (PL). Our observations can be explained if the interfacial van der Waals (vdW) bonding between MoS<sub>2</sub> monolayers and SrTiO<sub>3</sub> is greatest when maximum commensuration between the lattices is achieved. Therefore, a key finding of this study is that the vdW interaction between MoS<sub>2</sub> and SrTiO<sub>3</sub> substrates determines the supported crystal shapes and orientations by epitaxial relations.

Monolayer MoS<sub>2</sub> is also a wide-bandgap semiconductor suitable for use in high-temperature electronics. It is therefore important to understand its thermal stability. In the second part, we uncover the thermal degradation behavior of monolayer MoS<sub>2</sub> supported on SrTiO<sub>3</sub> in ultrahigh vacuum (UHV) because of sulfur loss. MoS<sub>2</sub> was found to degrade on the (111), (110), and (001) terminations of SrTiO<sub>3</sub> substrates in a similar way. The sulfur loss begins at 700 °C, at which point triangular etch trenches appear along the sulfur-terminated edge directions of the MoS<sub>2</sub> crystals (in scanning tunneling microscopy). The sulfur vacancies can be filled by annealing the crystals in a hot sulfur atmosphere, and the optical properties (by Raman spectroscopy and PL) of monolayer MoS<sub>2</sub> can nearly be fully recovered. At higher UHV annealing temperatures, the remaining Mo is oxidized by the SrTiO<sub>3</sub> substrates into MoO<sub>2</sub> and MoO<sub>3</sub>. The initial sulfur loss and the formation of MoO<sub>x</sub> are confirmed by X-ray photoelectron spectroscopy. The sulfur annealing no longer takes effect when all the Mo has been oxidized, which happens at a temperature

between 800 °C and 900 °C in UHV. The MoS<sub>2</sub> crystal shapes are stable upon annealing until the residual MoO<sub>3</sub> particles evaporate at above 1000 °C. This infers that any triangular crystals that look intact under low-magnification optical microscopy and SEM may not mean pristine MoS<sub>2</sub>.

9:00am **2D+EM+MI+NS-MoM3 3D Printed and Injection Molded Polymer Matrix Composites with 2D Layered Materials**, *Sangram Mazumder*, University of North Texas; *J.A. Catalan*, University of Texas at El Paso; *N. Hnatchuk, I. Chen*, University of North Texas; *P. Perez*, University of Texas at El Paso; *W. Brostow, A.B. Kaul*, University of North Texas

The two-dimensional layered materials (2DLMs), MoS<sub>2</sub> and WS<sub>2</sub>, as well as three-dimensional (3D) graphite were infused in thermoplastic polymer matrices, specifically acrylonitrile butadiene styrene (ABS) and polyethylene terephthalate glycol (PETG). Two techniques were explored for the production of these composites into dog-bone structures for mechanical testing, which included 3D printing and injection molding. The ductility of the composites was generally seen to decrease with the addition of the fillers compared to the otherwise ductile polymer matrix counterparts. Also, changes in Young's modulus, yield and tensile strengths, as well as percent strain at fracture, were analyzed as a function of filler loadings. The effect of processing technique on microstructures was also investigated by scanning electron microscopy of the fracture surfaces which revealed the presence of microstructural defects in the form of voids in the injection molded samples, which act as stress concentrators in the composite samples. Additionally, dynamic friction data of the composites was measured in an attempt to exploit the traditional, inherent solid phase lubricating properties of the 2DLMs. Graphite was indeed seen to lower dynamic friction in case of 3D printed PETG and injection molded ABS. Also, MoS<sub>2</sub> and WS<sub>2</sub> were found to reduce friction in 3D printed PETG and ABS. Graphite being an intrinsically good conductor, while the other 2DLMs explored, specifically MoS<sub>2</sub> and WS<sub>2</sub> given their semiconducting nature, can also be used as avenues for introducing electrical conductivity within these otherwise insulating parent polymer matrices. Thermal conductivity was also found to increase in both ABS and PETG composites containing graphite, MoS<sub>2</sub> and WS<sub>2</sub>, irrespective of their processing routes. The use of 2DLM-based polymer composites remains an area that is bound to open up avenues for a wide range of applications in the future related to wearable electronics and sensors with low-cost additive manufacturing approaches.

9:20am **2D+EM+MI+NS-MoM4 Semiconducting WS<sub>2</sub> and h-BN Inks for Printing Optically-active Nanodevices**, *Jay A. Desai*, University of Texas at El Paso; *S. Mazumder, A.B. Kaul*, University of North Texas

We present our work on dispersions of WS<sub>2</sub> and h-BN using cyclohexanone and terpineol (C/T) as the solvent to subsequently print prototype nanodevices. Current-voltage measurements, Raman spectroscopy, and photoluminescence spectroscopy were used to characterize the properties of these inks produced by various sonication techniques such as horn tip sonication, magnetic stirring and shear mixing. Both photodetector and capacitive heterostructure devices were formed with these materials. From this analysis, the photoresponsivity and detectivity of the graphene-WS<sub>2</sub>-graphene heterostructure devices were calculated to be ~ 0.86 A/W and ~ 10<sup>13</sup> J, respectively. Capacitance-voltage (C-V) and C-frequency (f) measurements were also conducted, where the V was swept from - 6 V to + 6 V, while the change in C was measured from f ~ 20 kHz up to 3 MHz to gain insights into the nature of the graphene-WS<sub>2</sub> interface. An all-inkjet-printed graphene-h-BN-graphene capacitors were fabricated and leakage current density, *J<sub>Leakage</sub>*, of up to ~ 0.072 μA/mm<sup>2</sup> and *capacitance density* of up to ~ 2.4 μF/cm<sup>2</sup> is reported. Finally, the influence of temperature, frequency, and LED illumination on the performance of the graphene-h-BN-based capacitor is explored with the help of *capacitance density*-voltage measurements at different parameters to promote the all-inkjet-printed capacitor for photosensitive detector applications.

10:40am **2D+EM+MI+NS-MoM8 Engineering Interfaces in the Atomically-Thin Limit**, *Deep Jariwala*, University of Pennsylvania **INVITED**

The isolation of a growing number of two-dimensional (2D) materials has inspired worldwide efforts to integrate distinct 2D materials into van der Waals (vdW) heterostructures. While a tremendous amount of research activity has occurred in assembling disparate 2D materials into "all-2D" van der Waals heterostructures, this concept is not limited to 2D materials alone. Given that any passivated, dangling bond-free surface will interact with another via vdW forces, the vdW heterostructure concept can be extended to include the integration of 2D materials with non-2D materials that adhere primarily through noncovalent interactions. I will present our work on emerging mixed-dimensional (2D + nD, where n is 0, 1 or 3)

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heterostructure devices. Two distinct examples of gate-tunable p-n heterojunctions with anti-ambipolar field effect will be presented. The anti-ambipolar field effect observed in the above systems is also shown generalized to other semiconducting heterojunction systems and extended over large areas with practical applications in wireless communication circuits. Recent work on high performance 2D/3D triodes will also be presented.

The second part of talk will focus on engineering interfaces on photovoltaic devices from 2D semiconductors such as transition metal dichalcogenides (TMDCs). High efficiency inorganic photovoltaic materials (e.g., Si, GaAs and GaInP) can achieve maximum above-bandgap absorption as well as carrier-selective charge collection at the cell operating point. Experimental demonstration of light confinement in ultrathin (< 15 nm) Van der Waals semiconductors (MoS<sub>2</sub>, WS<sub>2</sub> and WSe<sub>2</sub>) leading to nearly perfect absorption will be demonstrated concurrently with record high quantum efficiencies. Ongoing work on addressing the key remaining challenges for application of 2D materials and their heterostructures in high efficiency photovoltaics which entails engineering of interfaces and open-circuit voltage will be presented in addition to on going work on probing of buried metal/semiconductor interfaces with sub 50 nm resolutions as well as near field luminescence spectroscopy. I will conclude by giving a broad perspective of future work on 2D materials from fundamental science to applications.

**11:20am 2D+EM+MI+NS-MoM10 Ultrasoft Slip-mediated Bending in Few-layer Graphene, Jaehyung Yu, E. Han, E. Annevelink, J. Son, E. Ertekin, P.Y. Huang, A.M. van der Zande, University of Illinois at Urbana-Champaign**

A challenge and opportunity in nanotechnology is to understand and take advantage of the breakdown in continuum mechanics scaling laws as systems and devices approach atomic length scales. Such challenges are particularly evident in two-dimensional (2D) materials, which represent the ultimate limit of mechanical atomic membranes as well as molecular electronics. For example, after more than a decade of study, there is no consensus on the bending modulus of few layer graphene, with measured and predicted values ranging over two orders of magnitude, and with different scaling laws. However, comparing these studies is challenging because they probe very different and often fixed curvatures or magnitudes of deformation. To unravel the discrepancy, a systematic measurement of bending stiffness versus deformation is needed. The results have practical implications on predicting and designing the stiffness of many 2D mechanical systems like origami/kirigami nanomachines, stretchable electronics from 2D heterostructures, and resonant nanoelectromechanical systems.

In this study, we combine atomistic simulation and atomic scale imaging to theoretically and experimentally examine the bending behavior of few-layer graphene. First, we experimentally probe the nanoscale bending by laminating few-layer graphene over atomically sharp steps in boron nitride and imaging the cross-sectional profile using aberration-corrected STEM. Second, we use DFT simulations to examine the bending of few-layer graphene under compression. By measuring the nanoscale curvatures, we extract the simulated and experimental bending modulus while varying both the number of layers and the degree of nanoscale curvature.

We find remarkable agreement between the theory and experiment and observe an unexpected curvature dependent bending stiffness of few-layer graphene that deviates from continuum scale bending mechanisms. We find that the bending stiffness of few layer graphene versus curvature corresponds with a gradual change in scaling power with thickness from cubic to linear. We find that the transition in scaling behavior originates from a transition from shear, slip and the onset in superlubricity between the graphene layers at the van der Waals interface, verified by a simple Frenkel-Kontorova model. Our results provide a unified model for the bending of 2D materials and show that their multilayers can be orders of magnitude softer than previously thought, among the most flexible electronic materials currently known.

## Biomaterial Interfaces Division

### Room A120-121 - Session BI+AS+NS-MoM

#### Biofabrication, Bioanalytics, Biosensors, Diagnostics, Biolubrication and Wear

**Moderators:** Joe Baio, Oregon State University, Caitlin Howell, University of Maine

**8:20am BI+AS+NS-MoM1 Bio-inspired Peptide-polymer Hybrid Mucin Analogues: Applications in Osteoarthritis and Kidney Stone Disease, Daniel L. French, L.A. Navarro, S. Zauscher, Duke University**

Mucins play diverse and crucial roles in the body. These functions range from lubrication of articular joints and the eye, to protection of stomach endothelium, to modulation of oral and gut microflora populations. Despite their diversity, these functions commonly stem from modifications in a general structure shared by all mucins: a blocky polypeptide backbone comprised of terminal moieties for binding surfaces or crosslinking and a characteristic glycosylated bottlebrush. Inspired by this adaptable structure, we have created a mucin analogue platform which engenders key structural features preserved among native mucins. We have emulated the mucinous bottlebrush with a lysine-rich elastin-like polypeptide backbone, which provides primary amines for conjugation of synthetic polymer "bristles." Binding modules target surfaces of interest, to facilitate intramolecular associations, or to direct surface conformation of our construct. To demonstrate the application of our platform to clinically-relevant problems, we have tailored our mucin analogues to osteoarthritis and kidney stone disease, conditions infamous for profound morbidity and high prevalence. We will demonstrate that collagen-targeted mucin analogues adsorb to model surfaces and prevent protein fouling. This recapitulates the function of lubricin, a mucin downregulated in osteoarthritis. Similarly, we will show that we can target mineral surfaces relevant in kidney stone disease by exchanging the binding module of our analogue mucins. We will show that these altered analogues also inhibit protein-fouling, which is implicated in stone growth. In this platform technology, we have been inspired by the diverse functions of native mucins. By harnessing the general structure which gives rise to these properties, we endeavor not only to replicate the in vivo function of mucins, but also to harness the properties of natural mucins and apply them to systems not naturally protected by mucinous coatings, such as inhibiting the growth of kidney stones.

**8:40am BI+AS+NS-MoM2 Investigation of the Mechanical and Dielectric Properties of Bone Scaffolds, Kimberly Cook-Chennault, Rutgers University**

Despite the vast number of biomaterials and synthesis technologies available to treat bone defects and disease, few are readily employed for clinical use due in part to challenges in the development of materials that functionally mimic and facilitate the hierarchical processes of bone healing and regeneration. Calcium phosphate based bone replacement materials have been developed over the years for bioengineered bone structures due to their ability to mimic the general properties of mineralized bone. These bone replacement materials have mainly been fabricated in the form of hydroxyapatite (Hap), which can suffer from premature fracture when subjected to typical human load conditions. On the other hand, it is well known that enhanced osteobonding and bone growth results from the exposure of the bone to polarized Hap, which presents a negatively charged surface. Composite hydroxyapatite (Hap) – barium titanate scaffold materials are compared and contrasted with hydroxyapatite (Hap) samples for mechanical elastic moduli, compression strength and dielectric properties. Composite structures were observed to present better mechanical and dielectric properties when compared to Hap samples. For example, the elastic modulus of the Hap and composite samples were 2655.4 MPa and 3559.1 MPa, respectively. Understanding the interrelationship between scaffold architecture/material composition and mechano-transduction will improve our ability to realize patient specific solutions that eliminate hindrances to bone healing such as, lack of vascularization and lack of adequate mechanical stability.

**9:00am BI+AS+NS-MoM3 Bioelectronics with Graphene and Graphene-Based Hybrid-Nanomaterials – From Transparent to Fuzzy Interfaces, Tzahi Cohen-Karni, Carnegie Mellon University** **INVITED**

We focus on developing a new class of nanoscale materials and novel strategies for the investigation of biological entities at multiple length scales, from the molecular level to complex cellular networks. Our highly flexible bottom-up nanomaterials synthesis capabilities allow us to form unique hybrid-nanomaterials. Recently, we have demonstrated highly-controlled synthesis of 3D out-of-plane single- to few-layer fuzzy graphene

(3DFG) on a Si nanowire (SiNW) mesh template. By varying graphene growth conditions, we control the size, density, and electrical properties of the NW templated 3DFG (NT-3DFG). This flexible synthesis inspires formation of complex hybrid-nanomaterials with tailored optical and electrical properties to be used in future applications such as biosensing, and bioelectronics. Currently, we target the limits of cell-device interfaces using out-of-plane grown 3DFG, aiming at electrical recordings with subcellular resolution ( $<5\mu\text{m}$ ). Moreover, NT-3DFG unique optical properties allows formation of remote interfaces with tissue and cells. We demonstrate photostimulation of tissue and cells by using the photothermal effect of NT-3DFG. Last, we have developed a unique transparent graphene-based electrical platform that enables concurrent electrical and optical investigation of ES-derived cardiomyocytes' intracellular processes and intercellular communication. In summary, the exceptional synthetic control and flexible assembly of nanomaterials provide powerful tools for fundamental studies and applications in life science, and open up the potential to seamlessly merge either nanomaterials-based platforms or unique nanosensor geometries and topologies with cells, fusing nonliving and living systems together.

9:40am **BI+AS+NS-MoM5 Experimental Observation of Multiple Plasmon Induced Transparency and Fano Resonance in Titanium Nitride Based Devices**, *J.D. Asencios, Arturo Talleo, R.A. Moro, C.A. Luyo*, Facultad De Ciencias Universidad Nacional De Ingeniería, Perú

Abstract: We built three types of plasmonic structures based on titanium nitride thin films by using the technique dc magnetron sputtering and D-shaped prisms as substrates. The prisms were made of glass or sapphire. Devices with structure Prism/TiN, Prism/TiN/SiO<sub>2</sub> and Prism/TiN/SiO<sub>2</sub>/Nb<sub>2</sub>O<sub>5</sub> were called devices type 1, type 2 and type 3, respectively. Attenuated Total Reflection in the Kretschmann configuration was studied in the three types of devices. Experimental angular spectra were fitted by using a calculation program based on the solutions to Maxwell equations. ATR spectra of devices type 1 show a wide absorption band. The main feature for ATR spectra of devices type 2 was a series of maxima and minima of reflectance within a wide absorption band. ATR spectra of devices type 3 are identified with a very sharp window within the absorption band. The spectra of devices type 2 and type 3 were associated with the phenomena of Multiple Plasmon Induced Transparency (MPIT) and Fano Resonance, respectively. Based on calculations of the square of the electric fields in the involved media, we proposed some simple phenomenological explanations for the phenomena of MPIT and Fano resonance. Potential use of these structures as refractive-index sensors was also discussed.

10:00am **BI+AS+NS-MoM6 Breaking the Mass Resolution Limit of Shear Wave Resonators in Liquid through Integrated Microfluidic Channels**, *Z. Parlak, S. Zhao, D.L. French, Stefan Zauscher*, Duke University

Acoustic shear wave resonator sensors (SWRS), e.g., quartz crystal microbalance, are widely used in applications (e.g., thin film deposition) where their high quality factor in air or vacuum provides exquisite mass resolution. SWRS are also used as biosensors in liquid environments; however, they have not yet found widespread use outside the research environment despite their simple and robust detection modality. This is because current SWRS suffer from viscous contributions to shifts in resonance frequency, which inherently leads to low mass resolution. Furthermore, current SWRS require accurate temperature control and use large liquid volumes ( $\sim\text{ml}$ ). Together these limitations prohibit accurate and economic measurement of surface bound mass, e.g., in protein binding assays. We show through experiments and simulations that by confining fluid into small, rigid channels oriented perpendicularly to the shear direction of the SWRS, we can manipulate liquid to behave as a lossless layer and thus perform precise mass measurements of the confined liquid. Canceling viscous effects in  $\mu$ -fluidic SWRS not only enhances their mass resolution in liquid to levels observed in air/vacuum, but also enables efficient device miniaturization. Combined with the extremely small volume requirements for sensing ( $\sim\text{nL}$ ), we show that  $\mu$ -fluidic SWRS can overcome current barriers for their widespread use in diagnostic sensing and point of care applications.

11:20am **BI+AS+NS-MoM10 All Inkjet Printed Biosensor for Easy and Rapid Detection of Immunoglobulin G (IgG) Protein**, *Ridwan Fayaz Hossain, A.B. Kaul*, University of North Texas

Protein detection biosensors are interesting tools for detecting and measuring the levels of specific proteins in biological and environmental samples, offering certain operational advantages over standard photometric methods, notably with respect to rapidity, ease-of-use, cost,

simplicity, portability, and ease of mass manufacture. Although inkjet printed electrode based sensor is widely reported, the number of fully inkjet printed biosensors is still limited [1,2]. Here, we report the design, fabrication, and evaluation of a flexible field-effect transistor (FET) for biosensing based on the inkjet printing technique, where the insulator layer is uniquely functionalized for Immunoglobulin G (IgG) protein detection. IgG is a plasma-cell protein that is produced within the lymph nodes, spleen, bone marrow, respiratory tract mucosa, tissue, etc. Since IgG protein is produced as part of the body's response to bacteria, viruses, and tissue antigens, measurement of blood IgG levels can reveal any of the body's abnormal conditions. Until now, proteins are detected mostly by antibodies in analytical formats like ELISA, immunobead assay, western blotting, and microarrays, etc. but their performance is limited by low sensitivity. This new generation biosensor is more stable and well adapted to the conditions of real samples. The protein detection biosensor reported here represents an important starting point for the design and fabrication of flexible, rapid detection biosensing devices by inkjet printing. This work shows a promising aspect of protein detection that will pave the way for the development of a fully functional device for point-of-care diagnosis.

## Reference:

[1] Jensen, G. C., Krause, C. E., Sotzing, G. A., & Rusling, J. F. (2011). Inkjet-printed gold nanoparticle electrochemical arrays on plastic. Application to immunodetection of a cancer biomarker protein. *Physical Chemistry Chemical Physics*, 13(11), 4888-4894.

[2] Carvajal, S., Fera, S. N., Jones, A. L., Baldo, T. A., Mosa, I. M., Rusling, J. F., & Krause, C. E. (2018). Disposable inkjet-printed electrochemical platform for detection of clinically relevant HER-2 breast cancer biomarker. *Biosensors and Bioelectronics*, 104, 158-162.

11:40am **BI+AS+NS-MoM11 Biosensing Applications of Silver Nanorods Array Fabricated by Glancing Angle Deposition (GLAD)**, *Shashank Gahlaut*, Indian Institute of Technology Delhi, India

Silver being most widely used material due to its unique electrical and optical properties. Here we have investigated biosensing properties of silver nanorods array (AgNRs) fabricated by glancing angle deposition. GLAD grown silver nanorods are found to be highly sensitive and selective for hydrogen sulfide (H<sub>2</sub>S) gas. Color and water wetting (contact angle) of AgNRs array are parameters affected in the presence of this gas. H<sub>2</sub>S is one the major gaseous products evolved in bacterial metabolic process. On the basis of H<sub>2</sub>S production, we have shown the detection of viability as well as antibiotic resistance in different strains of bacteria.

Another potential application of as synthesized AgNRs array in Surface enhanced Raman scattering (SERS) based detection. The dengue is a viral disease and a serious global health concern. About 2.5 billion of world's population has been living at the risk of dengue infection. It causes a spectrum of illness ranges from acute febrile illness called dengue fever (DF) to more severe life threatening forms dengue hemorrhagic fever (DHF) and dengue shock syndrome (DSS) causing vascular leakage that may lead to death. So far, neither specific treatment nor effective vaccine available for the prevention and treatment. Therefore, early detection is the key of the survival of the patients. The earlier symptom starts with mild dengue fever, at this stage the concentration of the biomarkers are very less which pose a problem in early detection. In the present study, we have demonstrated the detection of dengue from clinical blood samples employing AgNRs array as SERS substrates with hand held Raman spectrometer. A notable change in SERS spectral signature observed in the blood of dengue infected patients in comparison to that of healthy subject. This change was further confirmed using the statistical tool principal component analysis (PCA) and the samples were differentiated as healthy, dengue positive and dengue negative. All the blood samples were also dually verified with Antigen (NS1) as well as Antibody (IgM) ELISA kit. This method provides a field deployable, rapid diagnosis of dengue at its early stage.

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## Materials and Processes for Quantum Information, Computing and Science Focus Topic

Room B231-232 - Session QS+EM+MN+NS-MoM

### High Coherence Qubits for Quantum Computing

**Moderators:** Vivekananda Adiga, IBM, T.J. Watson Research Center, Matteo Mariantoni, University of Waterloo, Canada

8:20am **QS+EM+MN+NS-MoM1 Measurement of a Two-Level-System Dipole Distribution in a Nanoscale Aluminum Oxide Barrier**, *Chih-Chiao Hung, N. Foroozani, K. Osborn*, University of Maryland

Random atomic-sized material defects, identified as two-level systems (TLS), have garnered wide interest because they cause decoherence in superconducting qubits. TLSs often arise in the nonlinear element, the Josephson junction, which is typically made of amorphous aluminum oxide. This material is a clear concern in qubits due to a substantial loss tangent in bulk: large area JJs. However, detail on the dipole moments of individual TLSs is generally lacking but is fundamental to defect-qubit coupling. We have recently developed a method to study individual dipole moments in thin dielectric films with a quantum regime resonator using an electrical bridge of capacitors. We have now extended this technique to a different material, aluminum oxide, using a smaller nanoscale thicknesses and barrier volume. The geometry of the device allows extraction of the individual dipole moments within the central layer of a superconductor-aluminum oxide-superconductor trilayer. This new study also produced a greater statistical sample of TLS dipoles than previous work. Preliminary analysis allows us to extract a dipole moment distribution with a clear mean value. This information on aluminum oxide can be used in the future modeling of qubits and the future characterization of qubit materials.

8:40am **QS+EM+MN+NS-MoM2 Mapping Quantum Systems to Quantum Computers using Symmetry**, *Daniel Gunlycke, S. Fischer, C.S. Hellberg, S. Policastro, S. Tafur*, U.S. Naval Research Laboratory

Quantum entanglement is a natural phenomenon in quantum mechanics that has enormous significance in quantum information science, including quantum computing. It enters quantum states in quantum algorithms through the application of multi-qubit quantum logic operations such as the CNOT and Ising gates. While deliberate entanglement adds power and efficiency to algorithms, unintentional entanglement can be undesirable for a variety of reasons. Unintentional entanglement adds complexity, making the outcome of a given algorithm more difficult to understand, as well as more sensitive to errors. Furthermore, it can be an indication that an algorithm has not been optimized. If we could transfer entanglement from our algorithms into the bases that define our systems, then we could potentially reduce our algorithms, including the qubit requirement. Such algorithm reductions will be of outmost importance for resource-limited, noisy intermediate-scale quantum (NISQ) computers.

In this presentation, we will demonstrate how such a reduction could be achieved for the simulation of quantum systems using symmetry. In addition to reducing the needed resources, our quantum computer calculations show a significant improvement in accuracy.

9:00am **QS+EM+MN+NS-MoM3 History of Superconducting Qubit Coherence and the Current Challenges**, *Hanhee Paik*, IBM T.J. Watson Research Center **INVITED**

Since the first demonstration of a few nanoseconds of coherent oscillations in 1999, a tremendous amount of effort has been put in to improve coherence of superconducting qubits. A modern day superconducting qubits show typically 100 microseconds of coherence times which allowed us to demonstrate a few simple quantum computing applications that led rapid growth of quantum computing industry. To build a full fault-tolerant universal quantum computing system, however, we still need a couple more orders of magnitude improvement in the superconducting qubit coherence, the solution to which, we believe, is in the qubit materials. In this talk, I will review the history of the superconducting qubit coherence research and what we learned about the materials for quantum computing at milli-kelvin temperatures, and I will discuss the current challenges of the coherence studies in the conjunction with the challenges in material science research.

9:40am **QS+EM+MN+NS-MoM5 Loss and Decoherence Benchmarking of Superconducting Transmon Qubits**, *Jonas Bylander*, Chalmers University of Technology, Sweden **INVITED**

We are engineering a superconducting quantum processor within the Wallenberg Center for Quantum Technology [1] in Sweden and the project OpenSuperQ [2] of the European Union's Flagship on Quantum Technology.

Here we will present our engineering approach for high-coherence superconducting quantum hardware. We have studied the temporal stability of relaxation and dephasing in transmon qubits [3]. Our qubits are made of aluminum on silicon; they have reached average  $T_1$  relaxation times of about 70  $\mu$ s. The  $T_2^*$  decoherence time, as measured in a Ramsey fringe, is practically relaxation-limited. By collecting statistics during measurements spanning several days, we reveal large fluctuations of qubit lifetimes – the standard deviation of  $T_1$  is about 15  $\mu$ s – and find that the cause of fluctuations is parasitic, near-resonant two-level-systems (TLS). Our statistical analysis shows consistency with an interacting-TLS model. Interacting TLS also cause low-frequency capacitance fluctuations, ultimately leading to frequency noise and dephasing of the qubit state. These discoveries are important for creating stable superconducting circuits suitable for high-fidelity quantum gates in quantum computing applications.

[1] [www.wacqt.se](http://www.wacqt.se)

[2] [www.opensuperq.eu](http://www.opensuperq.eu)

[3] J. J. Burnett, A. Bengtsson, M. Scigliuzzo, D. Niepce, M. Kudra, P. Delsing, and J. Bylander, "Decoherence benchmarking of superconducting qubits" arXiv:1901.04417

10:40am **QS+EM+MN+NS-MoM8 Towards PAMBE Grown Nitride Superconductors for Epitaxial Josephson Junctions and Quantum Circuits**, *Christopher Richardson, A. Alexander, C. Weddle*, Laboratory for Physical Sciences; *M. Olszta, B. Arey*, Pacific Northwest National Laboratory **INVITED**

Low microwave loss superconducting circuit components are a necessity of fabricating high-fidelity superconducting qubits. Accordingly, significant research has focused on making high-quality planar resonators from elemental and nitride superconductors. Josephson junctions are the nonlinear component of superconducting qubits, that also need to be high performance. Interestingly, superconducting qubits all use Josephson junctions fabricated from aluminum and aluminum oxide using the double angle evaporation process. Details of this alternative design will be presented.

Plasma assisted Molecular beam epitaxy (PAMBE) is used to grow niobium titanium nitride alloys ( $\text{Nb}_x\text{Ti}_{1-x}\text{N}$ ) and wide bandgap nitride (AlN) superconductors directly on sapphire wafers. This combination of nitride materials provides sufficient degrees of freedom that synthesis of an epitaxial Josephson junction may be possible. Using a structure first approach to design optimization, the structural, surface topology, chemical characteristics, and superconducting critical temperature of these films are used for optimization of the growth conditions before resonators are fabricated and tested.

Growth results of NbTiN and AlN films, bi-layer insulator-superconductor structures and trilayer superconductor-insulator-superconductor structures will be presented along with superconducting properties.

11:20am **QS+EM+MN+NS-MoM10 Josephson Junction Metrology for Superconducting Quantum Device Design**, *Ruichen Zhao, M. Bal, J.L. Long, R.E. Lake, X. Wu, C. Rae McRae, H.-S. Ku, H. Wang, D.P. Pappas*, National Institute of Standards and Technology (NIST)

Josephson junctions (JJs) are the power horses that drive the development of superconducting quantum technologies in the past decades. The non-linear inductance of JJs turns superconducting circuitry into a high-coherence two-level system that forms the foundation for quantum information processing [1]. They also enable Josephson parametric amplification that significantly improves the measurement of the fragile quantum state of superconducting qubits, mechanical oscillators or spins [2]. Consequently, the characterization of junction inductance becomes essential for the design and fabrication of these superconducting quantum devices.

Here, we present a systematic approach to characterize the micron-size JJs made from a new process. This new recipe extends from our previous work on nanoscale overlapping qubit junctions [1]. First, we collect statistics of the normal-state resistance over 2000 JJs through the room-temperature automated probing test. Second, we use Ambegaokar-baratoff formula to map the normal-state junction resistance into Josephson inductance [3]. Then we extract and investigate the process bias of our JJs. Based on this new information of JJs variation, we proposed a new JJ process which could potentially provide better control over the Junction inductance and therefore, deliver more reliable parameters for the device design.

[1] X. Wu, et al. "Overlap junctions for high coherence superconducting qubits." Applied Physics Letters 111.3: 032602 (2017).

# Monday Morning, October 21, 2019

[2] M. Malnou, et al. Optimal operation of a Josephson parametric amplifier for vacuum squeezing. *Physical Review Applied*, 9(4), 044023 (2018).

[3] V. Ambegaokar, & A. Baratoff, "Tunneling between superconductors." *Physical Review Letters*, 10(11), 486 (1963).

11:40am **QS+EM+MN+NS-MoM11 Superconducting Metamaterial Resonator Spectrum and Interaction with Qubit**, *Haozhi Wang, S. Indrajeet, M.D. Hutchings, M. LaHaye, B.L.T. Plourde*, Syracuse University; *B. Taketani, F. Wilhelm*, Saarland University

Metamaterial transmission line resonators fabricated from superconducting thin films can be designed to exhibit novel mode spectra like a high density of modes in the same frequency range where superconducting qubits are typically operated. We demonstrate the mode spectrum of a metamaterial resonator made of single layer of Nb and the coupling quality factor of the modes. We also present a series of low-temperature measurements of such a superconducting metamaterial resonator coupled to a flux-tunable transmon qubit. We observe Rabi vacuum crossing when performing transmission measurement of the metamaterial resonator as we tune the qubit frequency through many of the metamaterial resonances and we are able to track the qubit using a separate conventional resonator to read out the qubit state.

## 2D Materials

### Room A226 - Session 2D+AP+EM+MI+MN+NS+PS+TF-MoA

#### Nanostructures including Heterostructures and Patterning of 2D Materials

**Moderator:** Deep Jariwala, University of Pennsylvania

##### 1:40pm 2D+AP+EM+MI+MN+NS+PS+TF-MoA1 Tailoring and Patterning 2D Material Interfaces Through Chemical Functionalization, *Arend van der Zande*, University of Illinois at Urbana-Champaign

INVITED

Two-dimensional materials are all surface, so any change in the surface chemistry affects the entire material. This offers a challenge and an opportunity to engineering the material properties and new device behavior. There are many strategies to altering the chemical structure of 2D materials, yet one of the most successful is the chemical functionalization with low energy plasmas such as hydrogen and fluorine. Functionalization enables phase changes within materials to dramatically alter their properties, can be applied post synthesis and device fabrication, and is compatible with lithography for spatial patterning. Most studies of chemical functionalization focus on single functionalization of single 2D materials, yet there are many opportunities when applying the principles of chemical functionalization to spatially engineer the properties through in plane interfaces or out of plane in heterostructures.

First, we will examine selective etching with XeF<sub>2</sub> to pattern heterostructures using graphene etch stops. These techniques are self-limiting, yet scalable, and enable the patterning of 2D heterostructures into 3D multilayer circuitry. Moreover, devices like encapsulated graphene transistors fabricated with these techniques have exceptionally low contact resistances and mobilities which approach theoretical limits.

Second we will present a new strategy for tailoring the stoichiometry of functionalized graphene compounds through the systematic control of the ratio between adatoms. We demonstrate new ternary HFG compounds and reversible switching of material stoichiometry via the sequential exposure of graphene to low energy H plasma and XeF<sub>2</sub> gas. By patterning regions of different functionalization on a single chip, we perform direct comparisons and show spatially controlled tuning of the relative surface properties such as wettability, friction, electronic conductivity and molecular adhesion. Taken together, these studies show that chemical functionalization offers new atomically precise nanofabrication and materials engineering techniques for scalable engineering of circuitry along all three dimensions.

##### 2:20pm 2D+AP+EM+MI+MN+NS+PS+TF-MoA3 Dual-Route Hydrogenation of the Graphene/Ni Interface, *Rosanna Larciprete*, CNR-Institute for Complex Systems, Roma, Italy; *D. Lizzit*, Elettra - Sincrotrone Trieste, Trieste, Italy; *M.I. Trioni*, CNR-Institute of Molecular Science and Technologies, Milano, Italy; *P. Lacovig*, *L. Bignardi*, *S. Lizzit*, Elettra - Sincrotrone Trieste, Trieste, Italy; *R. Martinazzo*, Università degli Studi di Milano, Milano, Italy

Although the high surface-to-weight ratio would make graphene (Gr) one of the most promising material for hydrogen accumulation, up to now only moderate gravimetric density values of 1-2% have been obtained at room temperature (RT). The ultimate H coverage is limited by the competition between the adsorption and desorption/abstraction processes and by the elastic energy that accumulates in the C lattice once puckered by the local sp<sup>3</sup> hybridization of the C atoms binding hydrogen. Moreover, for epitaxial Gr on metals, the substrate-induced Gr corrugation might modulates periodically H adsorption. In this respect, the Gr/Ni(111) interface appears much more favorable than other graphene/metal systems, as the limitations due to the presence of the moiré supercell vanish due to commensurate relation between the Gr and Ni(111) lattices. Moreover, hydrogenation might be favored by the peculiar reactivity of Gr/Ni(111). This issues motivated a re-investigation of the interaction of this particular interface with hydrogen.

In this study [1] we used x-ray photoelectron spectroscopy (XPS) and near edge x-ray absorption fine structure spectroscopy (NEXAFS) to follow the RT hydrogenation of Gr/Ni(111) and determined the configuration of the hydrogenated interface by scanning tunneling microscopy (STM). We found that hydrogenation proceeds through a dual path that includes hydrogen chemisorption on top of the graphene followed by a slow but continuous intercalation below graphene. At low coverage H atoms predominantly adsorb as monomers and chemisorption saturates when ≈ 25% of the

surface is hydrogenated. The formation of C-H bonds determines new components in the C 1s core level spectrum that are attributed by DFT calculations to C atoms directly bonded to H and to their first neighbors. In parallel with chemisorption, with a much lower rate, H atoms intercalate below Gr and bind to Ni surface sites. Thermal programmed desorption measurements showed that chemisorbed hydrogen is released around 600 K, whereas the intercalated phase desorbs abruptly slightly below 400 K. Then the Gr cover, besides offering a storage volume for the intercalated H, stabilizes it above room temperature rising by a few tens of kelvins the H<sub>2</sub> release temperature with respect to the bare Ni(111) surface.

The effectiveness of these results can be expanded by using Ni substrates with large specific surface, as nanoparticles or nanostructured foils, which, when covered with Gr, might become media where hydrogen can be loaded and stored above room temperature.

[1] D. Lizzit et al. ACS Nano 13 (2019) 1828

##### 2:40pm 2D+AP+EM+MI+MN+NS+PS+TF-MoA4 Assembly of Arrays of Predefined Monolayer Features into vdW Heterostructure by a Continuous Exfoliate-align-Release Process, *Vu Nguyen*, *H. Taylor*, University of California at Berkeley

One of the major challenges of van der Waals (vdW) integration of 2D materials is the high-yield and -throughput assembly of pre-defined sequence of monolayers into heterostructure arrays. Although a variety of techniques have been developed to exfoliate the 2D materials from the source and deterministically place them onto a target substrate, they typically can transfer only either a wafer-scale blanket or a small flake at a time with uncontrolled size and shape. Here we present a method to exfoliate arrays of lithographically defined monolayer MoS<sub>2</sub> and WS<sub>2</sub> features from multilayer sources and directly transfer them in a deterministic manner onto target substrates. The continuous exfoliate-align-release process, without the need of an intermediate carrier substrate, was enabled by a new transfer medium fabricated by spin-coating a low-crosslinked and transparent adhesive on a transparent, electrostatically active backing material with low surface energy. MoS<sub>2</sub>/WS<sub>2</sub> vdW heterostructure arrays produced by this method were characterized, showing coupled photoluminescence between the monolayers. Light-emitting devices using WS<sub>2</sub> monolayer were also demonstrated, proving the functionality of the fabricated materials. This method promises to produce large-area monolayer and multiplex heterostructure arrays with capability to integrate with existing semiconductor manufacturing equipment.

##### 3:00pm 2D+AP+EM+MI+MN+NS+PS+TF-MoA5 van der Waals Heterojunction Photothermoelectric Effect in MoS<sub>2</sub>/Graphene Monolayers, *Yunqiu Kelly Luo*, The Ohio State University; *T. Zhou*, University at Buffalo, State University of New York; *M. Newburger*, The Ohio State University; *R. Bailey-Crandell*, *I. Lyalin*, The Ohio State University; *M. Neupane*, U.S. Army Research Laboratory; *A. Matos-Abiad*, Wayne State University; *I. Zutic*, University at Buffalo, State University of New York; *R. Kawakami*, The Ohio State University

Two-dimensional (2D) van der Waals (vdW) heterostructures provide a vast playground for exploring new phenomena due to its unique ability to tailor and combine dissimilar materials with atomic precision. In particular, the combination of graphene and transition metal dichalcogenides (TMDC) garners immense interest due to their novel optoelectronic, valleytronic and spintronic properties. Here, we report the observation of a highly tunable vdW heterojunction photothermoelectric effect (HPTE) in dual-gated MoS<sub>2</sub>/graphene heterostructures, identified by a signature six-fold photocurrent pattern as a function of heterojunction bias and carrier density. In stark contrast to photovoltaic and photothermionic effects, we discover a new mechanism arising from photoexcitation of hot electrons in graphene and subsequent thermoelectric transport across the vdW junction. While analogous to lateral photothermoelectric effects at quasi-1D junctions in single layers, the vertical geometry of HPTE offers area scaling of 2D active regions and establishes, for the first time, the photothermoelectric response in vdW heterostructures. Operating at both low (18 K) and room temperatures, the discovery of HPTE creates new

possibilities for electrically-tunable broadband photodetectors and atomically-thin spin caloritronic devices.

3:20pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA6 Formation of Edge-bonded MoS<sub>2</sub>-graphene Nanoribbons by On-surface Synthesis**, *Mark Hastrup, M. Mammen, J. Rodríguez-Fernández, J.V. Lauritsen*, Aarhus University, Denmark

2D materials exhibiting unique material properties have the potential for a huge impact on our future. Graphene, as the first discovered truly 2D material, has been extensively studied. However, the lack of an intrinsic band gap makes it inadequate for electronic and optical devices. MoS<sub>2</sub> from the family of transition metal dichalcogenides has been intensively investigated for its possibility to be used in future applications. The vision is to integrate various 2D materials to realise an actual device. However, the actual assembly of these materials with high controllability remains a challenge. Vertical heterostructures, supported by Van der Waals interactions, have already been realised by manually stacking 2D materials on top of each other [1]. An ultimate thin device can be realised by creating lateral heterostructures with atomically sharp interfaces where each material is directly bonded to another. Currently, methods for in-plane bonding of MoS<sub>2</sub> to other materials (e.g. graphene) are limited due to poor structural match. One possible solution is to develop selective bottom-up methods for synthesis of molecular nanostructures by self-assembly.

This study aims to investigate the fundamental nature of bonding of graphene nanoribbons (GNRs) to the edges of MoS<sub>2</sub> nanoparticles by scanning tunnelling microscopy (STM). The aim is to synthesise GNRs from precursor molecules through a thermally activated Ullmann reaction already used elsewhere [2,3]. After initial growth of MoS<sub>2</sub>, it is necessary to anneal in a hydrogen atmosphere to activate the edges to facilitate the attachment of an intermediate structure of poly(para-phenylene) (PPP) wires. STM reveals the PPP wires have an affinity for the corners of the MoS<sub>2</sub> nanoparticles with a distance, obtained from line scans across the adsorption site, consistent with a covalent C-S bond.

[1]: Pant et al., *Nanoscale*, 2016, 8, 7, 3870-3887

[2]: Cai et al., *Nature*, 2010, 466, 7305, 470-473

[3]: Basagni et al., *J. Am. Chem. Soc.*, 2015, 137, 5, 1802-1808

4:00pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA8 The Effects of Metal-modification and Two Dimensional (2D) Lamellar Structure on Catalytic Performance of MFI Zeolite for Ethylene Conversion into Liquid Aromatics**, *Laleh Emdadi, L. Mahoney, D. Tran, I. Lee*, US Army Research Laboratory

The effects of two dimensional (2D) meso-/microporous structure and metal modification with gallium or zinc on catalytic performances of lamellar MFI zeolites in ethylene conversion reaction to liquid aromatics were investigated. Dual template technique was used to synthesise the 2D zeolite and metal modification of the zeolite was carried out by wet impregnation method. The results of multiple analysis techniques such as TEM, XRD, Ar adsorption-desorption, UV-Visible spectroscopy, and H<sub>2</sub>-TPR showed that the zeolite structure is a pivotal factor for controlling the type of metal dopant species forming on zeolite, their size, and their distribution. Adding metal dopants to 2D zeolite structures improved the yield of liquid aromatics and selectivity for mono-benzene alkylated aromatics compared to their microporous commercial MFI analogies while decreased the coke formation rate. Zinc loaded lamellar MFI had the most efficient catalytic performance among all studied catalysts with lowest amount of total coke and highest fraction of light coke including mono-benzene alkylated aromatics determined by combination of different techniques such as FTIR, UV-Vis, MS-temperature programmed oxidation (TPO), FTIR-TPO, and GC-MS. This can be explained by higher accessibility of reactants to active sites and facilitated transport of products and coke precursors from lamellar structure of this zeolite and the lower Brønsted/Lewis acid site ratio of this catalyst provided by metal modification which is more suitable for ethylene aromatization and suppresses the formation of heavy coke species. The catalytic performance of zeolite catalyst can be tuned by modulating both the textural and acidity properties of the zeolite structure. The metal modified 2D lamellar MFI zeolites as bifunctional catalysts open an avenue for converting large reactant molecules to desired products by designing a catalyst with an optimal structure, acidity, and dispersion of metal dopants.

4:20pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA9 Structural Stability of Graphene Nanoflakes: From the View Point of Aromaticity**, *M. Ushirozako, H. Matsuyama, A. Akaishi, Jun Nakamura*, The University of Electro-Communications (UEC-Tokyo), Japan

Recently, nano-scale graphene nanoflakes (GNFs) have attracted great attention as one of the promising materials for electronics and spintronics. Kim *et al.* have successfully fabricated GNFs with various sizes up to 35 nm and have reported that the photoluminescence property of GNFs depends on the size and the edge shape [1]. From the view point of the structural stability of GNFs, we have not yet acquired the systematic comprehension with regard to effects of shapes and sizes of GNFs on the stability. In the present study, we have examined how the stability of GNFs is dominated by the edge shape and the size of GNFs, using first-principles calculations within the density functional theory.

In order to evaluate the stability of GNFs, we calculated the edge formation energy. First, we consider GNFs with the six-fold symmetry (D<sub>6h</sub>) and classify them into zigzag GNFs (ZZGNFs) and armchair GNFs (ACGNFs). ACGNFs have two subtypes, AC(1) and AC(2), depending on whether carbon atoms are just at the corner of the outermost envelope hexagon of GNFs. We define the edge purity as the ratio of the number of carbon atoms at the edge unambiguously regarded as the armchair to the total number of edge atoms. The purity of AC(1) is higher than that of AC(2). The chemical formulae associated with ZZ, AC(1), and AC(2) are C<sub>6n</sub><sup>2</sup>H<sub>6n</sub>, C<sub>18n</sub><sup>2-18n+6</sup>H<sub>12n-6</sub>, C<sub>18n</sub><sup>2-30n+12</sup>H<sub>12n-12</sub>, respectively. In addition, we also evaluate the structural stabilities of triangular and rhombus GNFs.

We calculated the edge formation energy of the GNFs having up to 1200 carbon atoms as a function of the number of edge carbon atoms [3]. The formation energy of ZZGNFs is higher than that of ACGNFs irrespective of the size of GNFs. This instability of ZZGNFs is attributed to the presence of the so-called edge state. Indeed, it has also been shown that the formation energy of the zigzag graphene nanoribbon is higher than that of the armchair one [4]. It is noted that AC(2) is slightly more stable than AC(1), whereas the purity of AC(2) is lower than that of AC(1). Such peculiar stabilization can be reasonably explained in terms of the aromaticity of GNFs. The Nucleus Independent Chemical Shifts (NICS) values, which is averaged for the six-membered rings in GNFs, for AC(2) are lower than those for AC(1). This means AC(2) is more aromatic than AC(1). We will discuss the quantitative relationship between the stability and the aromaticity of GNFs.

[1] S. Kim et al., *ACS Nano*, 6, 9, 8203 (2012)

[2] W. Hu et al., *J. Chem. Phys.* 141, 214704 (2014)

[3] A. Akaishi, M. Ushirozako, H. Matsuyama, and J. Nakamura, *Jpn. J. Appl. Phys.* 57, 0102BA (2018)

[4] S. Okada, *Phys. Rev. B*, 77, 041408 (2008)

4:40pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA10 Wafer-scale 2D-3D Mixed Heterostructures Enabled by Remote Epitaxy through Graphene**, *Jeehwan Kim*, Massachusetts Institute of Technology **INVITED**

The current electronics industry has been completely dominated by Si-based devices due to its exceptionally low materials cost. However, demand for non-Si electronics is becoming substantially high because current/next generation electronics requires novel functionalities that can never be achieved by Si-based materials. Unfortunately, the extremely high cost of non-Si semiconductor materials prohibits the progress in this field. Recently our team has invented a new crystalline growth concept, termed as "remote epitaxy", which can copy/paste crystalline information of the wafer remotely through graphene, thus generating single-crystalline films on graphene [1,2]. These single-crystalline films are easily released from the slippery graphene surface and the graphene-coated substrates can be infinitely reused to generate single-crystalline films. Thus, the remote epitaxy technique can cost-efficiently produce freestanding single-crystalline films including III-V, III-N, and complex oxides. This allows unprecedented functionality of flexible device functionality required for current ubiquitous electronics. I will also present detailed mechanism behind remote atomic interaction through graphene [2]. In addition, we have recently demonstrated a manufacturing method to manipulate wafer-scale 2D materials with atomic precision to form monolayer-by-monolayer stacks of wafer-scale 2D material heterostructures [3]. In this talk, I will discuss the implication of this new technology for revolutionary design of next generation electronic/photonics devices with combination of 3D/2D mixed heterostructures.

# Monday Afternoon, October 21, 2019

[1] Y. Kim, et al, and J. Kim, "Remote epitaxy through graphene enables two-dimensional material based layer transfer" *Nature*, Vol. 544, 340 (2017)

[2] W. Kong, et al, and J. Kim, "Polarity govern atomic interaction through two-dimensional materials", *Nature Materials*, Vol. 17, 999 (2018)

[3] J. Shim, S. Bae, et al, and J. Kim, "Controlled crack propagation for atomic precision handling of wafer-scale two-dimensional materials" *Science*, 362, 665 (2018)

## 2D Materials

### Room A216 - Session 2D+AP+EM+MI+NS+PS+TF-MoA

#### 2D Materials Growth and Fabrication

**Moderator:** Sarah Haigh, University of Manchester, UK

2:00pm **2D+AP+EM+MI+NS+PS+TF-MoA2 Synthesis of High Quality Monolayer Transition Metal Dichalcogenides using Direct Liquid Injection**, *Kathleen M. McCreary, E.D. Cobas, A.T. Hanbicki, M.R. Rosenberger, H.-J. Chuang, B.T. Jonker*, U.S. Naval Research Laboratory

In recent years, interest in monolayer transition metal dichalcogenides (TMDs) has rapidly increased, spurred by the possibility for integration into a variety of technologies such as photodetection, flexible electronics, and chemical sensing. While fundamental investigations can be performed on exfoliated flakes or chemical vapor deposition synthesized isolated islands, the limited size resulting from these techniques poses a significant barrier for implementation of TMDs in technological applications. To overcome these obstacles, new synthesis avenues should be explored. Here, we outline a novel technique that utilizes a commercially available Anneal Sys growth chamber equipped with direct liquid injection (DLI) heads for all precursors. The use of liquid, rather than solid precursors, provides fine control of both metal and chalcogen precursors leading to the synthesis of monolayer MoS<sub>2</sub> across cm<sup>2</sup> areas. Photoluminescence, Raman, XPS, and conductive AFM are used to evaluate DLI grown MoS<sub>2</sub>, and indicate high quality material having low defect density, with metrics comparable to or better than exfoliated and chemical vapor deposition grown MoS<sub>2</sub>.

2:20pm **2D+AP+EM+MI+NS+PS+TF-MoA3 Understanding and Controlling the Growth of 2D Materials with Non-Equilibrium Methods and in situ Diagnostics**, *David Geohegan, Y-C. Lin, Y. Yu*, Oak Ridge National Laboratory; *C. Liu, G. Duscher*, University of Tennessee Knoxville; *A. Strasser*, University of Texas at Dallas; *A.A. Puretzky*, Oak Ridge National Laboratory; *K. Wang*, Intel Corporation, USA; *M. Yoon, C.M. Rouleau*, Oak Ridge National Laboratory; *S. Canulescu*, DTU Nanolab, Technical University of Denmark; *P.D. Rack*, University of Tennessee Knoxville; *L. Liang, W. Zhang, H. Cai, Y. Gu, G. Eres, K. Xiao*, Oak Ridge National Laboratory

#### INVITED

Atomically-thin two-dimensional (2D) materials, including layered 2D transition metal dichalcogenide (TMD) semiconductors and their heterostructures, exhibit remarkable quantum properties that are envisioned for energy-efficient photovoltaics, flexible optoelectronics, catalysis, and quantum information science. However, significant synthesis and processing challenges currently limit the technologic development of these "all-surface" materials, including wafer-scale, bottom-up synthesis of uniform layers of crystalline 2D materials that are comparable in quality to exfoliated flakes of bulk materials. As-synthesized crystals of 2D TMDs display remarkable heterogeneity on both the atomistic level (e.g., vacancies, dopants, and edge terminations) and on the mesoscopic length scale (e.g., misoriented grains, layer orientations, and interactions with substrates and adsorbates) that can strongly influence the structure and electronic properties in 2D materials. This heterogeneity offers a serious challenge for synthesis and processing, yet offers a tremendous opportunity to tailor functionality.

Here we describe several approaches that are being developed for in situ diagnostic analysis and control of synthesis and heterogeneity. In addition to conventional vapor transport techniques, progress in laser-based approaches for 2D synthesis and modification, such as pulsed laser deposition (PLD) and pulsed laser conversion of precursors, are presented that permit control of the growth environment using time-resolved in situ diagnostics. The non-equilibrium advantages of PLD to form alloys and vertical heterojunctions are demonstrated using the tunable kinetic energy and digital nature of the process. Correlated atomic-resolution electron microscopy and atomistic theory are used to understand the size and stoichiometry of the "building blocks" deposited for synthesis and the forces that guide assembly. 2D crystals are grown directly on TEM grids

within custom chambers and transmission electron microscopes where the ability to 'see' every atom in these atomically-thin crystals permits a unique opportunity to understand the forces governing their synthesis and functionality. In situ optical spectroscopy techniques are described to characterize the material's evolving structure and properties, offering the opportunity to 'close the loop' between synthesis and optoelectronic functionality of 2D materials and heterostructures.

Research sponsored by the U.S. Dept. of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Div. (synthesis science) and Scientific User Facilities Div. (characterization science).

3:00pm **2D+AP+EM+MI+NS+PS+TF-MoA5 Area-Selective Atomic Layer Deposition of 2D WS<sub>2</sub> Nanolayers**, *Shashank Balasubramanyam<sup>1</sup>*, Eindhoven University of Technology, The Netherlands, Noord Brabant; *M.J.M. Merx*, Eindhoven University of Technology, The Netherlands; *W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands, Netherlands; *A.J.M. Mackus*, Eindhoven University of Technology, The Netherlands, Nederland; *A.A. Bol*, Eindhoven University of Technology, The Netherlands, Netherlands

With continued downscaling of device dimensions, ultra-thin two dimensional (2D) semiconductors like WS<sub>2</sub> are considered as promising materials for future applications in nanoelectronics. At these nanoscale regimes, device fabrication with precise patterning of critical features is challenging using current top-down processing techniques. In this regard, area-selective atomic layer deposition (AS-ALD) has emerged as a promising candidate for bottom-up processing to address the complexities of nanopatterning. Till date, AS-ALD of metals<sup>1</sup> and dielectrics<sup>2</sup> have been successfully demonstrated. However, AS-ALD of 2D materials has remained elusive. In this contribution, we demonstrate area-selective deposition of 2D WS<sub>2</sub> nanolayers by using a three-step (ABC-type) plasma-enhanced ALD process.

AS-ALD of WS<sub>2</sub> was achieved by using acetylacetone (Hacac) inhibitor (A), bis(tertbutylimido)-bis(dimethylamido)-tungsten precursor (B), and H<sub>2</sub>S plasma (C) pulses. This process resulted in immediate growth on SiO<sub>2</sub> while a significant nucleation delay was observed on Al<sub>2</sub>O<sub>3</sub>, as determined from *in-situ* spectroscopic ellipsometry (SE) and *ex-situ* X-ray photoelectron spectroscopy (XPS) measurements. The surface chemistry of this selective process was analysed by *in-situ* Fourier transform infrared spectroscopy (FTIR). The analyses revealed that the inhibitor adsorbed on the Al<sub>2</sub>O<sub>3</sub> surface, blocking precursor adsorption, while little or no inhibitor adsorption was detected on the SiO<sub>2</sub> surface where WS<sub>2</sub> was readily deposited. Furthermore, the area-selective growth was demonstrated on SiO<sub>2</sub> samples with patterned Al<sub>2</sub>O<sub>3</sub> on top. On SiO<sub>2</sub>, WS<sub>2</sub> could be deposited with angstrom-level thickness control.

To improve the crystallinity, the AS-ALD WS<sub>2</sub> films were annealed at temperatures within the thermal budget of industrial semiconductor processing ( $\leq 450^\circ\text{C}$ ). The annealed films exhibited sharp Raman peaks, which is a fingerprint of highly crystalline WS<sub>2</sub>. Furthermore, Raman line scans over the patterns showed very sharp peak intensity transitions at the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> interface which confirmed that annealing had no impact on selectivity.

To summarize, this work pioneered the combination of two key avenues in atomic-scale processing: area-selective growth and ALD of 2D materials. It is expected that the results of this work will lay the foundation for area-selective ALD of other 2D materials.

<sup>1</sup> R. Chen and S.F. Bent, *Adv. Mater.* (2006).

<sup>2</sup> A. Mamelì, M.J.M. Merx, B. Karasulu, F. Roozeboom, W.M.M. Kessels and A.J.M. Mackus, *ACS Nano* (2017).

3:20pm **2D+AP+EM+MI+NS+PS+TF-MoA6 Growth Behavior of Hexagonal Boron Nitride on Cu-Ni Binary Alloys**, *Karthik Sridhara*, Texas A&M University; *J.A. Wollmershauser*, U.S. Naval Research Laboratory; *L.O. Nyakiti*, Texas A&M University; *B.N. Feigelson*, U.S. Naval Research Laboratory

Controlled growth of large area n-layered chemical vapor deposited (CVD) hexagonal boron nitride (h-BN) is of great interest as a tunnel dielectric, and substrate for graphene and transition metal dichalcogenides (TMDs). The CVD growth of h-BN has been demonstrated on various transition metal catalytic substrates such as Cu, Ni, Pt and Fe. Of these metal substrates, Cu and Ni are frequently used due to their relative abundance and low cost. However, h-BN growth on Cu leads to monolayer films, and growth on Ni yields thicker, substrate grain-dependent films. Therefore, a

<sup>1</sup> TFD James Harper Award Finalist



cost-effective transition metal substrate is needed that will facilitate controlled n-layered h-BN growth.

In this work, we prepare isomorphous Cu-Ni binary alloys from 10-90 wt.% Ni by creating Ni-rich (Ni-Cu) and Cu-rich (Cu-Ni) alloys using electroplating of Cu on Ni foils and Ni on Cu foils, respectively. The electroplated foils are then annealed at  $\sim 1030^\circ\text{C}$  for  $>5$  hours to create Ni-Cu and Cu-Ni alloys. The alloys are subsequently polished mechanically to create a planarized surface suitable for h-BN growth. The surface morphology before and after polishing is assessed using a scanning electron microscope (SEM). Energy dispersive spectroscopy (EDS) characterization of the alloys confirms a designed stoichiometry at every weight percent. h-BN is grown on the alloys using atmospheric pressure chemical vapor deposition (APCVD) at  $1030^\circ\text{C}$ , with ammonia borane as the precursor, and  $\text{H}_2/\text{N}_2$  as the carrier gas flowing at  $\sim 200$  sccm. Cu and Ni foils are used as control samples for this study. Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS) is used to confirm and characterize h-BN growth directly on Cu, Ni and alloy substrates. SEM is performed to evaluate the h-BN film and crystal morphology. The results indicate that the h-BN growth behavior on Ni-Cu is different than on Cu-Ni alloys. A trend of decreasing h-BN amount with reducing Ni concentration is observed on Ni-Cu alloys while no such trend is observed on Cu-Ni alloys. Additionally, there are large ( $\sim 20\ \mu\text{m}$ ) multilayer and monolayer single crystals of h-BN on Ni-Cu alloys, and predominantly monolayer crystals and films of h-BN on Cu-Ni alloys. The difference in growth behavior is studied using x-ray photoelectron spectroscopy (XPS) and electron backscattering diffraction (EBSD), which reveal that the alloy surface composition determines the h-BN growth. This work demonstrates how Cu-Ni alloy substrate of different compositions, along with CVD growth conditions, can be used to control h-BN growth.

**4:20pm 2D+AP+EM+MI+NS+PS+TF-MoA9 Controlled Growth of Transition Metal Dichalcogenide Monolayers for Applications in Nanoelectronic and Nanophotonic Devices**, A. George, C. Neumann, D. Kaiser, R. Mupparapu, Friedrich Schiller University Jena, Germany; U. Hübner, Leibniz Institute of Photonic Technology, Jena, Germany; Z. Tang, A. Winter, I. Staude, **Andrey Turchanin**, Friedrich Schiller University Jena, Germany

Controlling the flow rate of precursors is highly essential for the growth of high quality monolayer crystals of transition metal dichalcogenides (TMDs) by chemical vapor deposition. Thus, introduction of an excess quantity of precursors affects the reproducibility of the growth process and results in the multilayer growth. Here, we demonstrate the use of Knudsen-type effusion cells for controlled delivery of sulfur precursor for the large area, high density, size-controlled and highly reproducible growth of monolayer TMD crystals [1]. The size of the grown crystals can be tuned between 10 - 200  $\mu\text{m}$ . We grow  $\text{MoS}_2$ ,  $\text{WS}_2$ ,  $\text{MoSe}_2$  and  $\text{WSe}_2$  monolayer crystals as well as  $\text{MoSe}_2$ - $\text{WSe}_2$  lateral heterostructures and characterize them by optical microscopy, atomic force microscopy, Raman spectroscopy, photoluminescence spectroscopy and electrical transport measurements. It has been found that they possess a high crystalline, optical and electrical quality based on their single crystalline nature. We demonstrate their implementation in novel field-effect and nanophotonic devices and discuss an influence of the point defect density on their functional characteristics [2-3]. Moreover, we present a novel synthetic route for the integration of TMDs into lateral heterostructures with other 2D materials [4].

[1] A. George et al., *J. Phys.: Mater.* 2 (2019) 016001.

[2] T. Bucher et al., *ACS Photonics* 6 (2019) 1002.

[3] R. Meyer et al., *ACS Photonics* 6 (2019) DOI: 10.1021/acsp Photonics.8b01716

[4] A. Winter et al., *Carbon* 128 (2018)106.

**4:40pm 2D+AP+EM+MI+NS+PS+TF-MoA10 Atomic Layer Deposition of BN as a Novel Capping Barrier for  $\text{B}_2\text{O}_3$** , **Aparna Pilli**, J. Jones, J.A. Kelber, University of North Texas; A. LaVoie, F. Pasquale, Lam Research Corporation

The deposition of boron oxide ( $\text{B}_2\text{O}_3$ ) films on Si and  $\text{SiO}_2$  substrates by atomic layer deposition (ALD) is of growing interest in microelectronics for shallow doping of high aspect ratio transistor structures.  $\text{B}_2\text{O}_3$ , however, forms volatile boric acid ( $\text{H}_3\text{BO}_3$ ) upon ambient exposure, requiring a passivation barrier, for which BN was investigated as a possible candidate. Here, we demonstrate, deposition of BN by sequential BCl/NH reactions at 600 K on two different oxidized boron substrates: (a) B O deposited using BCl /H O ALD on Si at 300 K ("B O /Si"); and (b) a boron-silicon oxide formed by sequential BCl /O reactions at 650 K on  $\text{SiO}$  followed by annealing to 1000 K ("B-Si-oxide"). X-ray photoelectron spectroscopy (XPS) data

demonstrate layer-by-layer growth of BN on  $\text{B}_2\text{O}_3/\text{Si}$  with an average growth rate of  $\sim 1.4\ \text{\AA}/\text{cycle}$ , accompanied by some  $\text{B}_2\text{O}_3$  removal during the first BN cycle. In contrast, continuous BN growth was observed on B-Si-oxide without any reaction with the substrate. XPS data also indicate that the oxide/nitride heterostructures are stable upon annealing in ultrahigh vacuum to  $>1000\ \text{K}$ . XPS data, after the exposure of these heterostructures to ambient, indicate a small amount of BN oxidation at the surface NH species, with no observable hydroxylation of the underlying oxide films. These results demonstrate that BN films, as thin as 13  $\text{\AA}$ , are potential candidates for passivating boron oxide films prepared for shallow doping applications.

**5:00pm 2D+AP+EM+MI+NS+PS+TF-MoA11 Atomic Layer Deposition of  $\text{SiO}_2$  on Group VIII Metals: Towards Formation of a 2D Dielectric**, T. Suh, R. Yaliso, **James Engstrom**, Cornell University

The atomic layer deposition (ALD) of many metals, particularly Group VIII (now known as Groups 8, 9 and 10), on  $\text{SiO}_2$  has been an active area of research in many fields, which include microelectronics and heterogeneous catalysis. There have been many fewer studies of the inverse—the deposition of  $\text{SiO}_2$  on many of these same metals. One possible reason to explore the ALD growth of  $\text{SiO}_2$  on transition metals is that it might provide a route to an atomically thick  $\text{SiO}_2$  dielectric, *silicatene*. Silicatene is a 2D material that consists of a bilayer of  $\text{Si}_2\text{O}_3$  linked to each other by bridging oxygen atoms (giving  $\text{SiO}_2$ ), where there are no dangling bonds or covalent bonds to the underlying substrate on which it is grown. For example, an established route to form silicatene involves deposition of elemental Si in UHV and subsequent high-temperature annealing on various single-crystalline metal surfaces including, but not limited to, Ru(0001), Pt(111), and Pd(100). Such a process, unfortunately, is likely not compatible with high-volume manufacturing. With this motivation we embarked on a study of the plasma-assisted ALD of  $\text{SiO}_2$  on e-beam deposited polycrystalline thin films of Ru, Pt and Pd using a commercial ALD reactor. We analyzed both the thin films and the starting substrates using a combination of techniques including contact angle, spectroscopic ellipsometry (SE) and X-ray photoelectron spectroscopy. Thin films of  $\text{SiO}_2$  were deposited using tris(dimethylamido)silane and an oxygen plasma at a substrate temperature of  $200^\circ\text{C}$ , and we examined growth for 5, 10, 20, 50 and 100 cycles. Contact angle measurements showed immediate evidence for  $\text{SiO}_2$  deposition on all metal surfaces, and the contact angle decreased and remained constant and  $< 10^\circ$  from 5 to 100 cycles of ALD. From SE we found little evidence of an incubation period, and growth was linear for the range of sample examined and the thickness deposited per cycle was remarkably constant at a value of  $0.76\text{-}0.78\ \text{\AA}/\text{cycle}$ . Analysis of these films using angle-resolved XPS was consistent with the formation of a thin film of  $\text{SiO}_2$  with uniform thickness. Having characterized the thin film thickness-ALD cycle relationship we subjected  $\text{SiO}_2$  thin films with thickness of  $\sim 7\text{-}15\ \text{\AA}$  to post-deposition high-temperature anneals in oxygen furnace. Initial attempts to form silicatene with an anneal at  $800^\circ\text{C}$ , produced a structure suggesting possible interfacial reaction between the  $\text{SiO}_2$  and Ru, perhaps involving silicide formation. We will end our presentation with a discussion of recent work involving a more extensive examination of the post-deposition annealing step, and deposition on patterned wafers.

**Materials and Processes for Quantum Information, Computing and Science Focus Topic**  
**Room B231-232 - Session QS+EM+MN+NS+VT-MoA**

**Systems and Devices for Quantum Computing**

**Moderators:** Jonas Bylander, Chalmers University of Technology, Sweden, Ruichen Zhao, National Institute of Standards and Technology (NIST)

**1:40pm QS+EM+MN+NS+VT-MoA1 DEMUXYZ Gate Using Single Microwave Drive Line for Multiple Qubits**, **Matteo Marantoni**, University of Waterloo, Canada; C.T. Earnest, University of Waterloo, Canada; J.H. Béjanin, University of Waterloo, Canada

Superconducting qubits have the potential to lead to large-scale quantum computers with  $10^5$  or more qubits in 2D arrays. As the number of qubits increases, finding methods to connect all the necessary control lines to each qubit can become a serious challenge. In this talk, we introduce a new demultiplexed one-qubit gate: DEMUXYZ. This gate makes it possible to decrease the number of microwave control lines from  $N^2$  to 1 by allowing multiple qubits to share a single microwave line. The shared line carries a continuous wave (CW) microwave tone, which is initially detuned from the qubits' idle frequency. When a qubit must undergo an arbitrary rotation on

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the Bloch sphere, the qubit is tuned on resonance with the CW tone and allowed to interact with the drive for the duration required to achieve the desired rotation. The rotation phase is tuned by detuning the qubit frequency away from the drive and idle frequency for the required time length. We demonstrate a first proof of concept for this gate performing experiments on Xmon transmon qubits. We characterize the gate ON/OFF ratio and perform quantum state tomography.

**Funding Acknowledgement:** This research was undertaken thanks in part to funding from the Canada First Research Excellence Fund (CFREF) and the Discovery and Research Tools and Instruments Grant Programs of the Natural Sciences and Engineering Research Council of Canada (NSERC).

2:00pm **QS+EM+MN+NS+VT-MoA2 Structural and Electronic Characterization of a Novel Si/SiGe Heterostructure for Quantum Computing**, *Thomas McJunkin, E.R. MacQuarrie, S.F. Neyens, B. Thorgrimsson, J. Corrigan, J.P. Dodson, D.E. Savage, M.G. Lagally, R. Joynt, M. Friesen, S.N. Coppersmith, M.A. Eriksson*, University of Wisconsin - Madison

In recent years, silicon-based quantum dots have been shown to be a promising avenue for quantum computing. However, dots formed in silicon quantum wells exhibit a near-degeneracy of the two low-lying valley states. Motivated by a desire to increase the magnitude and tunability of this valley splitting, we report the characterization of a novel Si/SiGe heterostructure grown with a thin layer of SiGe embedded within the Si quantum well, near the top of the well. The Si/SiGe heterostructure is grown via UHV-CVD on a linearly graded SiGe alloy with a final Ge concentration of 29%. STEM measurements reveal the quantum well structure to consist of a  $\sim 10$  nm Si layer, followed by a thin  $\sim 1$  nm SiGe layer, and subsequent  $\sim 2$  nm layer of pure Si. Above this quantum well, a  $\sim 35$  nm layer of SiGe with 29% Ge is grown to separate the quantum well from the surface. The intent of this  $\sim 1$  nm layer of SiGe, positioned just below the upper interface of the quantum well, is to modify the valley splitting of electrons in a 2-dimensional electron gas (2DEG) that reside near this interface. By modifying an external vertical electric field, the electron wavefunction can be moved on and off this spike in germanium concentration.

We report electronic measurements of both Hall bars and quantum dot devices that are fabricated on this heterostructure. Shubnikov-de Haas (SdH) and quantum Hall (QH) measurements reveal a peak transport mobility in excess of  $100,000 \text{ cm}^2/(\text{V s})$  at  $6 \times 10^{11} \text{ cm}^{-2}$  carrier density. We report SdH and QH measurements over a wide range of carrier density and magnetic field in the form of a fan diagram. Valley splitting values are measured in the quantum dot device by magnetospectroscopy, in which a few-electron dot transition is measured as the in-plane magnetic field is swept. Measuring at the second, third, and fourth electron transition in the quantum dot, we find valley splittings of 29, 48, and 65  $\mu\text{eV}$ , respectively. To measure tunability of valley splitting, nearby gate voltages are changed to vary the vertical electric field at constant charge occupation. We find that both the lowest lying valley splitting and the valley splitting in the first excited orbital can be tuned over a factor of 2 by means of such changes in gate voltage.

2:20pm **QS+EM+MN+NS+VT-MoA3 Efficient Quantum Computation using Problem-specific Quantum Hardware and Algorithms**, *Stefan Filipp*, IBM Research - Zurich, Switzerland **INVITED**

In recent years we have observed a rapid development of quantum technologies for the realization of quantum computers that promise to outperform conventional computers in certain types of problems. This includes problems in optimization, machine learning, finite element calculations, and in the computation of complex molecules. A key requirement to perform computations on current and near-term quantum processors is the design of quantum algorithms with short circuit depth that finish within the coherence time of the qubits. To this end, it is essential to implement a set of quantum gates that are tailored to the problem at hand and that can be directly implemented in hardware. To efficiently compute the ground and excited states of molecular hydrogen we utilize a parametrically driven tunable coupler to realize exchange-type gates that are configurable in amplitude and phase on two fixed-frequency superconducting qubits. Such gates are particularly well suited for quantum chemistry applications because they preserve the number of qubit excitations corresponding to the fixed number of electrons in the molecule. With gate fidelities around 95% we compute the eigenstates within an accuracy of 50 mHartree on average, a good starting point for the simulation of larger molecular systems.

3:00pm **QS+EM+MN+NS+VT-MoA5 Reconfigurable Magnetic Textures for Quantum Information Applications**, *Alex Matos-Abiague*, Wayne State University **INVITED**

Spintronic devices such as spin valves have extensively been used for non-volatile memory applications. The magnetic fringe fields generated by spin valves strongly depend on the magnetic state of the device. Thus, an array of electrically switchable spin valves allows for the generation of reconfigurable magnetic textures whose specific form and properties can be controlled on the nanometer scale. When combined with materials with large  $g$ -factor, such magnetic textures can have sizable effects not only on the spin but also on the localization, exchange, and transport properties of carriers. We show how the local control of the fringe-field-generated magnetic texture provides a unique tool for creating effective reconfigurable nanostructures and how it can be used for various quantum information applications. In particular, we focus on the use of reconfigurable magnetic textures as a new path to the realization of fault-tolerant topological quantum computing by enabling the generation and manipulation of Majorana bound states (MBSs) in superconductor/semiconductor heterostructures [1-4]. MBSs are emergent quasiparticles that obey non-Abelian statistics and can store quantum information that is immune against smooth local perturbations. Magnetic textures can provide not only synthetic spin-orbit and Zeeman fields -two important ingredients for the creation of MBSs- but also spatial confinement by creating closed domains in the form of effective topological wires. The effective wires can be re-shaped and re-oriented by properly changing the magnetic texture, allowing for the transportation of the MBSs [1,3] and the realization of quantum gates through braiding operations [2]. Other platforms combining the use of reconfigurable magnetic textures and Josephson junctions, as well as the main experimental challenges regarding materials, scalability, and detection are also discussed.

**ACKNOWLEDGMENTS:** This work is supported by DARPA Grant No. DP18AP900007 and US ONR Grant No. N000141712793

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[2] A. Matos-Abiague, J. Shabani, A. D. Kent, G. L. Fatin, B. Scharf, I. Žutić, *Solid State Commun.* **262**, 1 (2017).

[3] T. Zhou, N. Mohanta, J. E. Han, A. Matos-Abiague, and I. Žutić, *Phys. Rev. B* **99**, 134505 (2019).

[4] N. Mohanta, T. Zhou, J. Xu, J. E. Han, A. D. Kent, J. Shabani, I. Žutić, and A. Matos-Abiague, arXiv:1903.07834

4:40pm **QS+EM+MN+NS+VT-MoA10 Josephson Parametric Amplifiers based on Micron Scale Overlap Junctions (O-JPA)**, *Mustafa Bal, J.L. Long, R. Zhao, H. Wang*, National Institute of Standards and Technology (NIST); *C.R. McRae*, National Institute of Standards and Technology (NIST) and University of Colorado Boulder; *R.E. Lake, X. Wu, H.-S. Ku, D.P. Pappas*, National Institute of Standards and Technology (NIST)

Quantum limited amplifiers have become indispensable tools in superconducting quantum circuits. In recent years, quantum limited amplification has been demonstrated in parametric amplifiers based on high kinetic inductance superconductors as well as Josephson junctions. Previously, we have demonstrated submicron scale overlap Josephson junction fab process for qubits with long coherence times [1]. Here, we extend the overlap junction fab process to micron scale junctions to enable the realization of other superconducting quantum devices such as overlap junction-based Josephson parametric amplifiers (O-JPA). Our fab scheme yield frequency tunable O-JPAs with negligible insertion loss. We readily observe over 25 dB gain. Compared to other competing processes, overlap junction process for micron scale junctions allows the fabrication of O-JPAs with high yield and good device performance at a much lower infrastructure requirements. The fabrication details of overlap junction process as well as the results of O-JPA characterization will be presented. The metrology of overlap Josephson junctions will also be presented in this this symposium [2].

[1] X. Wu, J. L. Long, H. S. Ku, R. E. Lake, M. Bal, and D. P. Pappas, "Overlap junctions for high coherence superconducting qubits", *Appl. Phys. Lett.* **111**, 032602 (2017).

[2] R. Zhao *et al.*, "Josephson Junction metrology for superconducting quantum device design", also presented at AVS 66<sup>th</sup> International Symposium & Exhibition.

# Monday Afternoon, October 21, 2019

## New Challenges to Reproducible Data and Analysis Focus

### Topic

### Room A211 - Session RA+AS+NS+SS-MoA

### Quantitative Surface Analysis II/Big Data, Theory and Reproducibility

**Moderators:** Kateryna Artyushkova, Physical Electronics, Donald Baer, Pacific Northwest National Laboratory

1:40pm **RA+AS+NS+SS-MoA1 A Data-Centric View of Reproducibility, Anne Plant**, National Institute of Standards and Technology (NIST); *J. Elliott*, NIST; *R. Hanisch*, National Institute of Standards and Technology (NIST)

**INVITED**

Ideally, data should be shareable, interpretable, and understandable within the scientific community. There are many challenges to achieving this, including the need for high quality documentation and a shared vocabulary. In addition, there is a push for rigor and reproducibility that is driven by a desire for confidence in research results. We suggest a framework for a systematic process, based on consensus principles of measurement science, to guide researchers and reviewers in assessing, documenting, and mitigating the sources of uncertainty in a study. All study results have associated ambiguities that are not always clarified by simply establishing reproducibility. By explicitly considering sources of uncertainty, noting aspects of the experimental system that are difficult to characterize quantitatively, and proposing alternative interpretations, the researcher provides information that enhances comparability and reproducibility.

2:20pm **RA+AS+NS+SS-MoA3 Enhancing Data Reliability, Accessibility and Sharing using Stealthy Approaches for Metadata Capture, Steven Wiley**, Pacific Northwest National Laboratory

**INVITED**

Science is entering a data-driven era that promises to accelerate scientific advances to meet pressing societal needs in medicine, manufacturing, clean energy and environmental management. However, to be usable in big data applications, scientific data must be linked to sufficient metadata (data about the data) to establish its identity, source, quality and reliability. This has also driven funding agencies to require projects to use community-based data standards that support the FAIR principles: Findable, Accessible, Interoperable, and Reusable. Current concerns about data reproducibility and reliability have further reinforced these requirements. Truly reusable data, however, requires an enormous amount of associated metadata, some which is very discipline and sample-specific. In addition, this metadata is typically distributed across multiple data storage modalities (e.g. lab notebooks, electronic spreadsheets, instrumentation software) and is frequently generated by different people. Assessing and consolidating all of the relevant metadata has traditionally been extremely complex and laborious, requiring highly trained and motivated investigators as well as specialized curators and data management systems. This high price has led to poorly documented datasets that can rarely be reused. To simplify metadata capture and thus increase the probability it will indeed be captured, EMSL (Environmental Molecular Sciences Laboratory) has developed a general-purpose metadata capture and management system built around the popular ISA-Tab standard (Investigation-Study-Assay Tables). We have modified this framework by mapping it onto the EMSL workflow, organized as a series of "transactions". These transactions are natural points where metadata is generated, include specifying how samples will be generated and shipped, instrument scheduling, sample storage, and data analysis. Software tools have been built to facilitate these transactions, automatically capture the associated metadata and link it to the relevant primary data. This metadata capture system works in concert with automated instrument data downloaders and is compatible with commercial sample tracking and inventory management systems. By creating value-added tools that are naturally integrated into the normal scientific workflow, our system enhances scientific productivity, thus incentivizing adoption and use. The entire system is designed to be general purpose and extensible and thus should be a useful paradigm for other scientific projects that can be organized around a transactional model.

3:00pm **RA+AS+NS+SS-MoA5 From Electrons to X-rays: Tackling Big Data Problems through AI, Mathew Cherukara, Y. Liu, M.V. Holt, H. Liu, T.E. Gage, J.G. Wen, I. Arslan**, Argonne National Laboratory

**INVITED**

As microscopy methods and detectors have advanced, the rates of data acquisition and the complexity of the acquired data have increased, and these are projected to increase several hundred-fold in the near future. The unique electron and X-ray imaging capabilities at the Center for Monday Afternoon, October 21, 2019

Nanoscale Materials (CNM) are in a position to shed light on some of the most challenging and pressing scientific problems we face today. To fully leverage the capability of these advanced instruments, we need to design and develop effective strategies to tackle the problem of analyzing the data generated by these imaging tools, especially following facility upgrades such as the upgrade to the Advanced Photon Source (APS-U) and the commissioning of the ultrafast electron microscope (UEM).

The data problem is especially acute in the context of coherent imaging methods, ultra-fast imaging and multi-modal imaging techniques. However, analysis methods have not kept pace. It is infeasible for a human to sort through the large, complex data sets being generated from imaging experiments today. At the CNM, we apply machine learning algorithms to our suite of electron and X-ray microscopy tools. Machine learning workflows are being developed to sort through data in real-time to retain only relevant information, to invert coherently scattered data to real-space structure and strain, to automatically identify features of interest such as the presence of defects, and even to automate decision making during an imaging experiment. Such methods have the potential not only to decrease the analysis burden on the scientist, but to also increase the effectiveness of the instruments, for instance by providing real-time experimental feedback to help guide the experiment.

4:00pm **RA+AS+NS+SS-MoA8 Quantifying Shell Thicknesses of Core-Shell Nanoparticles by means of X-ray Photoelectron Spectroscopy, Wolfgang Werner**, Vienna University of Technology, Austria

**INVITED**

Determining shell thicknesses and chemistry of Core-Shell Nanoparticles (CSNPs) presently constitutes one of the most important challenges related to characterisation of nanoparticles. While for particulae number concentration various routine analysis techniques as well as methods providing reference measurements have been or are in the process of being developed, one of the most promising candidates for shell thickness determination is x-ray photoelectron spectroscopy (XPS).

Different approaches to quantify shell thicknesses will be presented and compared. These comprise: (1) The infinitesimal columns model (IC), (2) Shard's empirical formula (TNP-model) and (3) SESSA (Simulation of Electron Spectra for Surface Analysis) simulations with and (4) without elastic scattering.

CSNP XPS intensities simulated with SESSA for different combinations of core/shell-material combinations for a wide range of core and shell thicknesses have been evaluated with the TNP-model and the retrieved thicknesses are in good agreement with the nominal thickness, even when elastic scattering is turned on during the simulation, except for pathological cases. For organic shell materials these simulations fully confirm the validity of the (much simpler) TNP-method, which also coincides with the IC model.

Experimental data on of a round robin experiment of PMMA@PTFE CSNPs involving three research institutions were analysed with the aforementioned approaches and show a good consistency in that evaluations of the shell thicknesses among the institutions agree within 10% (and are in good agreement with the nominal shell thickness). This consistency is promising since it suggests that the error due to sample preparation can be controlled by following a strict protocol.

Use of the F1s signal leads to significant deviations in the retrieved shell thickness. Independent measurements using Transmission Electron Microscopy were also performed, which revealed that the core-shell structure is non-ideal, i.e. the particles are aspherical and the cores are acentric within the particles. SESSA simulations were employed to estimate the effect of various types of deviations of ideal NPs on the outcome of shell thickness determination.

The usefulness and importance of different kind of electron beam techniques for CSNP analysis and in particular shell thickness determination is discussed.

4:40pm **RA+AS+NS+SS-MoA10 Modeling the Inelastic Background in X-ray Photoemission Spectra for Finite Thickness Films, Alberto Herrera-Gomez**, CINVESTAV-Unidad Queretaro, México

The background signal in photoemission spectra caused by inelastic scattering is usually calculated by convolving the total signal with the electron-energy loss-function. This method, which was proposed by Tougaard and Sigmund in their classic 1982 paper [1], only works (as clearly indicated in [1]) for homogeneous materials. However, the method is commonly applied to finite thickness films. In this paper it is going to be described the proper way to remove the inelastic background signal of spectra from thin-conformal layers including buried layers and delta-doping

[2]. The method is based on the straight-line inelastic scattering path, which is expected to be a very good approximation for low energy losses (near-peak regime). It is also a common practice to use the parametric Tougaard Universal Cross Section [3] with the provision that, instead of using the theoretical values for the parameters valid for homogeneous materials, the B-parameter is allowed to vary until the experimental background signal  $\sim 50$  to  $100$  eV below the peak is reproduced. This is equivalent to scale the loss-function, which partially compensates the error from using the convolution method [1]. The error compensation on the modeling of the background of finite-thickness layers by scaling the loss-function will be quantitatively described.

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5:00pm **RA+AS+NS+SS-MoA11 R2R(Raw-to-Repository) Characterization Data Conversion for Reproducible and Repeatable Measurements, Mineharu Suzuki, H. Nagao, H. Shinotsuka**, National Institute for Materials Science (NIMS), Japan; *K. Watanabe*, ULVAC-PHI Inc., Japan; *A. Sasaki*, Rigaku Corp., Japan; *A. Matsuda, K. Kimoto, H. Yoshikawa*, National Institute for Materials Science (NIMS), Japan

NIMS, Japan, has been developing a materials data platform linked with a materials data repository system for rapid new material searching by materials informatics. The data conversion from raw data to human-legible/machine-readable data file is one of the key preparation techniques prior to data analysis, where the converted data file should include meta-information. Our tools can convert raw data to a structured data package that consists of (1) characterization measurement metadata, (2) primary parameters which we will not call “metadata” to distinguish from (1), (3) raw parameters as written in original raw data, and (4) formatted numerical data. The formatted numerical data are expressed as matrix type with robust flexibility, not obeying a rigid definition. This flexibility can be realized by applying the data conversion style of Schema-on-Read type, not Schema-on-Write type based on *de jure* standards such as ISO documents. The primary parameters are carefully selected from raw parameters and their vocabularies are replaced from instrument-dependent terms to general ones that everyone can readily understand. These primary parameters with linked specimen information are useful for reproducible and repeatable instrument setup. By this R2R conversion flow, we have verified that we can generate and store interoperable data files of XPS spectra and depth profiles, powder XRD patterns, (S)TEM images, TED patterns, EELS spectra, AES spectra, EPMA spectra and elemental mapping, and theoretical electron IMFP data. We have also developed a system to allow semi-automatic data transfer from an instrument-controlling PC isolated from the network, by adopting a Wi-Fi-capable SD card’s scripting capability, while keeping the PC offline. We are working on further software development for on-demand data manipulation after R2R data conversion. So far it has been possible to perform XPS peak separation using automated information compression technique. Using these components, high-throughput data conversion/accumulation and data analyses are realized, where human interaction is minimized. Using metadata extracted from raw data, other users can reproduce or repeat measurements even if they did not carry out the original measurement. Human-legible and machine-readable numerical data is utilized for statistical analyses in informatics.

## 2D Materials

### Room A216 - Session 2D+AS+MI+NS-TuM

#### 2D Materials Characterization including Microscopy and Spectroscopy

Moderator: David Geohegan, Oak Ridge National Laboratory

8:00am **2D+AS+MI+NS-TuM1 Near-field Infrared Spectroscopy of Single Layer MnPS<sub>3</sub>**, *Sabine Neal*, University of Tennessee Knoxville; *H-S. Kim*, Rutgers University; *K.A. Smith*, *A.V. Haglund*, *D.G. Mandrus*, University of Tennessee Knoxville; *H.A. Bechtel*, Advanced Light Source, Lawrence Berkeley National Laboratory; *G.L. Carr*, National Synchrotron Light Source II, Brookhaven National Lab; *K. Haule*, *D. Vanderbilt*, Rutgers University; *J.L. Musfeldt*, University of Tennessee Knoxville

In order to explore the properties of a complex van der Waals material under confinement, we measured the near-field infrared response of the magnetic chalcogenide MnPS<sub>3</sub> in bulk, few-, and single-layer form and compared the results with traditional far field vibrational spectroscopy and complementary lattice dynamics calculations. Trends in the activated  $B_u$  mode near 450 cm<sup>-1</sup> are particularly striking, with the disappearance of this structure in the thinnest sheets. Combined with the amplified response of the  $A_g$  mode and analysis of the  $A_u + B_u$  features, we find that the symmetry is unexpectedly *increased* in single-sheet MnPS<sub>3</sub>. The monoclinicity of this system is therefore a consequence of the long-range stacking pattern rather than local structure.

8:20am **2D+AS+MI+NS-TuM2 Multi-parameter Analysis of Genesis and Evolution of Secondary Electrons produced in the Low Energy Regime**, *Alessandra Bellissimo*, ETH Zürich, Switzerland; *G.M. Pierantozzi*, CNR - Istituto Officine Materiali, Italy; *A. Ruocco*, *G. Stefani*, Università degli Studi Roma Tre, Italy; *O. Ridzel*, *V. Astašauskas*, *W.S.M. Werner*, Technische Universität Wien, Austria; *M. Tadorelli*, CERN, Switzerland; *G. Bertolini*, *U. Ramsperger*, ETH Zürich, Switzerland; *O. Gürlü*, ETH Zürich, Switzerland, Turkey; *D. Pescia*, ETH Zürich, Switzerland

The mechanisms responsible for electron-induced Secondary Electron Emission (SEE) generation of these ubiquitous Secondary Electrons (SEs) in a solid surface is not yet fully understood. In particular, the question *how many* "true secondary" electrons are generated and emitted from the target per incident primary electron awaits resolution and is of great fundamental as well as technological importance. The present work reports on a study of these and related questions by means of a variety of spectroscopic tools of increasing finesse. The interaction of Low-Energy Electrons with surfaces exhibiting different long-range order, was investigated by combining measurements of the Total Electron Yield in absolute units, single-electron as well as (e,2e)-coincidence spectroscopy. This investigation has led to the disentanglement of the elementary processes that need to be considered and comprehended for the understanding of the SE-generation probability, fully taking into account both energy and momentum conservation in the collision and the band structure of the solid. Single ionising scattering events, assisted by collective excitations, i.e. *plasmons*, constitute one of the fundamental ingredients leading to SEE. In the Low-Energy-regime the electron yield of a material is constituted by the interplay of reflectivity and SEE, both strongly dictated by the target band structure. The gathered information is further used in an attempt to interpret the signal generation mechanisms relevant in Scanning Field-Emission Microscopy (SFEM) [1].

#### Reference:

[1] A. Bellissimo, PhD Thesis, "*Multiparameter Analysis of Genesis and Evolution of Secondary Electrons produced in the Low Energy Regime*", URL: [https://www.researchgate.net/publication/332684398\\_Multiparameter\\_Analysis\\_of\\_Genesis\\_and\\_Evolution\\_of\\_Secondary\\_Electrons\\_produced\\_in\\_the\\_Low\\_Energy\\_regime](https://www.researchgate.net/publication/332684398_Multiparameter_Analysis_of_Genesis_and_Evolution_of_Secondary_Electrons_produced_in_the_Low_Energy_regime)

8:40am **2D+AS+MI+NS-TuM3 Probing Point Defects, Folds and Interfaces in 2D Material Heterostructures using Scanning Transmission Electron Microscopy**, *Sarah Haigh*, University of Manchester, UK **INVITED**

Scanning Transmission Electron Microscopy (STEM) is one of the few techniques able to probe the structure and chemistry of 2D materials when these are stacked to form vertical heterostructures. By combining STEM with electron energy loss spectroscopy and energy dispersive X-ray spectroscopy it is possible to characterise individual point defects,[1] to measure interlayer distances for dissimilar materials [2] and to investigate the microstructure of mechanically deformed structures at the atomic scale [3]. We have extensively employed plan view and cross sectional STEM imaging to investigate complex 2D heterostructures. For example, we have

shown that protruding defects prevent the realisation of pristine interfaces between transition metal selenides (MoSe<sub>2</sub>, WSe<sub>2</sub>, NbSe<sub>2</sub>) and boron nitride, unless exfoliation is performed in an inert environment.[2]

We have analysed microstructures produced when 2D van der Waals materials (graphite, boron nitride, MoSe<sub>2</sub>) are subjected to mechanical deformation and find that the types of defect can be predicted from just the bend angle and thickness of the materials.[3] In particular we find that above a critical thickness the materials exhibit numerous twin boundaries and for large bend angles these can contain nanoscale regions of local delamination. Such features are proposed to be important in determining how easily the material can be thinned by mechanical or liquid exfoliation.[3]

2D material heterostructures are also enabling new STEM imaging capabilities. We show they can be used as a platform to study real time reactions in liquid environments with unprecedented spatial resolution and spectroscopic capabilities [4]. We further demonstrate that graphene encapsulation allows imaging of point defect dynamics, structural degradation and mechanically induced stacking faults in 2D monochalcogenides, GaSe and InSe [1].

#### References

- [1] D G Hopkinson et al, ACS Nano, (2019) 10.1021/acsnano.8b08253
- [2] A P Rooney et al. Nano Letters, (2017) 17, 5222.
- [3] A P Rooney et al. Nature Communications (2018) 9, 3597
- [4] D J Kelly et al Nano Letters, (2018) 18, 2, 1168

9:20am **2D+AS+MI+NS-TuM5 Low-Energy Electron Induced Disorder and Decomposition of Self-assembled Monolayers on Au(111)**, *Jodi Grzeskowiak*<sup>1</sup>, University at Albany - SUNY; *C.A. Ventrice, Jr.*, SUNY Polytechnic Institute

To study the interaction of low energy electrons with thin organic films, measurements have been performed on electron induced disordering and decomposition of 1-decanethiol molecules grown via vapor phase deposition on Au(111). Surface analysis techniques were used to characterize the monolayers before and after electron exposure. LEED was used to determine the structure of the SAM and the rate of disordering and decomposition. It was observed that the diffraction pattern of the lying down phase of the SAM, held near 100 K, almost completely disappears within about three minutes of exposure. However, when the temperature of the irradiated sample was raised to 300 K and then cooled back down to around 100 K, most of the intensity of the diffraction pattern returns, indicating that electron exposure is primarily inducing disorder. TPD was used to evaluate the thermal stability of the SAMs and the resulting desorption products after electron exposure. For the standing up phase SAM, two desorption features for the hydrocarbon fragments of the SAM are observed, one around 130 °C and a second near 220 °C. For the lying down phase, only the higher temperature desorption feature is observed, which indicates that the SAM is converting from the standing up phase to the lying down phase during the heating process. For both phases, desorption peaks for S and H<sub>2</sub>S at around 250 °C were observed, suggesting that there is a high probability for the alkane chain of the decanethiol molecule to detach from the sulfur head group. After electron exposure of the standing up phase, a large reduction in the intensity of the two desorption peaks for the masses monitored for the hydrocarbon fragments was observed. However, the intensities of the peaks associated with S and H<sub>2</sub>S were similar to those for the samples that were not irradiated with electrons. For the lying down phase, the intensities and positions of all of the desorption peaks were similar to the unexposed SAMs, which indicates that the cross-section for electron beam damage for the lying down phase is much lower than that for the standing up phase. Ex-situ XPS was used to monitor the decomposition of the SAMs. After irradiation with 80 eV electrons, an uptake of oxygen was observed in the XPS measurements for both samples. This oxygen uptake gives evidence that oxygen in the air is reacting with carbon and sulfur atoms whose bonds were broken during electron exposure.

9:40am **2D+AS+MI+NS-TuM6 Continuous Silicene, Silicene Ribbons and Surface Reconstructions on h-MoSi<sub>2</sub>**, *Anna Costine*, *C. Volders*, University of Virginia; *M. Fu*, Oak Ridge National Laboratory; *P. Reinke*, University of Virginia

Silicene has emerged as a 2D material of interest because of its spin-orbit coupling, tunable electronic structure, and Dirac type behavior. Synthesis of silicene with preserved Dirac-type electronic structure has proven

<sup>1</sup> ASSD Student Award Finalist

challenging, but is critical to realizing theoretically predicted quantum states and devices. To date, Ag(111) remains the most popular substrate for silicene synthesis, but is discussed controversially due to its similarity with surface alloys. Silicene has also been synthesized on other substrates including Ir, IrSi<sub>3</sub>, and ZrB<sub>2</sub>. Silicene synthesis on a semiconducting substrate with a low buckling conformation to conserve the Dirac-type behavior would be ideal. The synthesis of silicene on new substrates that allow for direct device integration is an important next step.

We developed an alternate approach to silicene synthesis that allows for silicene synthesis on semiconducting silicides. The (0001) surface of h-MoSi<sub>2</sub> has hexagonal symmetry and a lattice constant close to that of silicene. Our recent measurements support the assumption that silicene is electronically decoupled from the substrate. The h-MoSi<sub>2</sub> crystallites, which are terminated by the (0001) plane are grown by depositing Mo onto a Si (001) or Si(111) surface. Upon annealing to ~800°C the Si atoms decouple from the underlying surface and form a weakly buckled silicene layer with the  $\sqrt{3} \times \sqrt{3}$  surface as seen by STM.

Our recent work expands this study and uses STM/S at 77 K to achieve a comprehensive description of silicene-on-silicide. The amount of Mo deposited (0.3 nm - 18 nm) and annealing temperature (700- 1000°C) were varied. All surface structures discussed here are on h-MoSi<sub>2</sub> crystallites in the (0001) plane. Three distinct surface structures coexist - silicene ribbons, a 4x4 reconstruction, and a complex reconstruction which is very sensitive to variations in the bias voltage. The electronic structure of silicene-ribbons shows a V-shaped density of states close to EF, indicative of Dirac-like behavior, while the other reconstructions are semiconducting. The surface and electronic structures observed on h-MoSi<sub>2</sub> crystallites as a function of the synthesis conditions will be discussed. The preference for silicene-ribbons in the low T STM/STS measurements is currently attributed to a faster post-deposition cooling rate, but the exact mechanism is still open to debate. We will present a detailed discussion of the electronic structure of silicene and silicene ribbons, and suggest mechanisms for the transition from the (0001) surface to silicene. Our goal is to develop synthesis approaches suitable for device integration of both silicene conformations.

**11:00am 2D+AS+MI+NS-TuM10 Epitaxial Growth and Characterization of Single-Orientation Single-Layer Transition Metal Dichalcogenides on Au(111).** *L. Bignardi*, University of Trieste, Italy; *Daniel Lizzit*, Elettra - Sincrotrone Trieste, Trieste, Italy; *B. Harsh*, *E. Travaglia*, Department of Physics, University of Trieste, Italy; *C.E. Sanders*, iNANO, Aarhus University, Denmark, UK; *M. Dendzik*, Aarhus University, Denmark, Germany; *P. Lacovig*, Elettra-Sincrotrone Trieste, Italy; *M. Michiardi*, iNANO, Aarhus University, Denmark, Canada; *M. Bianchi*, Aarhus University, Denmark; *R. Larciprete*, CNR-Institute for Complex Systems, Roma, Italy; *J.I. Flege*, *J. Falta*, University of Bremen, Germany; *P.K. Das*, Abdus Salam International Centre for Theoretical Physics, Trieste, Italy; *J. Fujii*, *I. Vobornik*, IOM-CNR, Laboratorio TASC, Trieste, Italy; *M. Ewert*, *L. Buß*, University of Bremen, Germany; *A. Baraldi*, University of Trieste, Italy; *P. Hofmann*, Aarhus University, Denmark; *S. Lizzit*, Elettra - Sincrotrone Trieste, Trieste, Italy

It has been widely demonstrated that Transition Metal Dichalcogenides (TMDs), and in particular MoS<sub>2</sub> and WS<sub>2</sub> could be good candidates for future electronic devices because of their intrinsic electronic properties and their potential for ultimate device scaling. In the single layer (SL) form, the inversion symmetry breaking and the strong spin-orbit coupling of the heavy transition metals (Mo or W) open new possibilities for data storage and computing thanks to the spin and valley degrees of freedom. However, in order to investigate the fundamental physics behind these materials and to produce high quality electronic devices, SL TMDs with enough large area and high quality are demanded. In particular, single domain oriented layers, that are SLs without mirror domains, allow to strongly suppress defects due to the absence of grain boundaries which are known to degrade the overall performances.

We here present a successful synthesis method based on physical vapor deposition that consists in dosing W or Mo in H<sub>2</sub>S atmosphere onto Au(111), and provide an in-depth characterization of the synthesized SL TMDs through different surface science techniques. Synchrotron radiation based photoelectron spectroscopy in the fast modality (fast-XPS) was used to carefully tune the growth parameters whereas high resolution (HR-XPS) was used for the characterization. In particular fast-XPS allowed to optimize the growth parameters which turned out to be different for MoS<sub>2</sub> [1] with respect to WS<sub>2</sub>[2]. Then, photoelectron diffraction (XPD) was employed to find the structural parameters of the SLs and to unambiguously determine their single orientation character and the relative alignment with respect to the underlying substrate. Scanning Tunneling Microscopy (STM), Low Energy Electron Diffraction (LEED) and

Microscopy (LEEM) added further insight into the lateral extension of the SLs and the structural order at the atomic level.

[1] H. Bana, E. Travaglia, L. Bignardi, P. Lacovig, C. E. Sanders, M. Dendzik, M. Michiardi, M. Bianchi, D. Lizzit, F. Presel, D. D. Angelis, N. Apostol, P. K. Das, J. Fujii, I. Vobornik, R. Larciprete, A. Baraldi, P. Hofmann and S. Lizzit, 2D Materials, 2018, 5, 035012.

[2] L. Bignardi, D. Lizzit, H. Bana, E. Travaglia, P. Lacovig, C. E. Sanders, M. Dendzik, M. Michiardi, M. Bianchi, M. Ewert, L. Buss, J. Falta, J. I. Flege, A. Baraldi, R. Larciprete, P. Hofmann, and S. Lizzit, Physical Review Materials 3, 014003 (2019).

**11:20am 2D+AS+MI+NS-TuM11 Surface Reactivity of MoS<sub>2</sub> by ambient pressure X-ray Photoelectron Spectroscopy, Rafik Addou, D. Dardzinsky, G.S. Herman**, Oregon State University

Molybdenum disulfide (MoS<sub>2</sub>) has potential applications as a low-cost catalyst for the hydrogen evolution reaction (HER). Defect sites in MoS<sub>2</sub> have been demonstrated to have high catalytic activities, where edge sites and sulfur vacancies are the major active sites for HER. Intentionally inducing defects offers a simple way to enhance the reactivity of MoS<sub>2</sub> and other 2D materials. In this study, we have characterized the surface reactivity and the catalytic activities of bulk MoS<sub>2</sub> samples using ambient pressure X-ray photoelectron spectroscopy (APXPS). The pristine surface was exposed to 1 mbar of H<sub>2</sub>O vapor for temperatures ranging from 300 to 573 K. APXPS Mo 3d, S 2p, and O 1s core levels do not show any significant changes under these reaction conditions due to the inert nature of the MoS<sub>2</sub> surface. To activate the MoS<sub>2</sub> basal plane to improve surface reactivity, we have formed well-controlled densities of defects using Ar<sup>+</sup> sputtering. The defective surfaces were exposed to 1 mbar of H<sub>2</sub>O vapor for temperatures ranging from 300 to 600 K. Changes in the APXPS Mo 3d, S 2p, and O 1s core levels indicate that the surface is much more reactive to H<sub>2</sub>O, with the formation of Mo-O bonds. These results are consistent with the reduction in the H<sub>2</sub>O gas phase which was measured by operando mass spectrometry. We have found that the reactivity strongly depends on the temperature and the size and density of defects. Following this first report of APXPS on MoS<sub>2</sub> acquired at more realistic pressure, we will also report the HER activity and X-ray absorption spectroscopy (XAS) on the pristine surface and compare it with defective surfaces. Our findings demonstrate that the reactivity and the catalytic activity of MoS<sub>2</sub> are significantly improved through the formation of defects.

**11:40am 2D+AS+MI+NS-TuM12 Surface Characterization of 2D Materials and their 3D Analogues using XPS, Jonathan Counsell, S.J. Coultas, C.J. Blomfield, N. Gerrard, Kratos Analytical Limited, UK; C. Maffitt, Kratos Analytical Limited; A.J. Roberts, Kratos Analytical Limited, UK**

Since the synthesis of Graphene in 2004 there has been significant interest in novel 2D materials. Indeed this area has produced an abundance of high impact publications and so far >\$10bn has been committed globally to both fundamental research and commercialisation. This interest has been due to the unique properties exhibited such as mechanical strength and charge/heat transfer. The potential commercial possibilities are diverse with applications as varied as heat management and dissipation to increasing computer processing power. To fully understand the nature and potential of these materials a comprehensive surface characterisation is necessary.

Herein we illustrate how by applying conventional surface analysis techniques with novel methodologies it is possible to create a more complete picture of the chemical and physical nature of deposited 2D materials. Both organic and inorganic 2D materials will be explored to demonstrate the methods and capabilities. Dichalcogenide materials (sulphides and selenides) containing different metal centres were analysed with XPS, and angular resolved methods, to calculate layer thicknesses, stoichiometry and chemical states. The lateral distribution of CVD ultra-thin films was studied using both macro and micro area XPS imaging modes to distinguish uniformity and evenness. The application of UPS will explore the bonding structure, sensitivity of the materials and as a potential tool for identifying damage/defects in the surface lattice. The merits and pitfalls of ion etching will be discussed and a complete method and protocol will be proposed for limiting spectral artefacts and therefore misleading results. The effects of deposition and analysis on the 2D materials' structure and composition will be highlighted as will the characterisation of unwanted reduction/oxidation, contamination and structural defects. Utilising the complete surface analysis tool box allows the analyst to gain further insight and to fully understand the complex nature of these novel materials.

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12:00pm **2D+AS+MI+NS-TuM13 Characterization of Catalytic Active Sites on the Surface of MoS<sub>2</sub> 2-D Materials, Miguel Jose Yacamán**, University of Texas at San Antonio; *T. Zepeda, S. Fuentes Moyado, CNyN UNAM Ensenada, Mexico*

Materials such as the MoS<sub>2</sub> have been used in catalysis at industrial level for many decades mostly on the hydrodesulfurization of naftas.

However more stringent regulations about the sulfur amount in diesel has printed the need to improve the catalysts. In order to achieve that it is important to understand the nature of the active sites and ways to improve the activity. In this presentation we discuss the use of in-situ techniques to study the surfaces of MoS<sub>2</sub> materials made of few layers and discuss the role of the sites on the crystal edges. We also demonstrate that during the reaction the MoS<sub>2</sub> material becomes crumpled and changes from semiconductor to metallic.

## 2D Materials

### Room A226 - Session 2D+EM+MI+MN+NS+QS-TuM

#### Novel Quantum Phenomena

**Moderator:** Arend van der Zande, University of Illinois at Urbana-Champaign

8:00am **2D+EM+MI+MN+NS+QS-TuM1 Charge Density-Wave States in Single-Layer Transition-Metal Dichalcogenides, Phil King**, University of St Andrews, UK

INVITED

Control over materials thickness down to the single-atom scale has emerged as a powerful tuning parameter for manipulating not only the single-particle band structures of solids, but increasingly also their interacting electronic states and phases. A particularly attractive materials system in which to explore this is the transition-metal dichalcogenides, both because of their naturally-layered van der Waals structures as well as the wide variety of materials properties which they are known to host. Yet, how their interacting electronic states and phases evolve when thinned to the single-layer limit remains a key open question in many such systems. Here, we use angle-resolved photoemission to investigate the electronic structure and charge density wave (CDW) phases of monolayer TiSe<sub>2</sub>, TiTe<sub>2</sub>, and VSe<sub>2</sub>. Three-dimensionality is a core feature of the electronic structure of all of these parent compounds, but we show how their CDW phases not only persist, but are strengthened, in the monolayer limit. In TiSe<sub>2</sub>, we observe an orbital-selective CDW, necessarily without a  $k_z$ -selectivity in band hybridisation that is of key importance for the bulk instability,<sup>1</sup> while TiTe<sub>2</sub> is driven into a charge-ordered phase in the monolayer which is not stable in the bulk at all. In VSe<sub>2</sub>, we show how the monolayer hosts a much stronger-coupling CDW instability than the bulk, which in turn drives a metal-insulator transition, removing a competing instability to ferromagnetism.<sup>2</sup> Together, these studies point to the delicate balance that can be realized between competing interacting states and phases in monolayer transition-metal dichalcogenides.

*This work was performed in close collaboration with M.D. Watson, A. Rajan, J. Feng, D. Biswas, and colleagues from the Universities of St Andrews, Oxford, Keil, Diamond, Elettra, and SOLEIL.*

<sup>1</sup>Watson *et al.*, Phys. Rev. Lett. 122 (2019) 076404.

<sup>2</sup>Feng *et al.*, Nano Lett. 18 (2018) 4493.

9:00am **2D+EM+MI+MN+NS+QS-TuM4 Indirect Transition and Opposite Circular Polarization of Interlayer Exciton in a MoSe<sub>2</sub> WSe<sub>2</sub> van der Waals Heterostructure, Hsun-Jen Chuang**, A.T. Hanbicki, M.R. Rosenberger, C.S. Hellberg, S.V. Sivaram, K.M. McCreary, I.I. Mazin, B.T. Jonker, U.S. Naval Research Laboratory

An emerging class of heterostructures involves monolayer semiconductors such as many of the transition metal dichalcogenides (TMDs) which can be combined to form van der Waals heterostructures (vdWHs). One unique new optical property of heterostructure is an interlayer exciton (ILE), a spatially indirect, electron-hole pair with the electron in one TMD layer and the hole in the other. Here, we fabricated MoSe<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer encapsulated in h-BN with the alignment angle close to 60 degree between MoSe<sub>2</sub> and WSe<sub>2</sub>. Followed by the state-of-the-art preparation techniques (Nano-squeegee) to ensure the optimal contact between the TMDs. The Strong ILE emission is observed with the emission energy around 1.35 eV at room temperature and resolve this emission into two distinct peaks (ILE1 and ILE2) separated by 24 meV at zero field at 5 K. Furthermore, we demonstrate that the two emission peaks have opposite circular polarizations with up to +20% for the ILE1 and -40% for ILE2 when excited

by circularly polarized light. *Ab initio* calculations provide an explanation of this unique and potentially useful property and indicate that it is a result of the indirect character of both electronic transitions. These peaks are double indirect excitons. *i.e.* indirect in both real and reciprocal space, split by relativistic effects.

This research was performed while H.-J.C. held an American Society for Engineering Education fellowship and M.R.R. and S.V.S. held a National Research Council fellowship at NRL. This work was supported by core programs at NRL and the NRL Nanoscience Institute. This work was also supported in part by a grant of computer time from the DoD High Performance Computing Modernization Program at the U.S. Army Research Laboratory Supercomputing Resource Center.

9:20am **2D+EM+MI+MN+NS+QS-TuM5 Integrating 2D Magnet 1T-MnSe<sub>2</sub> with Topological Insulator Bi<sub>2</sub>Se<sub>3</sub>, Tiancong Zhu**, The Ohio State University; *D. O'Hara*, University of California, Riverside; *J.J. Repicky, S. Yu, M. Zhu, B.A. Noesges, T. Liu, M. Brenner, L.J. Brillson, J. Hwang, F.Y. Yang, J.A. Gupta, R. Kawakami*, The Ohio State University

Integrating two-dimensional (2D) magnet with topological insulator is an exciting topic. Other than the possible proximity induced magnetic ordering inside topological insulator, the 2D magnet/topological insulator heterostructure can also lead to more efficient spin orbit torque switching, or the formation of magnetic skyrmions. The recent discovery of room temperature ferromagnetic ordering in 2D material MnSe and VSe further brings more potential in such heterostructure systems. In this talk, we report the synthesis and characterization of 2D magnet 1T-MnSe on topological insulator Bi<sub>2</sub>Se<sub>3</sub>. Monolayer of MnSe is grown on Bi<sub>2</sub>Se<sub>3</sub> with molecular beam epitaxy, and subsequently characterized with various techniques, including X-ray diffractometry (XRD), X-ray photoemission spectroscopy (XPS) and scanning tunneling microscopy (STM). STM measurement reveals the co-existence of monolayer a-MnSe(111) and 1T-MnSe<sub>2</sub> on Bi<sub>2</sub>Se<sub>3</sub> surface. By performing spin-polarized STM measurement with Cr tip, we observed directly the magnetic signal from 1T-MnSe<sub>2</sub> on Bi<sub>2</sub>Se<sub>3</sub>. The growth of 1T-MnSe<sub>2</sub> on Bi<sub>2</sub>Se<sub>3</sub> further leads to the MBE synthesis of magnetic topological insulator Bi<sub>2</sub>MnSe<sub>4</sub>, which also shows ferromagnetism down to the monolayer limit. The structural and magnetic characterization of the material will also be discussed in this talk.

9:40am **2D+EM+MI+MN+NS+QS-TuM6 Effect of Exchange-correlation Functional and Structural Constraints on the Transition Temperature of Two-Dimensional Ferroelectrics, Shiva P. Poudel**, J. Villanova, B. Miller, A. Pandit, S. Barraza-Lopez, University of Arkansas, Fayetteville

In this presentation, I will discuss two inconsistent models for obtaining the transition temperature ( $T_c$ ) of two-dimensional (2D) ferroelectrics. It will be shown that the inconsistency arises from the choice of exchange-correlation functional and structural constraints [1-4] by obtaining  $T_c$  for a SnSe monolayer with PBE and vdW exchange-correlation functional, and with increased constraints. It has been found that vdW functional gives a larger  $T_c$  in comparison with PBE functional. Also, the increasing constraint raises  $T_c$  as well. Afterward, a complete analysis of the converged unit cell with seven different exchange-correlation functional will be provided. These results represent the most comprehensive theoretical benchmarks for these intriguing 2D ferroelectric materials.

This work was funded by an Early Career Grant from the DOE (Grant No. DE-SC0016139). Calculations were performed on Cori at the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility operated under Contract No. DE-AC02-05CH11231 and Arkansas High-Performance Computing Center's *trestles*, which is funded through the multiple National Science Foundation grants and the Arkansas Economic Development Commission.

References:

1. M. Mehboudi *et al.*, Nano Lett. **16**, 1704 (2016).
2. M. Mehboudi, *et al.*, Phys. Rev. Lett. **117**, 246802 (2016).
3. S. Barraza-Lopez, *et al.*, PRB **97**, 024110 (2018).
4. R. Fei, *et al.*, Phys. Rev. Lett. **117**, 097601 (2016).

11:00am **2D+EM+MI+MN+NS+QS-TuM10 Sign-change Pairing Symmetry in Single Layer FeSe/SrTiO<sub>3</sub> Film, Huimin Zhang**, West Virginia University; *Z. Ge, M. Weinert*, University of Wisconsin; *L.L. Li*, West Virginia University  
Single layer FeSe film epitaxially grown on SrTiO<sub>3</sub>(001) substrate has drawn much interest for its novel interfacial effects, which have led to the highest superconducting temperature ( $T_c$ ) to date amongst all Fe-based superconductors. While several pairing states, such as sign-persevering  $s_{\pm}$ -wave, sign-changing nodeless  $d$ -wave and  $s_{\pm}$ -wave have been suggested,

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the pairing symmetry remains to be experimentally validated. Here we investigate the intrinsic impurity-induced in-gap bound states and quasiparticle interference (QPI) patterns in single layer FeSe/SrTiO<sub>3</sub> by scanning tunneling microscopy/spectroscopy. We observed bound states induced by nonmagnetic impurities, which strongly suggests a sign-changing order parameter. Through detailed analysis of the phase-sensitive QPI patterns, we further confirm that the order parameter indeed changes sign within the electron pockets. This identification of a sign change pairing symmetry in single layer FeSe/SrTiO<sub>3</sub> presents a critical step towards the understanding of its high  $T_c$  superconductivity.

11:20am **2D+EM+MI+MN+NS+QS-TuM11 High Temperature Superconductivity in Epitaxial Single Layer FeTe<sub>1-x</sub>Se<sub>x</sub>/STO(001), Qiang Zou, Z. Ge, C. Yan, H. Zhang, L.L. Li, West Virginia University**

Single crystal FeTe exhibits a distinct long-range bicollinear antiferromagnetic order that can be suppressed by alloying with Se, where superconductivity emerges at a critical Se concentration of 0.3 with a  $T_c$  of 10 K. In this work, we show that this phase transition can be further modulated by reducing the thickness of FeTe<sub>1-x</sub>Se<sub>x</sub> down to the single atomic layer limit. High quality single layer FeTe<sub>1-x</sub>Se<sub>x</sub> films are grown on SrTiO<sub>3</sub>(001) substrate by molecular beam epitaxy and characterized by scanning tunneling microscopy/spectroscopy and angle-resolved photoemission spectroscopy. We find the electronic properties are strongly dependent on the Se content. For  $x < 0.1$ , hole-like bands cross the Fermi level and form a hole-pocket at the  $\Gamma$  point with no states observed around the M point, indicating no superconductivity. With increasing Se content, the top of the valence bands moves away from the Fermi level, accompanied by a decrease in effective mass at the  $\Gamma$  point. For  $x > 0.1$ , the hole pocket at  $\Gamma$  point moves below the Fermi level, and an electron-pocket emerges at M point where a superconducting gap opens with a  $T_c$  of  $\sim 50$  K. These findings and their implications for the emergence and stabilization of superconductivity in Fe-based superconductors at reduced dimensions will be presented at the meeting.

11:40am **2D+EM+MI+MN+NS+QS-TuM12 The Observation of Majorana Zero Mode and Conductance Plateau in an Iron-based Superconductor, Hong-Jun Gao, Institute of Physics, Chinese Academy of Sciences, China INVITED**

Majorana zero-modes (MZMs) are spatially-localized zero-energy fractional quasiparticles with non-Abelian braiding statistics that hold great promise for topological quantum computing. Recently, by using scanning tunneling microscopy/spectroscopy (STM/STS), a new breakthrough of Majorana zero mode (MZM) was achieved in a single material platform of high- $T_c$  iron-based superconductors, FeTe<sub>0.55</sub>Se<sub>0.45</sub>, which combined advantages of simple material, high- $T_c$ , and large ratio of  $\Delta/E_F$  [1]. A detail STM/STS study of a FeTe<sub>0.55</sub>Se<sub>0.45</sub> single crystal, also revealed the mechanism of two distinct classes of vortices present in this system, which directly tied with the presence or absence of zero-bias peak [2]. To further investigated the MZM, it is still needed to find a "smoking-gun" type of evidence for the existence of MZM, and a quantized conductance plateau is widely believed to be one of them. Here we report an observation of the Majorana conductance plateau in vortices on the iron superconductor FeTe<sub>0.55</sub>Se<sub>0.45</sub> surface by using STM/STS [3]. We found that both extrinsic instrumental convoluted broadening and intrinsic quasiparticle poisoning can reduce the conductance plateau value. When extrinsic instrumental broadening is removed by deconvolution, the plateau is found to nearly reach a  $2e^2/h$  quantized value. The direct observation of a conductance plateau on a single zero-mode in a vortex strongly supports the existence and protection of MZMs in this iron-based superconductor, which can serve as a single-material platform for Majorana braiding at relatively high temperature.

\* In collaboration with, D.F. Wang<sup>1,2</sup>, L.Y. Kong<sup>1,2</sup>, P. Fan<sup>1,2</sup>, H. Chen<sup>1</sup>, S.Y. Zhu<sup>1,2</sup>, W.Y. Liu<sup>1,2</sup>, L. Cao<sup>1,2</sup>, Y.J. Sun<sup>1,2</sup>, S.X. Du<sup>1,2,3</sup>, J. Schneeloch<sup>4</sup>, R.D. Zhong<sup>4</sup>, G.D. Gu<sup>4</sup>, Liang Fu<sup>5</sup>, Hong Ding<sup>1,2,3</sup>.

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## Electronic Materials and Photonics Division Room A214 - Session EM+2D+AP+NS+PS-TuM

### New Devices and Materials for Electronics and Photonics

**Moderators:** Sean W. King, Intel Corporation, Michelle M. Paquette, University of Missouri-Kansas City

8:00am **EM+2D+AP+NS+PS-TuM1 Performance Modeling and Design for Spintronic Logic and Memory Devices, Azad Naeemi, Georgia Institute of Technology INVITED**

As scaling conventional logic and memory devices becomes more and more challenging, there is a global search for novel materials and devices that can augment mainstream technologies used for data storage and processing. To this end, spintronic materials and devices are promising candidates as they provide dense non-volatile storing elements that enable novel computing paradigms such as in memory-computing and neural networks.

This talk will present physical models for various read and write spintronic mechanisms and quantifies the potential performances of Boolean circuits based on various spintronic logic devices. It will be shown that without major breakthroughs such circuits will not be able to compete with their CMOS counterparts. However, novel circuit paradigms that take advantage of the physics of these devices can potentially provide significant benefits. For example, cellular neural networks based on spintronic devices are projected to perform better compared to their analog CMOS implementation.

While spin-transfer-torque random access memory (STT-RAM) is becoming commercially available, it suffers from relatively large switching currents that limits its density and causes reliability challenges. Novel read and write mechanisms such as spin-orbit torque or magneto-electric effects can potentially address or partially mitigate some of these challenges. In this talk, the array-level potential performance of various magnetic memory devices will be quantified and benchmarked.

8:40am **EM+2D+AP+NS+PS-TuM3 High Yield, Low Variability HfO<sub>2</sub> 1T1R Cells Fabricated in 65nm CMOS, J.H. Hazra, M.L. Liehr, K. Beckmann, Nathaniel C. Cady, SUNY Polytechnic Institute**

Hafnium Oxide (HfO<sub>2</sub>) based Resistive Random Access Memory (ReRAM) devices are promising candidates for non-volatile memory, having a wide variety of applications in neuromorphic computing, artificial intelligence and future memory solutions. Stochastic conductive filament (CF) generation and rupture processes, however, contribute to high variability resistive switching in these devices. In order to address this issue, an extensive characterization of HfO<sub>2</sub> 1 transistor 1 RRAM (1T1R) cells was performed to investigate switching yield and cell-to-cell variability. 1T1R devices were integrated into a 300mm wafer platform utilizing the IBM 65nm 10LPe process technology, in which the memristor device stack is implemented between the M1 and M2 metallization layers, using a custom designed FEOL compatible process flow. The ReRAM device stack is comprised of a TiN bottom electrode followed by conformal deposition of the HfO<sub>2</sub> switching layer, Ti oxygen scavenging layer and TiN top electrode. The HfO<sub>2</sub> switching layer was deposited using an atomic layer deposition (ALD) process with an organic precursor. For statistical significance, the performance of 50 different 1T1R cells was compared for cell-to-cell variability in operating voltage and resistance in the on and off state. An impressive 100% switching yield and low cell-to-cell switching variability were observed for these devices. 1T1R cells were also investigated for long term endurance and high temperature retention, exhibiting excellent endurance of up to 1 billion switching cycles with an average  $R_{off}/R_{on}$  ratio of 10:1. As compared to 1T1R cells that we have fabricated with alternative ALD precursors/methods, these devices show superior yield and performance. We are currently performing compositional and structural comparisons between these sets of devices, to elucidate the impact of ALD precursor choice and processing methods on yield and electrical performance.



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9:00am **EM+2D+AP+NS+PS-TuM4 Heat Transfer Proximity Effects in Resistive Memory Crossbar Arrays**, *Marius Orlowski, M.S. Al-Mamun*, Virginia Tech

Evidence for thermal cross talk in resistive RAM memory arrays is presented. Frequent switching of a resistive memory cell (Cu/TaO<sub>x</sub>/Pt) may lead to a considerable local accumulation of Joules heat. The heat generated in a stressed device spreads via common electrode lines to the neighboring cells impacting their switching behavior. As a probe into degraded performance of the neighbor cells we choose the cell itself set into the on-state under specific conditions. The cell is set at a critical compliance current  $I_{cc}$  that allows repeated switching for no more than ~15 cycles. After the maximum number of cycles the on-state becomes volatile. For a lower  $I_{cc}$ , the cell produces a volatile on-state, and for higher  $I_{cc}$  the cell switches for hundred of times with a stable on-state. We find that the cells in close proximity of the heated device display various degrees of degradation indicated by a reduced number of cycles of the probed cell. The 1<sup>st</sup> neighbor cell experiences the greatest, and the 4<sup>th</sup> neighbor cell the smallest degradation. This indicates the spread of the heat from the heated device to its neighbors. After a sufficient cooling off period (10 minutes or longer), all the neighboring cells and the heated device display again the maximum number of cycles i.e. 15, when set under the critical compliance current and reset, repeatedly. Also cells that don't share any of the common electrode metal lines with the heated source cell, may degrade provided that the intermediate cells are set to on-state, thus enabling a continuous thermal conduction path between the heated cell and the probed cell. The heat dissipation from the heated device is slower for narrow and thin metal electrode lines than for wide and thick metal lines. However, in case of wide and thick metal lines more distant neighbor cells are affected by the parasitic cell-to-cell heat transfer.

We have performed the characterization of the neighboring cells along the Cu and Pt electrode lines. We find that the performance degradation of the neighboring cells along the Cu line is significantly stronger than along the Pt metal line. This observation is consistent with the much better heat conductivity of Cu lines (385W/(mK) and 150nm thick) than the Pt (72W/(mK) and 50nm thick) lines, but is at odds with the assumption of the standard electro-chemical metallization model postulating a conical shape of the Cu filament with a broad base of the cone at the Pt electrode and a tip at the Cu electrode. We discuss the extant controversial experimental evidence and models for the filament's shape and propose an hour-glass shape for the filament reconciling the extant findings and our thermal results.

9:20am **EM+2D+AP+NS+PS-TuM5 High Performance Memristive Action in Methylammonium Bismuth Iodide([MA]3Bi2I9) Films**, *P. Cheng*, Vanderbilt University; *G. Luo*, Washington University in St. Louis; *Z. Gao*, University of Central Florida; *A. Thind*, *R. Mishra*, Washington University in St. Louis; *Parag Banerjee*, University of Central Florida

We demonstrate high performance (ON/OFF ~ 2.4x10<sup>5</sup>) resistive switching in methylammonium bismuth iodide ((CH<sub>3</sub>NH<sub>3</sub>)<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> or, MBI) thin films.<sup>1</sup> MBI has a post-perovskite structure and consists of 2D layers of face-shared

BiI<sub>6</sub> octahedra. This talk focuses on the structure, composition and associated defect chemistry that is critical for memristive behavior in MBI films.

Memristors are formed by contacting MBI films with aluminum electrodes. The switching for a 200 nm film is observed at voltages ~ 0.5 V. High frequency performance of these memristors shows a peak ON/OFF ratio 2.4x10<sup>5</sup> at 50 KHz. The ON state retention is maintained at 50C for > 10<sup>6</sup> seconds. Stable room temperature endurance is noted for up to 1000 cycles. Energy dispersive x-ray spectroscopy on planar memristor devices show that, postswitching,

a detectable change in the I- concentration is observed closer to the anode side. Density-functional theory (DFT) calculations show low activation barrier for iodine migration in agreement with the experimental results. The DFT calculations also provide insights about the migration pathway and strategies to control this behavior.

From a synthesis perspective, MBI films can be deposited using solution as well as low temperature (< 200C), atmospheric CVD technique.<sup>2</sup> The compounds are air stable. This family of ternary compounds offers a large compositional and structural tunability; unlike binary metal oxides commonly used for memristors. As opposed to recent 2D MoS<sub>2</sub> based planar, tunneling RAM devices<sup>3</sup>, the vertical stack of the 2-terminal memristor bodes well for scalability. Thus, we propose that hybrid organic-

inorganic thin films may offer strategic materials and design advantages together with seamless process integration into current Si-based devices.

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9:40am **EM+2D+AP+NS+PS-TuM6 Mechanism of Chalcogen Passivation of GaAs Surfaces**, *Takayuki Suga*, *S. Goto*, UEC-Tokyo, Japan; *A. Ohtake*, *NIMS*, Japan; *J.N. Nakamura*, UEC-Tokyo, Japan

GaAs surfaces are stabilized by surface treatments with Se or S through the reduction of the dangling bond density [1,2]. It has long been thought that the Se- or S-treated GaAs(111)B-(1x1) surface has a simple structure; the outermost As atoms of the ideal (111)B surface are completely replaced by Se or S atoms, the Se- or S-terminated model [3]. In general, the structural stability of compound semiconductor surfaces can be explained in terms of the so-called electron-counting rule (ECR) [4]. The Se- or S-terminated model, however does not satisfy ECR. Recently, the atomic structure of the Se-treated GaAs(111)B surface has been revisited [5] and another structure model has been proposed, where the Se atoms substitute 3/4 of the topmost surface As atoms in a (2x2) unit [6]. This mixed Se/As-terminated model satisfies ECR, being electronically stable [6]. We have depicted phase diagrams of Se- or S- treated GaAs(111)B surface at 0K as functions of the chemical potentials of Se ( $\Delta\mu_{\text{Se(S)}}$ ) and As ( $\Delta\mu_{\text{As}}$ ). The (2x2) As-trimer and the mixed Se(S)/As-terminated surfaces appear under Se poor condition. It is noted that the Se- or S-terminated surface also becomes stable as  $\Delta\mu_{\text{Se}}$  or  $\Delta\mu_{\text{S}}$  increases, respectively, even though these surfaces are not qualified for ECR.

The Se(S)-treated GaAs(111)B surface is prepared experimentally by molecular beam epitaxy under a finite temperature and a gas pressure. Therefore, it is necessary to consider the free energy of a molecule in vapor phase. In this study, we investigate the stabilization of the Se- or S-treated GaAs(111)B surface structures by considering the beam equivalent pressure of As and Se(S) in a growth temperature using the first-principles calculations within the density functional theory. The chemical potentials of molecules are derived from the partition functions for the translation, the rotation, and the vibrational motions.

In the phase diagram for the actual experiment condition, T=800K, the mixed Se/As terminated surface appears in the Se pressure of 10<sup>-15</sup>-10<sup>-5</sup> Torr, being consistent with the recent experiment [5]. Surprisingly, the Se-terminated surface also becomes stable as the Se pressure increases. We will discuss the stabilization mechanism of the chalcogen-treated GaAs surfaces.

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11:00am **EM+2D+AP+NS+PS-TuM10 Combining 2D and 1D Atomic Scale Tailored Nanowire Surfaces for Novel Electronics and Photonics**, *Anders Mikkelsen*, Lund University, Sweden

INVITED

The III-V nanowire (NW) technology platform has reached a level of advancement that allows atomic scale control of crystal structure and surface morphology as well as flexible device integration. In particular, controlled axial stacking of Wurtzite (Wz) and Zincblende (Zb) crystal phases is uniquely possible in the NWs. We explore how this can be used to affect electronic, optical and surface chemistry with atomic scale precision opening up for 1D, 2D and 3D structures with designed local properties.

We have previously demonstrated atomically resolved Scanning Tunneling Microscopy/Spectroscopy (STM/S) on a wide variety of these III-V NWs and on operational NW devices[1-4]. We now use these methods for studying atomic scale crystal phase changes, the impact on local electronic

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properties and demonstrating full atomic resolution STM during device operation[5-7]. We explore the surface alloying of Sb into GaAs NWs with controlled axial stacking of Wz and Zb crystal phases[5] demonstrating a simple processing-free route to 1D and 2D compositional control at the monolayer level. Further we show how Bi can form unique 1D and 2D structures in particular on the unique Wz GaAs NW segments. Using 5K STM/S we measure local density of states of Zb crystal segments in Wz InAs NWs down to the smallest possible atomic scale crystal lattice change [6], which is effectively a small 2D material segment in a 1D structure. We find that the general Zb electronic structure is preserved locally in even the smallest segments and signatures of confined states in them.

Characterization to the atomic scale during electrical and optical operation is necessary to understand and develop the functionality of structures as discussed above. We demonstrate a novel device platform allowing STM/S with atomic scale resolution across a III-V NW device simultaneously with full electrical operation and high temperature processing in reactive gases[7]. Using 5-15 femtosecond laser pulses combined with PhotoEmission Electron Microscopy (PEEM) we explore local dynamic response of carriers in the 1D Wz and Zb crystal phases down to a few femtoseconds temporally and a few tens of nanometer spatially[8].

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11:40am **EM+2D+AP+NS+PS-TuM12 Nanoflower Decorated GaN and AlGaIn/GaN based Catalyst-free CO Sensors**, *Monu Mishra, G. Gupta*, National Physical Laboratory, India

III-Nitride semiconductors owing unique material properties have proven their potential in the detection of light, chemical, biomolecules and toxic/explosive gases. Despite of numerous advantages viz. biocompatibility, high temperature/frequency tolerance and harsh/adverse environmental condition sustainability, the use of expensive catalysts (e.g. platinum) and higher operation temperature (>250°C) for gas sensing has plagued the development of GaN based cost-effective sensing technology. Upto the best of our knowledge, literature lacks any scientific report on the development of catalyst-free CO sensors operating at room-temperature using GaN or AlGaIn/GaN structures indicating the necessity of dedicated scientific attention in this area. Therefore, we report the fabrication of nanoflowers-decorated GaN and AlGaIn/GaN heterostructure based catalyst-free CO sensors operating at lower (including room) temperature. Planar as well as nanostructured GaN & AlGaIn/GaN thin films were employed for sensors fabrication which exhibited significant CO sensing associated with its superior surface and interface properties. For in-depth understanding, the obtained results were thoroughly analyzed and correlated to investigate the underlying science/phenomenon which revealed that CO sensing on GaN (and AlGaIn/GaN) is governed by the chemical nature of ambient-oxidation induced amorphous oxide ( $O_2^-$ ,  $O^{2-}$  or OH<sup>-</sup> species) layer grown on the surface and acting as a donor/acceptor state. Besides, electron accumulation at AlGaIn/GaN interface influenced the critical parameters like Schottky barrier height, ideality factor etc. perturbed the effective carrier transport and ultimately the device performance. The study demonstrates that development of catalyst-free room temperature operating GaN based CO sensors is feasible using nanostructured surfaces, though further research is required for optimization of device performance.

12:00pm **EM+2D+AP+NS+PS-TuM13 Surface Transfer Doping of Diamond by Complex Metal Oxides for Power Electronics: A Combined Experimental and Simulation Study**, *Vihar Georgiev, A.J. Moran, A. McGhee*, University of Glasgow, UK

Diamond has unique properties that make it an attractive wide band-gap material to produce future high-performance electronic devices. With a wide band-gap of 5.5eV, a thermal conductivity 5 times greater than 4H-SiC, a high breakdown field and high hole and electron carrier velocities, diamond is a clear stand out candidate for high frequency and high power devices. However, the lack of a suitable doping mechanism has hindered

the application of diamond in electronic devices. Conventional substitutional doping techniques are limited as it is difficult to substitute atoms into the diamond crystal lattice.

Surface Transfer Doping (STD) gives the use of diamond for such applications more promise. For STD to occur there are typically two prerequisites: hydrogen terminated diamond (H-diamond) and an electron accepting material in intimate contact with the H-diamond surface. The hydrogen termination gives the diamond a negative electron affinity which facilitates the transfer of electrons from the diamond to the electron-accepting material, creating a shallow, quasi two-dimensional hole gas (2DHG) in the diamond. This doping process traditionally relies upon interfacial electron transfer between the diamond valence band and favourable energy states provided by atmospheric molecules dissolved in a water layer naturally adsorbed on the diamond surface. However, the stability of this atmospheric layer, upon which the transfer doping process relies, has been a significant limiting factor in the production of high-power handling and robust operation devices.

One of the materials that can improve the performance and stability of STD in diamond are the metal oxides such as MoO<sub>3</sub> which acts as an alternative electron acceptor medium on the H-diamond surface. In order to validate and understand the physical and the chemical process in such STD, in this work we have combined experimental and simulation studies. The electrical characterisation is done by high temperature Hall measurements. Those experimental results are compared to numerical simulation based on the first principle methods such as Density Functional Theory. Comparing the simulation and experimental results revealed that the electrons are transferred from the diamond to the metal oxides, leading to formation of a sub-surface 2DHG in the diamond. Due to this transfer of electrons to the oxide the hole carrier concentration increases in comparison to the air-exposed H-diamond. Our work shows the potential to improve the stability and performance of hydrogen-terminated diamond electronics devices through incorporation of high electron affinity transition metal oxides.

## 2D Materials

### Room A216 - Session 2D+EM+MI+NS-TuA

#### Properties of 2D Materials including Electronic, Magnetic, Mechanical, Optical, and Thermal Properties II

Moderator: Roland Wiesendanger, University of Hamburg, Germany

2:40pm **2D+EM+MI+NS-TuA2 Resolving the Structural and Electronic Properties of Graphene/Ge(110)**, *Luca Camilli*, Technical University of Denmark, Denmark; *M. Galbiati*, Technical University of Denmark; *L. Persichetti*, *M. De Seta*, Università degli Studi Roma Tre, Italy; *F. Fabbri*, Italian Institute of Technology, Italy; *A. Scaparro*, Università degli Studi Roma Tre, Italy; *A. Notargiacomo*, Centro Nazionale di Ricerca, Italy; *V. Miseikis*, *C. Coletti*, Italian Institute of Technology, Italy; *L. Di Gaspare*, Università degli Studi Roma Tre, Italy

Unraveling the structural and electronic properties of the interface between graphene and conventional semiconductors is critical to enable novel graphene-based applications [1].

In this framework, the graphene/Ge(110) system has since last year received unprecedented attention [2-6]. Notably, graphene can be grown via chemical vapor deposition directly on the surface of germanium, similarly to the case of graphene grown on metals [7]. From a structural point of view, the graphene/Ge system is very dynamic, and the Ge surface has been shown by scanning tunneling microscopy (STM) studies to undergo a number of changes (i.e., reconstructions). However, the conclusions drawn in those studies do not always agree, probably also due to the strong dependence of the STM images on the applied voltage bias that makes comparison between different images rather difficult. In Ref. [6], for instance, the authors report three different surface reconstructions that are driven by thermal annealing, while the authors in Ref. [4] find only the unreconstructed surface and a (6x2) reconstruction, which again can reversibly change to unreconstructed surface after annealing at high temperature in hydrogen.

In this study, we aim at resolving the rich phase diagram of the Ge surface protected by graphene. We carry out annealing of the sample at different temperatures, and use a low-temperature STM to investigate the surface structure with atomic precision. At each stage, images at different applied biases are collected in order to allow a more straightforward comparison of the results.

Moreover, we perform electron energy loss spectroscopy (EELS) and scanning tunneling spectroscopy (STS) at temperature below 10 K to shed light on the electronic properties of the graphene/Ge interface, and to get more insights into their interaction.

Finally, we also show through a combination of STM and Raman spectroscopy that graphene can protect the germanium surface from oxidation even after continuous exposure to ambient conditions for more than 12 months, which is surprisingly a far more efficient protection than that offered by graphene on metals [8, 9].

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3:00pm **2D+EM+MI+NS-TuA3 Array of Strain Induced Quantum Dots in Graphene**, *Md Tareq Mahmud*, *N. Sandler*, Ohio University

Local Gaussian-shaped deformations induce strain fields that are represented by scalar and vector potentials in a continuum model description of electron dynamics in graphene. The ubiquitous strain changes the charge distribution in a very peculiar way, introducing a sublattice symmetry breaking, as has been reported in the literature. This feature can be exploited to design specific charge profiles by combining several deformations. Naturally, a combination of two or more is expected to introduce interference effects that can enhance charge accumulation in specific regions. We have investigated the effects of two overlapping deformations with different separations on the local density of states

(LDOS). We showed that the overlap term can enhance the LDOS leading to stronger charge confinement in certain regions. Motivated by the work of Mason et al (2018) we have extended these studies to a closed pack structure with a unit cell of 3 distinct deformations. This arrangement can be extended by symmetry to a lattice superstructure, thus creating a periodic array of confined charge regions, i.e. quantum dots. This array can be tailored by appropriately choosing the parameters of the deformations and their distances. The total charge distribution in these systems is similar to those observed in twisted bilayer systems, known as 'Moire patterns'. We discuss optimal tuning of deformations to control the physical properties of these graphene devices.

3:20pm **2D+EM+MI+NS-TuA4 Ultrafast Spin and Charge Dynamics in Monolayer WSe<sub>2</sub>-Graphene Heterostructure Devices**, *Michael Newburger*, *Y.K. Luo*, The Ohio State University; *K.M. McCreary*, U.S. Naval Research Laboratory; *I. Martin*, *E. McCormick*, The Ohio State University; *B.T. Jonker*, U.S. Naval Research Laboratory; *R. Kawakami*, The Ohio State University

Monolayer transition metal dichalcogenides (TMDs) have attracted attention due to their long spin/valley lifetimes and ability to couple the helicity of light to spin/valley polarization. Additionally, a strength of TMDs lies in their ability to complement other materials, such as graphene, by acting as a means of optical spin injection or proximity coupling. Recently, multiple groups have demonstrated proximity mediated charge transfer and optical spin injection in TMD/graphene heterostructures. However, the spin transfer dynamics across a TMD/graphene interface remain largely unexplored.

Here we utilize time-resolved Kerr rotation (TRKR) microscopy to image the spatial dependence of spin/valley dynamics in monolayer WSe<sub>2</sub>/graphene heterostructure devices. Spatial maps demonstrate long-lived spin/valley lifetimes on the bare WSe<sub>2</sub> but reveal a quenching of spin-valley signal at the WSe<sub>2</sub>/graphene interfaces. Time delay scans show these interface lifetimes to be quenched up to 3 orders of magnitude in comparison to bare WSe<sub>2</sub>. Furthermore, photoluminescence mapping exhibits quenching at the interfaces while photoconductivity is enhanced in these regions, demonstrating efficient charge transfer from WSe<sub>2</sub> to graphene. Consequently, we attribute the ultrafast spin/valley quenching to the transfer of spin information by conducted charge carriers.

4:20pm **2D+EM+MI+NS-TuA7 Spatially Selective Enhancement of Photoluminescence in MoS<sub>2</sub> by Exciton-Mediated Adsorption and Defect Passivation**, *Saujan V. Sivaram*, *A.T. Hanbicki*, *M.R. Rosenberger*, *G. Jernigan*, *H.-J. Chuang*, *K.M. McCreary*, *B.T. Jonker*, U.S. Naval Research Laboratory

Monolayers of transition metal dichalcogenides (TMDs) are promising components for flexible optoelectronic devices due to their direct band gap and atomically thin nature. The photoluminescence (PL) from these materials is often strongly suppressed by non-radiative recombination mediated by mid-gap defect states. Here, we demonstrate up to a 200-fold increase in PL intensity from monolayer MoS<sub>2</sub> synthesized by chemical vapor deposition (CVD) by controlled exposure to laser light in ambient. This spatially resolved passivation treatment is air and vacuum stable. Regions unexposed to laser light remain dark in fluorescence despite continuous impingement of ambient gas molecules. A wavelength dependent study confirms that PL brightening is concomitant with exciton generation in the MoS<sub>2</sub>; laser light below the optical band gap fails to produce any enhancement in the PL. We highlight the photo-sensitive nature of the process by successfully brightening with a low power broadband white light source (< 10 nW). We decouple changes in absorption from defect passivation by examining the degree of circularly polarized PL. This measurement, which is independent of exciton generation, confirms that laser brightening reduces the rate of non-radiative recombination in the MoS<sub>2</sub>. A series of gas exposure studies demonstrate a clear correlation between PL brightening and the presence of water. We propose that H<sub>2</sub>O molecules passivate sulfur vacancies in the CVD-grown MoS<sub>2</sub>, but require photo-generated excitons to overcome a large adsorption barrier. This work represents an important step in understanding the passivation of CVD-synthesized TMDs and demonstrates the interplay between adsorption and exciton generation.

This research was performed while S.V.S and M.R.R held a National Research Council fellowship and H.-J.C. held an American Society for Engineering Education fellowship at NRL.

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4:40pm **2D+EM+MI+NS-TuA8 Strained Graphene in the Quantum Hall Regime: Valley Splitting and Extra Conducting Channels**, *Daiara Faria*, Ohio University / Universidade do Estado do Rio de Janeiro; *C. León*, Brigham Young University; *L. Lima*, Universidade Rural do Rio de Janeiro, Brazil; *A. Latgé*, Universidade Federal Fluminense, Brazil; *N. Sandler*, Ohio University

The coupling between electronic and mechanical properties in 2D materials has become an important tool to control valleytronics. Graphene experiments have been reported with common deformations such as membrane bending that induces strain in the samples [1]. It has also been shown that strain affects charge distributions and graphene transport properties. Motivated by these responses, we have studied the effect of folds and wrinkles in graphene. New 'edge'-like states along the graphene folded region, that are valley polarized, were found and explored [2]. To take advantage of the existence of these new states, it would be desirable to separate their contribution from the continuum extended states that make graphene a semimetal.

Here we present a theoretical study of folds effects on a graphene membrane in the quantum Hall regime. We show that the addition of an external magnetic field allows the isolation of the valley polarized edge states in energy and in real space. Local density of state calculations in the deformation region predict the valley split peaks, as observed in recent experimental [3]. Using recursive Green's function method, we are able to reveal new extra conducting channels due to the "new edges" at the deformation region. These extra conducting channels could be detected in transport measurements.

A discussion is presented to bring attention on the role of the deformation parameters on the graphene quantum Hall regime and their relations with the magnetic lengths. With this in mind, we perform an analytic study based on the continuum (Dirac) description of electrons in graphene. In this model, the deformation is considered as a perturbation to the Landau Level states. The results show the existence of two different regimes, characterized by the ratio between the magnetic length and the deformation width ( $\gamma = l_B/b$ ). For  $\gamma < 1$  the magnetic confinement allows the electrons to follow the strain potential profile. In this regime, the spatial separation between the polarized currents is larger. This could encourage the design of devices where contacts can efficiently detect these polarized currents.

[1] Y. Jiang et al., Nano Lett. 17, 2839 (2017).

[2] R. Carrillo-Bastos et al., PRB 94, 125422 (2016).

[3] S. Li, arXiv:1812.04344.

5:00pm **2D+EM+MI+NS-TuA9 Unraveling the Novel Quantum Phenomena in Two-dimensional Materials using Transport and Photoemission Spectroscopy**, *Jyoti Katoch*, Carnegie Mellon University **INVITED**

The extreme surface sensitivity of two-dimensional (2D) materials provides an unprecedented opportunity to engineer the physical properties of these materials via changes to their surroundings, including substrate, adsorbates, defects, etc. In addition, 2D materials can be mechanically assembled layer-by-layer to form vertical or lateral heterostructures, making it possible to create new material properties merely by the choice of the constituting 2D layers and the relative twist angle between them. In this talk, I will discuss our recent transport [1] and photoemission [2, 3] results that shed light on the intricate relationship between controlled external perturbations, substrate, and electronic properties of 2D materials. I will show that the decoration of the 2D materials with adatoms, such as sub-lattice selective atomic hydrogenation of graphene and alkali metal doping of single layer  $WS_2$  can be utilized to tailor electronic properties and induce novel quantum phenomena in 2D landscape.

[1] Katoch et. al., Physical Review Letters 121, 136801 (2018).

[2] Katoch et. al., Nature Physics 14, 355-359 (2018).

[3] Søren Ulstrup, et. al., arXiv:1904.06681 (2019).

5:40pm **2D+EM+MI+NS-TuA11 Electronic Properties and Charge Density Wave Transition in Single-layer  $VSe_2$** , *Kien Nguyen-Cong*, *P. Neto*, *M. Batzill*, *I.I. Oleynik*, University of South Florida

Single-layer  $VSe_2$  has been recently attracted attention due to experimental observations of ferromagnetism and charge density wave (CDW) transition. There are controversies from both theory and experiment concerning ferromagnetism in both bulk and single layer  $VSe_2$ . In addition, CDW transition in  $VSe_2$  is not well understood. In this work, structural, electronic, magnetic and CDW properties of this system are investigated using first-principle calculations. The calculated electronic structure is compared with

recent APPRES measurements and conclusions concerning its magnetic state are made. The calculated phonon spectra are used in investigation of CDW transition mechanism. Crystal structure of the CDW state is determined using the evolutionary crystal structure prediction combined with lattice dynamics.

6:00pm **2D+EM+MI+NS-TuA12 Tunable Band Gap and Thermal Conductivity Measurements of Monolayer  $MoSe_2$  by S Incorporation**, *Shyama Rath*, *V. Singh*, University of Delhi, India

Monolayer  $MoSe_2$  was grown on insulating  $SiO_2/Si$  substrates by chemical vapor deposition. Scanning electron microscopy and optical contrast images were used to determine the domain size, morphology, and the number of layers. The crystallinity, and thickness of the synthesized domains were determined by Raman spectroscopy. The band gap was determined from Photoluminescence (PL) spectroscopy. The PL emission was absent for more than 4 layers, and the peak position varied from 1.48 eV for 4 layers to 1.55 eV in the monolayer limit. Sulphur incorporation was done to obtain  $MoS_xSe_{2-x}$  so as to obtain a further tunability of the bandgap. The band gap changes from 1.55 eV for monolayer  $MoSe_2$  to 1.64 eV for monolayer  $MoS_{0.32}Se_{0.68}$ . Further, larger area domains were achieved in the alloy as compared to binary. The thermal conductivity of the monolayer  $MoSe_2$  and  $MoS_xSe_{2-x}$  were determined from temperature-dependant Raman spectroscopy.

## Nanometer-scale Science and Technology Division Room A222 - Session NS-TuA

### Recent Advances in Nanoscale Probing and Fabrication

Moderator: Jay Mody, GlobalFoundries Inc

4:20pm **NS-TuA7 Electrical, Photovoltaic, and Nano-Optical Characterization of TMD Lateral Heterostructures**, *Marudachalam Shanmugasundaram*, HORIBA Scientific; *A. Elias*, *M. Terrones*, The Pennsylvania State University; *H. Terrones*, Rensselaer Polytechnic Institute

The growth of lateral heterostructures of transition metal dichalcogenides (TMDs) was recently demonstrated, which has created the potential for fabricating semiconductor devices with novel electronic properties. Specifically, it would combine distinct properties of materials derived from different sources into one device. It has been shown that under well-controlled growth conditions,  $MoS_2$ - $WS_2$  lateral heterostructures with atomically sharp interfaces can be synthesized. While the growth of such materials can be challenging, the development of analytical methods with the capability of providing chemical information, in addition to morphological information, with nanometer-scale spatial resolution is equally challenging.

Raman spectroscopy is used to study chemical composition of materials with high specificity, but it lacks sensitivity due to the inherent weakness of the Raman scattering phenomenon. Besides, its spatial resolution is diffraction-limited to  $\sim 0.5 \lambda$ . These drawbacks can be overcome by combining Raman spectroscopy with Scanning Probe Microscopy (SPM) in which certain metal particles placed at the end of the SPM tip act as plasmonic substrate. This technique is referred to as tip-enhanced Raman spectroscopy (TERS). This combination provides not only the benefits of both SPM and Raman microscopy at the same time, but also enables Raman mapping with spatial resolution proportional to the size of the coated SPM tip (well below the diffraction limit) due to plasmonic enhancement of Raman signal.

In this work, we present characterization of  $MoS_2$ - $WS_2$  lateral heterostructures based on morphology, electrical properties, photovoltaic properties, and chemical composition, using a single platform. Scanning Kelvin imaging was used to map the surface potential as well as electro-mechanical contrast proportional to capacitance from the heterostructures. Their surface potential and capacitance change dramatically in a reversible manner when the heterostructures are illuminated by a laser, highlighting their photovoltaic properties. Raman and photoluminescence (PL) maps were recorded with 532 nm excitation, which enabled collection of Raman and PL bands from both materials simultaneously with reasonable separation. In addition, tip-enhanced Raman and PL maps were collected across the interface, with sub-diffraction limited spatial resolution. In summary, a unique collection of characterization techniques were used based on AFM-Raman instrumentation to study morphological, electrical, photovoltaic properties, and chemical composition of  $MoS_2$ - $WS_2$  lateral heterostructures.

4:40pm **NS-TuA8 Development of Near-Field Electrospinning for 3D Nanofabrication for tissue engineering applications**, *Alex Nagle*, University of Wollongong, Australia

The major goal in this work was to mimic the nanofibrous proteins found in the neural extracellular matrix (nECM). NFES is a versatile nanofiber patterning technique, utilising additive layer-by-layer deposition to create nanofibrous microstructures. However, high volume can be a difficult to achieve due to inhibition of the ejection process by polymer build-up. To mimic the 3D nECM, led to the development of a new technique: Suspension Near-Field Electrospinning (SNFES).

Suspended, aligned fibres can be printed across void space between electrodes and so a strategy of using free standing electrode pillars to support distributed PEO fibres within space was investigated. This strategy relied on a high accuracy, software integrated NFES system as well as 3D printed pillar electrodes, fabricated by Selective laser melt (SLM). Interpillar motion of the emitter, drew fibers between four-pillar electrodes, demonstrating SNFES.

The process parameters, working distance, maximum stage speed, voltage, PEO solution concentration, and pattern iteration effects of SNFES through orthogonal experiments. The need for more complex structures in TE, led to the development of further pattern types, working around the simple four-pillar structure, to produce crossing arrays. Alignment of the arrays was accurate to  $\pm 5^\circ$ ; diameter was modulated by the process parameters; while density exponentially decayed at high iteration by the electrostatic inhibitory effects.

Finally, ultrafine polycaprolactone (PCL) fiber arrays prepared using SNFES, then encapsulated into a biocompatible gellan gum methacrylate (GGMA) hydrogel matrix, to mimic the nanofibrous proteins of the nECM. Parametric studies varying fiber diameter, as well as electrode pillar design and pattern iteration; elucidated the encapsulated array effects. It was found that fiber encapsulation led to dramatic improvements in the constructs mechanical properties, raising the storage modulus from 0.17 up to 1.28 kPa, (native tissue 0.5 -1kPa) upon minimising the fiber diameter below 1 micron.

The findings of this research are significant as it creates for the first time a suspended polymer nanoarray, in a directed manner, which can be extended across multiple working 3D planes in situ. The hybrid fiber-gel systems can be mechanically tailored based on the findings of the parametric experiments. The increase in nanoarray volume and density achieved here is expected to address challenges of producing hierarchical tissue constructs in 3D.

## Acknowledgements

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5:20pm **NS-TuA10 The Effects of Atomic-Scale Strain Relaxation on the Electronic Properties of Monolayer  $\text{MoS}_2$** , *Daniel Trainer*, *Y. Zhang*, Argonne National Laboratory; *F. Bobba*, University of Salerno, Italy; *X. Xi*, Temple University; *S-W. Hla*, Argonne National Laboratory; *M. Iavarone*, Temple University

The ability to control nanoscale electronic properties by introducing macroscopic strain is of critical importance for the implementation of two-dimensional (2D) materials into flexible electronics and next-generation strain engineering devices. In this work, we correlate the atomic-scale lattice deformation with a systematic macroscopic bending of monolayer molybdenum disulfide films by using scanning tunneling microscopy and spectroscopy implemented with a custom-built sample holder to control the strain. Using this technique, we are able to induce strains of up to 3% before slipping effects take place and relaxation mechanisms prevail. We find a reduction of the quasiparticle bandgap of about 400 meV per percent local strain measured with a minimum gap of 1.2 eV. Furthermore, unintentional nanoscale strain relaxation of van der Waals monolayer sheets can negatively impact strain engineered device performance. Here we investigate such strain relaxation mechanisms that include one-dimensional ripples and 2D wrinkles which alter the spatial electronic density of states and strain distribution on the atomic scale.

5:40pm **NS-TuA11 Probing the Viscoelastic Properties of Polymer Composites with AFM-based Dynamic Mechanical Analysis**, *B. Pittenger*, *S. Osechinskiy*, *J. Thornton*, *S. Loire*, **Thomas Mueller**, Bruker Corporation

The mechanical performance and function of polymer composites and thin films are controlled by the properties of the components as well as the microstructure of the material. As confinement effects and interphase

formation can alter properties of the microphases, only measurements performed directly on the composite can provide the needed local property distribution. Mechanical properties of polymers are generally time dependent, so a full understanding requires measurements over a range of frequencies and temperatures. Ideally, one would like to observe the mechanical behavior of these microscopic domains while they pass through their glass transitions to appreciate the influence of size effects and confinement on time dependent mechanical properties.

With its proven ability to map mechanical properties at the nanometer level [1], Atomic Force Microscopy (AFM) has the resolution and mechanical sensitivity needed to investigate these domains. Unfortunately, established AFM measurement modes do not yield results that allow direct comparison to established rheological techniques like Dynamic Mechanical Analysis (DMA). Contact resonance [2] provides mechanical property maps at well-defined frequencies, but cantilever resonances are many orders of magnitude higher than DMA, making comparisons indirect at best. Intermittent contact methods like TappingMode [3], force volume, and PeakForce Tapping [4] face challenges in calculating intrinsic mechanical properties like storage and loss modulus (or  $\tan \delta$ ) due to the non-linear process of making and breaking contact [5].

AFM based nano-DMA (AFM-nDMA) provides viscoelastic results that can be directly compared with bulk DMA. Like bulk DMA, it provides spectra of storage and loss modulus across frequency and temperature allowing construction of master curves through Time Temperature Superposition (TTS) [6]. In addition, it allows high resolution measurements localized to the microscopic structures within heterogeneous samples. This presentation will examine the capabilities of this new mode with examples in a wide range of polymers and composites.

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[3] O. Sahin, C. Quate, O. Solgaard, and A. Atalar, *Phys. Rev. B*, 2004, 69, 1.

[4] B. Pittenger and D. G. Yablon, Bruker Application Note, 2017, AN149, 1. doi: 10.13140/RG.2.2.15272.67844

[5] M. Chyasnavichyus, S. L. Young, and V. V. Tsukruk, *Langmuir*, 2014, 30, 10566.

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## Complex Oxides: Fundamental Properties and Applications Focus Topic

### Room A220-221 - Session OX+EM+HC+MI+NS+SS+TF-TuA

## Complex Oxides: Catalysis, Dielectric Properties and Memory Applications

**Moderators:** Alexander Demkov, University of Texas at Austin, Jeffrey Kelber, University of North Texas

2:20pm **OX+EM+HC+MI+NS+SS+TF-TuA1 Novel Multiferroic and Ferroelectric Ferrite Thin Films**, *Peter A. Dowben*, *C. Binek*, *X. Xu*, University of Nebraska-Lincoln **INVITED**

Ferroelectricity and ferromagnetism are foundational to numerous technologies, yet the combination of ferroelectricity and ferromagnetism, namely multiferroicity, may be even more desirable. Multiferroic materials are believed to be a route to voltage controlled spintronic devices. Yet very few single phase materials are known to be ferroelectric and ferromagnetic at the same time, i.e. multiferroic. Even fewer materials are fewer materials are magneto-electric, that is to say materials with magneto-electric coupling, i.e. voltage control of magnetization, but without separate order parameters for magnetism (or antiferromagnetism) and ferroelectricity. This talk will review the electronic structure of the tri-rutile magneto-electric antiferromagnets, like  $\text{Fe}_2\text{TeO}_6$ , as well as rare earth ferrites like  $\text{ReFeO}_3$  (Re = rare earth) stabilized in the hexagonal phase. Both types of materials are frequently antiferromagnetic, and, in principle, both can exhibit magneto-electric coupling. The surface termination affects the measured spin polarization of the surface and the interface with other materials. This will have a significant influence on the voltage control of magnetization. We have investigated the structural and electronic properties at the surface of these more unusual multiferroic materials using angle-resolved x-ray photoemission spectroscopy (ARXPS), complemented by x-ray diffraction (XRD), x-ray photoemission electron

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microscopy (X-PEEM), and X-ray circular dichroism. We find that the low local symmetry, especially at surfaces, will split the electronic states, via spin-orbit coupling. In some cases, the result is a net spin polarization at the surface, under electric field cooling. Because of the strongly preferential surface termination of these types of materials, the boundary polarization is roughness insensitive, in some cases making spintronic device applications plausible.

3:00pm **OX+EM+HC+MI+NS+SS+TF-TuA3 Potential Applications and Challenges for Complex Oxides in Advanced Memory and Computing Applications**, *Sebastian Engelmann, T. Ando, V. Narayanan*, IBM T.J. Watson Research Center **INVITED**

As the semiconductor industry continues to push for and develop higher performance computing systems, there is also a growing trend of redeveloping or optimizing fundamental computing approaches to be more energy efficient. The development of hardware for novel AI systems is no exception. New integration schemes, novel materials, multi-component materials or even nanoscale materials and the ability to integrate all of these approaches together becomes the compounded challenge. Deposition and etch technologies that offer differentiating solutions to these issues therefore need to meet somewhat conflicting demands, such as low damage processing as well as high rate processing beside many other issues.

Novel thin films, thin film laminates and alloys promising unprecedented performance are very interesting candidates to enable such computing paradigm shifts. In particular the class of complex oxides is a very interesting area of research as they offer new phenomena such as ferroelectricity, ferromagnetism or high temperature conductivity. While new phenomena are being discovered, unraveling the fundamental physics behind these properties is a critical element for an industrial exploitation of these properties.

In addition, these new and complex materials are growing the need for the ultimate process solution: atomic layer precision processing. Atomic layer etching is a promising path to answer the processing demands of new devices at the Angstrom scale. Self-limiting reactions, discrete reaction and activation steps or extremely low ion energy plasmas are some of the pathways being pursued for precise material removal control and maintaining the original film performance. Depending on the nature of the material, the etch response may be either too much or not enough chemical modifications of the material. Resulting modifications of the films is an important variable to consider in the readiness of material systems. In particular synergy to deposition approaches such as atomic layer deposition has been proposed as a solution, but more work is needed.

4:20pm **OX+EM+HC+MI+NS+SS+TF-TuA7 Epitaxial Design of Complex Oxides for Catalysis and Electrocatalysis**, *Yingge Du*, Pacific Northwest National Laboratory **INVITED**

Predictive synthesis of highly active and cost-effective catalysts and electrocatalysts for energy conversion and storage is critical for leveraging intermittently available energy sources. Transition metal oxides with perovskite (ABO<sub>3</sub>) and perovskite-related structures (e.g., Brownmillerite and Ruddlesden-Popper) have been identified as robust catalysts with high oxygen reduction reaction (ORR) and/or oxygen evolution reaction (OER) activities that rival the performance of noble metals and their compounds. The study of perovskites as epitaxial thin films enables measurement of their intrinsic catalytic activity, deconvolved from the effects of surface roughness and polycrystalline defects (e.g., grain boundaries and edges between facets). In addition, epitaxial growth facilitates accurate control over the composition, crystallographic orientation, and strain in thin films.

In this talk, our recent efforts in the design of epitaxial complex oxides for catalysis and electrocatalysis will be highlighted. Using LaNiO<sub>3</sub>, a bifunctional electrocatalyst, as an example, I will show how isovalent substitution, aliovalent substitution, and interfacial strain can be used to tune the structural, electronic, and optical properties of the resultant films, and how these observed changes correlate with their (electro)catalytic performance. The use of complex oxide thin films as support or anti-corrosion layers during catalytic reactions will also be discussed.

5:20pm **OX+EM+HC+MI+NS+SS+TF-TuA10 Vanadia/Tungsten Oxide on Anatase TiO<sub>2</sub>(101): a Model Catalyst Study by STM and XPS**, *Tao Xu, J.V. Lauritsen, K.C. Adamsen*, Aarhus University, Denmark; *S. Wendt*, iNANO, Aarhus University, Denmark

Nitrogen oxides (NO<sub>x</sub>) from flue gas are in concern as major sources of air pollution. Increasingly stricter NO<sub>x</sub> emission control policies (e.g. Euro VI) demand innovation and better performance of NO<sub>x</sub> reduction technology.

The Selective Catalytic Reduction (SCR) of NO<sub>x</sub> by vanadia supported on anatase titania, with tungsten oxide (WO<sub>3</sub>) as promoter, has been widely used for this service and attracted much research attention. However, many aspects of the SCR catalysis process remain poorly understood at the atomic level. Particularly, the synergistic effect of tungsten oxide and vanadia remain elusive in literature, despite intensive RAMAN and infrared spectroscopy studies.

In this work, we use mineral  $\alpha$ -TiO<sub>2</sub> single crystals exposing the (101) facets as the model surface and deposit V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> in our ultrahigh vacuum chamber (UHV) chamber by e-beam evaporation in oxygen. Combining Scanning Tunneling Microscope (STM) and X-ray photon-electron Spectroscopy (XPS), we systematically investigated the morphology and oxidation state changes of the model catalyst upon heating and reactant adsorption.

The STM results illustrate the distribution of V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> on anatase TiO<sub>2</sub>(101) at the atomic level. It is found that both species are highly dispersed in the sub-monolayer region. For the deposition of surface oxide species, we explored different methods to achieve the highest oxidation state of vanadium (5+) and tungsten (6+). The thermal stability of the as-deposited V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> are investigated by XPS and STM systematically. We found that when V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> co-exist on the  $\alpha$ -TiO<sub>2</sub> surface the stability of V<sub>2</sub>O<sub>5</sub> is improved. This work provides atomic level understanding on the V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub> SCR catalyst and new insights into the synergistic interactions between vanadia and tungsten oxide on the  $\alpha$ -TiO<sub>2</sub> surface.

5:40pm **OX+EM+HC+MI+NS+SS+TF-TuA11 Observation of Memory Effect and Fractal Surface in SrRuO<sub>3</sub> Epitaxial Thin Films**, *Ratnakar Palai*, University of Puerto Rico; *H. Huhtinen*, University of Turku, Finland

Integration of multifunctional oxide materials (ferroelectrics and multiferroics) into silicon technology is of great technological and scientific interests. The current interest in functional oxides is largely based on engineered epitaxial thin films because of their superior properties compared to the bulk and polycrystalline thin films and their technological applications in dynamic random access memories, magnetic recording, spintronics, and sensors. Most of these applications require bottom and top electrodes to exploit the electronic properties of the functional materials.

SrRuO<sub>3</sub> (SRO) has been found to be very useful for electrodes and junctions in microelectronic devices because of its good electrical and thermal conductivities, better surface stability, and high resistance to chemical corrosion, which could minimize interface electrochemical reactions, charge injection in oxide, and other detrimental processes, thus improving retention, fatigue resistance, and imprint. It also has good work function to produce the required large Schottky barrier on most ferroelectric oxide capacitors.

The bulk SRO exhibits several useful properties, such as extraordinary Hall effect, strong magnetocrystalline anisotropy, itinerant ferromagnetism, and spin-glass behavior. Spin-glass materials are currently frontier field of research and the most complex kind of condensed state of matter encountered so far in solid-state physics. Despite of the enormous importance of spin-glass models in neural networks, our knowledge of the underlying mechanistic processes involved is extremely limited. Although memory effect has been reported in bulk SRO, to our knowledge, the behavior is not well understood and there was no such report in thin films.

In this work, we report on the observation of memory effect and strong magnetic anisotropy in extremely smooth 1–3 Å roughness epitaxial (110) and (010) SrRuO<sub>3</sub> thin films. The observation of non-zero imaginary susceptibility and frequency dependent cusp at freezing temperatures confirms the spin-glass behavior, which agrees well with the dc magnetization measurement. The origin of memory effect can be attributed to the magnetic frustration and random interaction, which is affected by dynamics of cooling and will be discussed in details.

6:00pm **OX+EM+HC+MI+NS+SS+TF-TuA12 In situ Auger Electron Spectroscopy of Complex Oxide Thin Film Surfaces Grown by Pulsed Laser Deposition**, *Thomas Orvis, M. Surendran, Y. Liu, A. Cunniff, J. Ravichandran*, University of Southern California

Complex oxides can enhance the functionality of electronic and photonic devices by supplementing them with interesting properties such as ferroelectricity, superconductivity, and magnetoresistivity. Furthermore, low dimensionality in these materials can result in additional useful properties, inspiring the continued study of complex oxides in thin film form. However, the deposition of these materials is typically governed by

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notoriously complex growth mechanisms, revealing the need for *in situ* probes to observe and understand their precise nature. To this end, we report the *in situ* observation of chemical composition of complex oxide thin film surfaces with Auger electron microscopy during growth by pulsed laser deposition. Our implementation of real-time monitoring techniques for complex oxide thin films sheds an important light on the intricacies of the relationships between processing conditions and resulting composition.

## Materials and Processes for Quantum Information, Computing and Science Focus Topic

Room B231-232 - Session QS+2D+EM+MN+NS-TuA

### Materials for Quantum Sciences

**Moderators:** Matthew R. Rosenberger, U.S. Naval Research Laboratory, Robert Walko, The Ohio State University

2:20pm **QS+2D+EM+MN+NS-TuA1 Electrically Detected Electron Nuclear Double Resonance Study of Defects in 4H-SiC Bipolar Junction Transistors, Ryan Waskiewicz, B.R. Manning, D.J. McCrory, P.M. Lenahan, Pennsylvania State University**

There is growing interest in the possibilities of SiC in spin-based quantum computation. The development of such spin-based quantum computation will require a fundamental understanding of spin physics of paramagnetic defects in SiC including both electron and nuclear paramagnetism. We utilize electrically detected magnetic resonance (EDMR) detection through spin dependent recombination (SDR). In this study we demonstrate relatively high signal to noise electron nuclear double resonance (ENDOR) in a single fully processed SiC pn junction at room temperature. The electrically detected ENDOR (EDENDOR) involves nitrogen nuclei in close proximity to deep level centers within the depletion region of the pn junction; the deep levels are almost certainly silicon vacancies.

We believe these observations are of importance for at least two reasons: (1) they demonstrate that the enormous analytical power of ENDOR can be extended to the study of problems in conventional solid-state electronics and (2) the results demonstrate a way to directly monitor small numbers of nuclear spins through the measure of electronic currents.

In our EDMR measurements, a slowly varying magnetic field and an oscillating microwave frequency magnetic field are applied to the sample inside a microwave cavity. As in conventional EPR, energy is absorbed by paramagnetic sites when the resonance condition is met. For a simple case, this resonance condition is  $h\nu = g\mu_B B \pm \sum m_i A_i$ , where  $h$  is Planck's constant,  $g$  is an orientation dependent number typically expressed in a  $g$ -tensor,  $\mu_B$  is the Bohr magneton,  $B$  is the magnetic field,  $m_i$  is the spin quantum number of the  $i^{\text{th}}$  nucleus, and  $A_i$  is the hyperfine interaction of the  $i^{\text{th}}$  magnetic nucleus. In EDMR, the EPR response is detected through a change in device current, in our case due to SDR.

The devices in this study are 4H-SiC BJTs. The EDMR response obtained on these BJTs is very similar to an EDMR spectrum that has been linked to a silicon vacancy in 4H-SiC MOSFETs. To perform the EDENDOR measurement, the magnetic field is held constant and an NMR frequency sweep is applied to the device. The device current is measured and a large response is measured at what is unambiguously the nuclear frequency of nitrogen. These results demonstrate the analytical power of the EDENDOR measurement, measuring nitrogen in the vicinity of the silicon vacancy defect centers that are measured with EDMR.

This work was supported by the Air Force Office of Scientific Research under award number NO. FA9550-17-1-0242.

2:40pm **QS+2D+EM+MN+NS-TuA2 Scanning Tunneling Microscopy Studies of Er Adatoms on GaAs (110), Rebekah Smith, A. Benjamin, J.A. Gupta, The Ohio State University**

Rare earth dopants in III-V semiconductors are of interest as high quality optical sources due to the preservation of sharp intra- $f$ -shell transitions. The long optical coherence lifetime and narrow energy width of these transitions, at 1.54  $\mu\text{m}$ , make them a candidate for quantum communication. Here we investigate Er interactions with host GaAs (110) surface with atomic resolution using STM. Er atoms were deposited via electron beam evaporation onto the GaAs surface at 5 K. We find three different  $\text{Er}_{\text{ad}}$  configurations with varying abundance upon deposition, each with a different surface site location. All three configurations exhibit long-range depressions in STM topographic images, attributed to band bending associated with a positive adatom charge state. Individual Er adatoms can be switched between these states by applying a positive voltage pulse with

the STM tip. Tunneling spectroscopy on Er adsorbed at the interstitial sites reveals prominent states within the GaAs bandgap, but no evidence of sharp  $f$ -shell transitions inferred from bulk optical studies. We also form substitutional  $\text{Er}_{\text{Ga}}$  by applying a larger positive voltage pulse. Substitutional Er appears neutral, which we attribute to it being isoelectronic with Ga. This work acknowledges funding from the DOE (DE-SC0016379).

3:00pm **QS+2D+EM+MN+NS-TuA3 Defect-based Quantum Systems in Hexagonal Boron Nitride, Trong Toan Tran, University of Technology Sydney, Australia**

INVITED

Engineering solid state quantum systems is amongst grand challenges in realizing integrated quantum photonic circuitry. While several 3D systems (such as diamond, silicon carbide, zinc oxide) have been thoroughly studied, solid state emitters in two dimensional (2D) materials are still in their infancy. In this talk I will introduce hexagonal boron nitride (hBN) as a promising layered material that hosts ultra bright quantum emitters. I will present several avenues to engineer these emitters in large area hBN multilayers and monolayers using chemical vapour deposition techniques. I will then show unique tuning experiments and promising results for controlling the emission wavelength of these quantum emitters. At the second part of my talk, I will discuss promising avenues to integrate the emitters with plasmonic and photonic cavities to achieve improved collection efficiency and Purcell enhancement. These are fundamental experiments to realize integrated quantum photonics with 2D materials. I will summarize by outlining challenges and promising directions in the field of quantum emitters and nanophotonics with 2D materials and other wide band gap materials.

4:20pm **QS+2D+EM+MN+NS-TuA7 Specific Placement of  $V_{\text{Si}}$  in 4H-SiC for Quantum Technologies using  $\text{Li}^+$  Implantation, S.P. Pavunny, Rachael L. Myers-Ward, D.K. Gaskill, U.S. Naval Research Laboratory; E.S. Bielejec, Sandia National Laboratories; H.B. Banks, A.L. Yeats, U.S. Naval Research Laboratory; M.T. DeJarlid, Raytheon; S.G. Carter, U.S. Naval Research Laboratory**

Silicon carbide has been a material of interest in the quantum technology field for future applications in communication and sensing due in part to the long spin ( $S = 3/2$ ) coherent lifetime of the Si vacancies ( $V_{\text{Si}}$ ). Additional benefits to using SiC for quantum technologies is wafer scalability and fabrication capability using standard processing techniques, making it a favorable material. To improve emission rates of photoluminescence from the vacancies, exact placement of the  $V_{\text{Si}}$  within microcavities is necessary. Here we show implanted  $\text{Li}^+$  into Si-face, 4H-SiC homoepitaxy creates  $V_{\text{Si}}$  in desired locations. The epitaxial material had no measurable  $V_{\text{Si}}$  prior to  $\text{Li}^+$  implantation. The dose of 100 keV  $\text{Li}^+$  ranged from  $10^{12} - 10^{15} \text{ cm}^{-2}$  and was directed using a maskless focused ion beam technique with a positional accuracy of  $\sim 25 \text{ nm}$ . The arrays were characterized with high-resolution scanning confocal fluorescence microscopy. Using a 745 nm excitation source, the photoluminescence ranging from 860 - 975 nm produced the characteristic  $V1'$ ,  $V1$  and  $V2$  lines, with the  $V1'$  zero-phonon line being consistent for all measurements. In addition, the  $V1'$  intensity showed a linear dependence with implantation dose. Moreover, near single photon emission is obtained from  $V_{\text{Si}}$  at the lowest doses.

Research at NRL is supported by the Office of Naval Research. Ion implantation was performed at Sandia National Laboratories through the Center for Integrated Nanotechnologies, an Office of Science facility operated for the DOE (contract DE-NA-0003525) by Sandia Corporation, a Honeywell subsidiary.

4:40pm **QS+2D+EM+MN+NS-TuA8 Silicon Vacancy Point Defect in High-quality Nanobeam Photonic Crystal Cavities in 4H Silicon Carbide, Mena Gadalla, X. Zhang, A.S. Greenspon, Harvard University; D.O. Bracher, Harvard GSAS; R.K. Defo, E. Hu, Harvard University**

Silicon carbide (SiC) has recently found promise and applications in the quantum world, because of various fluorescent point defects that serve as an intriguing platform for solid-state quantum information and quantum sensing technologies. One such native point defect is the negatively charged silicon vacancy ( $V_{\text{Si}}^-$ ) in the 4H polytype of SiC. This color center can occupy two inequivalent lattice sites, resulting in two distinct zero-phonon-lines (ZPL) at 862nm and 916nm.  $V_{\text{Si}}^-$  possesses good spin coherence properties, with spin states that can be initialized and read out optically. Unfortunately, low branching ratio is a characteristic of the  $V_{\text{Si}}^-$  spectrum where a small fraction of the total emission is coupled into the ZPL and the rest is emitted into the phonon sideband. This low emission fraction limits the ability to employ  $V_{\text{Si}}^-$  in various quantum information schemes. To increase the fraction of light emitted into the ZPL and increase the defect emission rate, we fabricated high-quality factor nanophotonic crystal

# Tuesday Afternoon, October 22, 2019

cavities designed to match the ZPL frequency. Through tuning of the cavity into resonance with the ZPLs, we have demonstrated a 75-fold Purcell enhancement at 4K. This talk will describe the fabrication process for 1D nanobeam photonic crystal cavities, leading to quality factors in excess of  $10^4$ . The highest cavity-defect interactions depend on resonance in frequency and high spatial overlap of the defect with the maximum electric field within the cavity. Using the cavity as a “nanoscope”, revealing defect position, we used laser irradiation annealing at varying times and different laser frequencies to infer the diffusive motion of defects within the cavity. We showed that a systematic and controlled laser annealing can increase the ZPL of the implanted cavity mode by a factor of 4.

5:00pm **QS+2D+EM+MN+NS-TuA9 Tailoring the Heterogeneities in 2D Materials by Controlled Synthesis and Processing, Kai Xiao, X. Li, K. Wang, A. Oyedele, M. Yoon, S. Xia, M. Mahjouri-Samani, C.M. Rouleau, A.A. Puzetky, L. Liang, R.R. Unocic, D. Geohegan**, Oak Ridge National Laboratory Two-dimensional (2D) materials are intrinsically heterogeneous, therefore controlling defects, understanding the impact of boundaries and interfaces and developing means to exploit these heterogeneities is a transformative opportunity that could underpin future technologies and energy applications. In this talk, I will discuss the fundamental understanding of the roles of heterogeneities including defects, dopants, edges, strain, and phases in 2D materials on their optoelectronic properties. Through isoelectronic doping in monolayer of MoSe<sub>2</sub>, the Se vacancies are effectively suppressed and photoluminescence is significantly enhanced. In addition, we demonstrate the non-equilibrium, bottom-up growth approach not only can tailor the defect density far beyond intrinsic levels in monolayers of 2D MoSe<sub>2-x</sub> but also create new antisite defects in monolayers of WS<sub>2</sub> during the synthesis. The build-in localized strain in 2D crystals directly grown on patterned curved surface can tune the bandgap of 2D crystals for possible quantum emitting applications. The bottom up synthesis of 2D materials discussed here provides excellent control over the heterogeneity in 2D materials, which can modulate the optical and electrical properties in 2D materials and their heterostructures for ultra-thin and flexible electronics.

**Acknowledgment:** Synthesis science was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division and characterizations were performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

5:20pm **QS+2D+EM+MN+NS-TuA10 Epitaxial Al Films for Plasmonic and Quantum Computing Applications, Ka Ming Law, S. Budhathoki, S. Ranjit, F. Martin, A.J. Hauser**, The University of Alabama

Superconducting resonators are important for application in quantum computing but require high quality factors. Much work has been done on superconducting resonators fabricated from aluminum thin films on sapphire, and superconducting Josephson tunnel junctions made from aluminum are used as the basis for quantum bit designs. In addition, epitaxial aluminum films has attracted attention in plasmonics due to their superior performance in the UV regime compared to Au and Ag, and their compatibility with current CMOS technology. Sapphire substrates are chemically stable and have low lattice mismatch with aluminum, allowing higher film quality without the need for elaborate substrate preparation and time-consuming growth procedures.

Epitaxial aluminum films were successfully grown by off-axis magnetron sputtering on c-plane sapphire. This study assessed the effects of varying both substrate preparation conditions and growth and prebake temperatures on crystallinity and smoothness. X-ray diffraction and reflectivity measurements demonstrate superior crystallinity and surface smoothness for films grown at 200°C in 15mTorr Ar. An additional substrate preparation procedure which involves 1) a modified RCA procedure and 2) prebake in oxygen environment is shown by atomic force microscopy to be highly effective in reducing void density and depth.

5:40pm **QS+2D+EM+MN+NS-TuA11 2019 AVS Mid-Atlantic Student Awardee Talk: Minimizing Coulomb Oscillation Linewidth on Silicon Quantum Dots, Yanxue Hong<sup>1</sup>, A.N. Ramanayaka, M.D. Stewart, Jr., X.Q. Wang, R.V. Kashid, P. Nambodiri, R.M. Silver, J.M. Pomeroy**, National Institute of Standards and Technology (NIST)

In quantum science research, both cryogenic temperatures and low measurement noise are required for high fidelity. For silicon quantum dot devices, an increase in either one causes broadening of Coulomb blockade

peaks, which is usually referred to as a high electron temperature. Here we report on temperature-dependent (T-dependent) conductance measurements and evaluation of effective electron temperature ( $T_{\text{eff}}$ ) using an STM-patterned atom-scale silicon single-electron transistor (SET). Measurements are made in various cryogenic systems over temperatures varying from 10 mK to 25 K. The effective electron temperature is extracted by fitting the experimental data using a theoretical model. We initially find that the measured peak width has a linear dependence on the bath temperature above 1 K and saturates below 1 K. In addition, a considerable mismatch ( $> 2$  K) between the lattice (thermometer) temperature and the carrier temperature ( $T_{\text{eff}}$ ) is observed. Therefore, the Coulomb resonance is not only thermally broadened by  $T_{\text{eff}}$  but also broadened by other T-independent sources such as gate noise, triboelectric noise, etc. We study the origins of the saturation at low temperature regime and analyze factors inducing high  $T_{\text{eff}}$ . We report on progress to reduce the noise and reach an effective temperature of  $< 300$  mK. Since our silicon SETs have high charging energies and large energy level spacings, we also seek to measure the transition from classical (multilevel) regime to quantum (single-level) regime by manipulating the bath temperature.

6:00pm **QS+2D+EM+MN+NS-TuA12 Micro-magnetic Simulations of Correlated Switching in Touching Nano-magnetic Elements, Tejmade Durowade, V. Metlushko**, University of Illinois at Chicago

Nanomagnets hold significant potential for use as building blocks for room temperature quantum computers. Bistability based on stable ground magnetization states means power dissipation can be extremely low and their small size allows magnetization to be maintained for a long period time [1]. With packing density on the order of  $10^{10}$  /cm<sup>2</sup> and switching frequency in the terahertz range, nanomagnets are a promising replacement for current state of art metal oxide semiconductor processes that are already at the limits of continued scaling. In this work, we present the results of simulations of touching nanomagnetic disks that can be used for room operable quantum computing. Like gears in a mechanical system, the chirality of the magnetization in each disk is determined through interaction with its neighbors. These simulations offer insight into the switching dynamics within the disks as current experimental techniques lack the combined temporal and spatial resolution needed to observe the formation and annihilation of the magnetic domains that facilitate the switching process. The switching of touching symmetric disks can be achieved at zero applied field as the disks settle into a remanent vortex state, meaning minimal energy loss during the process. Due to the quantum exchange force, at the point of contact between disks, the magnetization vectors rotate in the same direction giving rise to opposite chiralities in the disks. Since logic states can be represented using the chirality of the in-plane magnetization, configurations of touching disks can potentially be used to implement basic or complex logic functions. Maintaining coherence of opposite chirality in chains of disks was achieved with the introduction of a biasing element to eliminate the bidirectionality of interaction between disks.

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## 2D Materials

### Room A216 - Session 2D+AS+MI+NS-WeM

#### 2D Materials Characterization by Scanning Probe Microscopy and Spectroscopy

Moderator: Adina Luican-Mayer, University of Ottawa, Canada

##### 8:20am 2D+AS+MI+NS-WeM2 Silicene like Domains on IrSi<sub>3</sub> Crystallites, *Nuri Oncel, D. Cakir, F. Fatima, D. Nicholls*, University of North Dakota

Recently, silicene, the graphene equivalent of silicon, has attracted a lot of attention due to its compatibility with Si-based electronics. So far, silicene has been epitaxially grown on various crystalline surfaces such as Ag(110), Ag(111), Ir(111), ZrB<sub>2</sub>(0001) and Au(110) substrates. Here, we present a new method to grow silicene via high temperature surface reconstruction of hexagonal IrSi<sub>3</sub> nanocrystals. The h-IrSi<sub>3</sub> nanocrystals are formed by annealing thin Ir layers on Si(111) surface. A detailed analysis of the STM images shows the formation of silicene like domains on the surface of some of the IrSi<sub>3</sub> crystallites. We studied both morphology and electronic properties of these domains by using both scanning tunneling microscopy/spectroscopy and first-principles calculation methods.

##### 8:40am 2D+AS+MI+NS-WeM3 Interfacial and Topological Superconductivity in 2D Layers Studied by Spin-Resolved Scanning Tunneling Spectroscopy, *Roland Wiesendanger*, University of Hamburg, Germany

INVITED

In this presentation, we will first focus on interfacial superconductivity in novel types of heterostructures. In particular, we will present a low-temperature SP-STs study of ultrathin FeTe<sub>1-x</sub>Sex (x = 0, 0.5) films grown on prototypical Bi-based bulk topological insulators. We observe fully developed U-shaped superconducting gaps in FeTe<sub>0.5</sub>Se<sub>0.5</sub> layers of one unit cell (UC) thickness with a transition temperature (T<sub>c</sub>) of ~11 K, close to the one of the corresponding bulk system (T<sub>c</sub> ~ 14.5 K) [1]. Surprisingly, we also find clear evidence for superconductivity up to T<sub>c</sub> ~ 6 K for one UC thick FeTe layers grown on Bi<sub>2</sub>Te<sub>3</sub> substrates [2], in contrast to the non-superconducting FeTe bulk compound which exhibits bicollinear antiferromagnetic (AFM) order in a wide temperature range up to 70 K. Even more surprisingly, detailed investigations of the atomic-scale spin-resolved local density of states by SP-STs reveal that superconductivity in one UC layers of FeTe grown on Bi<sub>2</sub>Te<sub>3</sub> appears to spatially coexist with bicollinear AFM order. By using 3D-vector-resolved SP-STM techniques [3] we find an unusual reorientation of the diagonal double-stripe spin structure at Fe<sub>1+y</sub>Te thin film surfaces [4]. Moreover, variable-temperature SP-STM studies [5] reveal an enhanced Néel temperature for AFM spin ordering of the ultrathin FeTe films grown on topological insulators [6]. These findings open novel perspectives for theoretical studies of competing orders in Fe-based superconductors as well as for experimental investigations of exotic phases in heterostructures of topological insulators and superconducting layers.

In a second part, we will address experimental and theoretical studies of monolayer topological superconductivity and chiral Majorana edge modes in model-type 2D magnetic Fe islands on elemental superconducting Re [7]. In particular, we demonstrate that interface engineering by an atomically thin oxide layer is crucial for driving the studied hybrid system into a topologically non-trivial state as confirmed by theoretical calculations of the topological invariant, the Chern number.

This work is supported by the EU via the ERC Advanced Grant No. 786020 "ADMIRE".

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##### 9:20am 2D+AS+MI+NS-WeM5 Geometric Imaging of Borophene Polymorphs, *Xiaolong Liu*, Northwestern University; *L. Wang*, Rice University; *S. Li, M. Rahn*, Northwestern University; *B. Yakobson*, Rice University; *M.C. Hersam*, Northwestern University

Two-dimensional (2D) boron, known as borophene, has recently been experimentally realized<sup>1,2</sup> revealing a number of polymorphic structures. A common characteristic of those borophene polymorphs is the presence of

hollow-hexagons (HH) in an otherwise triangular lattice. The vast number of possible HH lattices underlies the polymorphic nature of borophene. Superlattices of HHs could be further realized when borophene phases periodically intermix in the form of line defects<sup>3</sup>. While scanning tunneling microscopy (STM) of borophene with conventional metal probes has revealed key features of borophene, significant ambiguity of the exact atomic lattice structure exists due to the convolution of electronic and structural details. With CO-functionalized atomic force microscopy, we unambiguously resolve the HH lattice and reveal features corresponding to B-B covalent bonds<sup>4</sup> that are supported by numerical simulations. We further show that CO-functionalized STM is an equivalent but more accessible technique for HH imaging, allowing us to assemble a growth phase diagram of borophene involving non-rotated, 30°-rotated and randomly rotated borophene phases on Ag(111), confirming the  $v_{1/5}$  and  $v_{1/6}$  models as the unifying structures for all observed phases. In particular, a transition from rotationally commensurate to incommensurate phases is observed at high growth temperatures, corroborating the chemically discrete nature of borophene.

\*Current affiliation of Xiaolong Liu: Kavli Postdoc Fellow, LASSP, Cornell University

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##### 9:40am 2D+AS+MI+NS-WeM6 Atomic Manipulation of Defects in the Layered Semiconductor 2H-MoTe<sub>2</sub>, *Sara Mueller, S. Deng*, The Ohio State University; *B. St. Laurent*, University of New Hampshire; *Y. Wang, W. Windl*, The Ohio State University; *S. Hollen*, University of New Hampshire; *J.A. Gupta*, The Ohio State University

Here we present a charge control of native defects in the bulk transition metal dichalcogenide, MoTe<sub>2</sub> by scanning tunneling microscopy (STM). Bulk MoTe<sub>2</sub> was cleaved at room temperature in ultrahigh vacuum and imaged with a cut PtIr tip at 9K. Native defects in the MoTe<sub>2</sub> are present throughout the sample and image with complex structure. In topographic imaging, the long-range protrusion of a bright defect indicates the species is charged and we image the defects at different depths below the surface. They present with an ionization feature in tunneling spectroscopic mapping which indicates that the charge state of this defect can be manipulated by the band bending caused by the tip. Voltage pulses from the tip migrate the subsurface defects to the surface layer. The migrated defects present with the same spectroscopic signature as native surface defects. We also present DFT results that we use to clarify the identification of these native defects and energy barriers for migration between layers of 2H-MoTe<sub>2</sub>.

##### 11:00am 2D+AS+MI+NS-WeM10 Scanning Tunneling Microscopy and Spectroscopy of a Heterotriangulene-based 2D Polymer, *Zachery Enderon, H. Murali, R. Dasari, T.C. Parker, S.R. Marder, H. Li, Q. Dai, S. Thomas, J.-L. Brédas, P.N. First*, Georgia Institute of Technology

Covalent Organic Frameworks (COFs) and similar materials synthesized from bottom-up procedures grant scientists a means to customize a 2D material's final properties from its initial precursors. The dimethylmethylen-bridged triphenylamine (DTPA) COF is an excellent example of the unique systems one can fabricate with these techniques<sup>1</sup>. The DTPA COF is initially synthesized on Au(111) or Ag(111) which facilitates crystalline growth through Ullman-type coupling. With an even number of electrons per unit cell, theory predicts a semiconducting electronic structure for the COF. Further heating in vacuum selectively cleaves the dimethyl groups but leaves the framework intact. This final COF resembles an ultra-flat covalent network of triangulene molecules with enticing proposed electronic properties, which depend on how the demethylated sites are terminated. In the case of hydrogen termination at these sites, calculations indicate that the "radical" COF on a metallic substrate will be a half-metal (fully spin-polarized density of states at the fermi energy)<sup>2</sup>. Using a low-temperature scanning tunneling microscope, the work outlined in this talk presents new information on the electronic structure of the DTPA COF in both its intact (methylated) and radical (demethylated) forms.

# Wednesday Morning, October 23, 2019

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11:20am **2D+AS+MI+NS-WeM11 Scanning Tunneling Microscopy Investigations of Molecules Adsorbed on Semiconducting Graphene Nanoribbons**, *Sineth Premaratna, K.Z. Latt, S.-W. Hla*, Ohio University

Unlike graphene, semiconducting graphene nanoribbons possess a band gap and they have the capability to electronic decouple the molecules from the supporting substrate. Here, we study the structural, electronic and vibrational properties of individual para-sexiphenyl molecules adsorbed on semiconducting graphene nanoribbons. The graphene nanoribbons here are grown on the surface of Au(111) using DBBA molecules as the initial building blocks. Para-sexiphenyl molecules adsorb on the graphene nanoribbons with their long molecular axis positioning parallel to the long axis of the graphene nanoribbons. As expected, the tunneling spectroscopy data reveal the HOMO-LUMO gap of the molecule on graphene nanoribbons much closer to their gas phase values. Moreover, the vibration spectroscopy measurements of the molecules further provide a strong vibration mode associated with the C=C ring stretching of the molecules. This work provides single molecule level information on the electronic, vibronic and structural properties of the molecules adsorbed on vertically stacked heterostructures formed by graphene nanoribbons on Au(111) surface.

Acknowledgement: This work is supported by the DOE-BES, DE-FG02-02ER46012 grant.

11:40am **2D+AS+MI+NS-WeM12 Molecular Flexure and Atom Trapping with Sexiphenyl Molecules by Scanning Tunneling Microscope Manipulation**, *Y. Zhang, Shaoze Wang, K.-F. Braun, S.-W. Hla*, Ohio University

Molecular flexure, and molecule-metal contact of para-sexiphenyl molecules on a Ag(111) surface are investigated by using low temperature scanning tunneling microscopy, and molecular manipulations. Atom trapping with sexiphenyl molecules is realized by laterally manipulating the molecules onto individual silver atoms and up to three silver atoms have been trapped. We also demonstrate breaking of a silver dimer into individual silver atoms by atom trapping. STM manipulation experiments show that the molecule-metal complexes formed by the atom trapping are mechanically stable. Moreover, lateral manipulation of a single sexiphenyl across a Ag(111) atomic step highlights how the molecule moves across step-edges; the molecule can easily conform across the step and it recovers original configuration after the manipulation.

Acknowledgement: This work is supported by the DOE-BES, DE-FG02-02ER46012 grant.

12:00pm **2D+AS+MI+NS-WeM13 Localized Strain Effects in Spin-Polarized Density of States for 2D-MnGaN – a Room Temperature Ferromagnetic Monolayer**, *Y. Ma*, Ohio University; *K. Meng*, The Ohio State University; *D. Hunt, M.A. Barral, V. Ferrari*, CAC-CNEA, Argentina; *F.Y. Yang*, The Ohio State University; *Arthur Smith*, Ohio University

We recently demonstrated the first observation of a 2D *room-temperature-ferromagnetic monolayer* of MnGaN (2D-MnGaN) using spin-polarized scanning tunneling microscopy and spectroscopy. The sample is grown by molecular beam epitaxy on gallium nitride substrates. We resolved ferromagnetic domains using SP-STM, demonstrated magnetic hysteresis using small *out-of-plane* magnetic fields, observed magnetic rim states, and measured magnetic DOS profiles using tunneling spectroscopy which are in excellent agreement with the predicted spin-polarized & spin-split DOS peaks obtained from first-principles theory. This work was published online in December 2017 in *Nano Letters*. [1]

More recently, we are investigating the dependence of magnetization anisotropy on *in-plane* lattice strain. First of all, we have observed from the spectroscopy measurements that the position of the spin-polarized Mn DOS peak varies from spectrum to spectrum, ranging from -1.69 eV up to -1.22 eV (relative to  $E_{\text{Fermi}}$ ). In order to investigate if these variations could be related to structural variations, we have also carried out theoretical calculations based on first principles for both isotropic and local anisotropic lattice strains. The isotropic strain case shows that the occupied-states Mn peak can indeed shift by many tenths of an eV if the

2D-MnGaN is strained *in-plane*; for example,  $E = -1.58$  eV for the no-strain case, whereas  $E = -1.33$  eV for tensile strain (+9.1%) and  $E = -2.22$  eV for compressive strain (-6.0%). On the other hand, we find an opposite behavior in the local anisotropic calculation.

Using atomic resolution STM, we have also found that significant strain variations exist within the 2D-MnGaN. As compared to an ideally periodic hexagonal lattice, the 2D-MnGaN lattice displays local spacing variations, and the spacing distribution is highly non-Gaussian and may instead be characterized as *tri-modal* with the central peak matching closely the expected average for 2D-MnGaN of 5.52 Å, but with left and right peaks centered around 5.00 Å and 5.92 Å. Therefore, the Mn atoms, centered between Ga adatoms, are under highly varying strains, ranging from tensile to compressive.

By mapping the observed Mn peak energies onto theoretical energy-strain curves, we can then estimate the expected lattice parameters corresponding to particular energies and compare with the lattice spacing distribution. These results will be discussed as well as the additional discovery of a dependence of the spin anisotropy on the lattice strain.

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## 2D Materials

### Room A226 - Session 2D+EM+MI+MN+NS+QS-WeM

#### Novel 2D Materials

**Moderator:** Phil King, University of St Andrews

8:00am **2D+EM+MI+MN+NS+QS-WeM1 A Safari Through Thousands of Layered Materials Guided by Data Science Techniques**, *Evan Reed, G. Cheon*, Stanford University

INVITED

We have utilized data mining approaches to elucidate over 1000 2D materials and several hundred 3D materials consisting of van der Waals bonded 1D subcomponents, or molecular wires. We find that hundreds of these 2D materials have the potential to exhibit observable piezoelectric effects, representing a new class of piezoelectrics. A further class of layered materials consists of naturally occurring vertical hetero structures, i.e. . bulk crystals that consist of stacks of chemically dissimilar van der Waals bonded layers like a 2-D super lattice. We further combine this data set with physics-based machine learning to discover the chemical composition of an additional 1000 materials that are likely to exhibit layered and two-dimensional phases but have yet to be synthesized. This includes two materials our calculations indicate can exist in distinct structures with different band gaps, expanding the short list of two-dimensional phase change materials. We find our model performs five times better than practitioners in the field at identifying layered materials and is comparable or better than professional solid-state chemists. Finally, we find that semi-supervised learning can offer benefits for materials design where labels for some of the materials are unknown.

8:40am **2D+EM+MI+MN+NS+QS-WeM3 2D Ferroelectric Semiconductor  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> for Non-Volatile Memory Applications**, *M. Si, Peide Ye*, Purdue University

$\alpha$ -In<sub>2</sub>Se<sub>3</sub> is a novel two-dimensional (2D) ferroelectric semiconductor. It has a bandgap of  $\sim 1.39$  eV, room temperature ferroelectricity, the ability to maintain ferroelectricity down to a few atomic layers and the feasibility for large-area growth. Based on the ferroelectric and semiconducting nature of the material, a ferroelectric semiconductor field-effect transistor (FeS-FET) was proposed and experimentally demonstrated [1]. In the FeS-FET, a ferroelectric semiconductor is employed as the channel material while the gate insulator is the dielectric. The two non-volatile polarization states in FeS-FETs exist in the ferroelectric semiconductor channel. Therefore, a high quality amorphous gate insulator can be used instead of the common polycrystalline ferroelectric insulator for Fe-FETs. The fabricated FeS-FETs exhibit high performance with a large memory window, a high on/off ratio over  $10^8$ , a maximum on-current of 862  $\mu\text{A}/\mu\text{m}$ , low supply voltage with scaled gate insulator and the potential to exceed the existing Fe-FETs for non-volatile memory applications.

[1] M. Si, S. Gao, G. Qiu, J. Qin, Y. Duan, J. Jian, H. Wang, W. Wu, and P. D. Ye, "A Ferroelectric Semiconductor Field-Effect Transistor," arXiv:1812.02933.

# Wednesday Morning, October 23, 2019

9:00am **2D+EM+MI+MN+NS+QS-WeM4 *Ab initio* Informed Theory of Axis-dependent Conduction Polarity in Goniopolar Materials, Yaxian Wang, B. He, M.Q. Arguilla, N.D. Cultrara, M.R. Scudder, J.E. Goldberger, J.P. Heremans, W. Windl**, The Ohio State University

$\text{NaSn}_2\text{As}_2$  has recently been synthesized and was found to be an exfoliatable van der Waals Zintl phase, opening new opportunities for electronic design on the few-atom-thick scale. Although the band structure may suggest a range of metal to semi-metal, it shows strong anisotropy especially in its “polarity”, characterized by its dominant carrier type, which strongly affects its electronic and thermal properties. We used DFT calculations to investigate bandstructure and Fermi surface. In addition, we employed BoltzTraP code to calculate the transport behavior in in/cross-plane directions, predicting strongly anisotropic carrier transport and directionally dependent polarity – “goniopolarity” – in this layered material. It is confirmed by experimental thermopower measurements. We show from simulations on a model band structure the Fermi surface geometry origin in a single-band toy model, and we utilize the bandwidth concept from a tight-binding model to give an insight of real space orbital contributions and nature of the bonding states in this layered crystal. Based on that, additional candidate materials for goniopolarity can be proposed, and the design space for goniopolar materials in general will be defined.

9:20am **2D+EM+MI+MN+NS+QS-WeM5 In-Plane Mechanical Properties and Strain Engineering of 2D Hybrid Organic-Inorganic Perovskites, Qing Tu, I. Spanopoulos, S. Hao, C. Wolverton, M. Kanatzidis, G. Shekhawat, V. David**, Northwestern University

Two-dimensional (2D) hybrid organic-inorganic perovskites (HOIPs) are new members of the 2D materials family with wide tunability, highly dynamic structural features and excellent physical properties. Mechanical strain is inevitable in 2D-HOIP-based applications due to materials processing, thermal expansion and substrate deformation. Understanding the mechanical properties and strain engineering of such functional materials are both fundamentally and practically important to achieve high performance and mechanically stable (flexible) devices. Here the in-plane mechanical properties and the impact of in-plane uniaxial tensile strain on the electronic properties of 2D lead iodide perovskites with a general formula  $(\text{CH}_3(\text{CH}_2)_n\text{NH}_3)(\text{CH}_3\text{-NH}_3)_{n-1}\text{Pb}_{n+1}\text{I}_{3n+1}$  were reported for the first time. The in-plane Young's modulus and breaking strength of ultrathin 2D HOIP flakes were measured by AFM-based nanoindentation of suspended 2D HOIP membranes.[1] The in-plane Young's moduli of 2D HOIPs are smaller than that of conventional covalently bonded 2D materials like graphene and  $\text{MoS}_2$  due to the much more deformable  $[\text{PbI}_6]^{4-}$  octahedra structure. Both the Young's modulus and breaking strength first decrease and then plateau as the thickness of 2D HOIP flake increases from monolayer to 4 layers, which is attributed to interlayer slippage during deformation. Ultrathin 2D HOIPs exhibit outstanding breaking strength/Young's Modulus ratio compared to many other widely used engineering materials and polymeric flexible substrates, which renders them suitable for application into flexible electronic devices. Furthermore, the uniaxial tensile strain was found to increase the band gap of 2D HOIPs.[2] Such strain effect on the band gap of 2D HOIPs is fully reversible and depends on the structural unit of the materials. For 2D HOIP with  $n = 5$ , the strain response of the band gap can be as high as 13.3 meV/%. First-principles simulations show that the strain response of the band gap arises from the rotation of the inorganic  $[\text{PbI}_6]^{4-}$  octahedra and the consequential Pb-I bond stretching and increase of Pb-I-Pb angle. The observed band gap-strain relationship can be harnessed to map the local mechanical strain in 2D HOIP-based devices and allow 2D HOIPs for sensing applications.

## References

- [1]. Tu Q, Spanopoulos I, Yasaei P, Stoumpos CC, Kanatzidis MG, Shekhawat GS, et al. Stretching and Breaking of Ultrathin 2D Hybrid Organic-Inorganic Perovskites. *ACS Nano*. 2018;12(10):10347-54.
- [2]. Tu Q, Spanopoulos I, Hao S, Wolverton C, Kanatzidis MG, Shekhawat GS, et al. Probing Strain-Induced Band Gap Modulation in 2D Hybrid Organic-Inorganic Perovskites. *ACS Energy Letters*. 2019;4(3):796-802.

9:40am **2D+EM+MI+MN+NS+QS-WeM6 Collective Electronic States of Epitaxial Monolayer 1T-NbSe<sub>2</sub>, Zhuozhi Ge**, University of Wisconsin; H. Zhang, L. Liu, C. Yan, West Virginia University; M. Weinert, University of Wisconsin; L.L. Li, West Virginia University

At the single layer limit, transition metal dichalcogenides (TMDs) can adopt two different structural variants depending on the anionic environment around the metal ions: the anions are arranged in trigonal prismatic fashion in the 1H polymorph, whereas in 1T the arrangement is octahedral. While bulk 1T NbSe<sub>2</sub> doesn't exist in nature, here we show that single layer 1T

NbSe<sub>2</sub> polymorph can be grown by molecular beam epitaxy on epitaxial graphene/SiC(0001) substrates. A (Ö13xÖ13) Star-of-David charge density waves is observed by *in situ* scanning tunnelling microscopy, which persists above room temperature. A gap of 0.50 eV is further observed by tunnelling spectroscopy and angle resolved photoemission spectroscopy, indicating that this monolayer 1T phase of NbSe<sub>2</sub> is also a Mott insulator, similar to that of bulk 1T TaS<sub>2</sub>. Our findings indicate that the presence of epitaxial constraints can generate structural configurations that are prohibited in fully-bonded TMD crystals. These findings and their implication on the collective electronic states of single layer 1T-NbSe<sub>2</sub> will be discussed at the meeting.

11:00am **2D+EM+MI+MN+NS+QS-WeM10 Magnetic Interfaces of MnSe<sub>2</sub> Monolayer, Tomas Rojas, S. Ulloa**, Ohio University

Until recently, 2D magnetism was thought to occur together with defects or doping on different substrates. This situation changed drastically, as intrinsic Cr-based ferromagnetic monolayer materials were discovered, namely CrI<sub>3</sub> and Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub>. A different material, MnSe<sub>2</sub>, was predicted as stable ferromagnetic monolayer by first-principles calculations, and it has been successfully grown on several substrates. In this study, the authors confirm the intrinsic ferromagnetism of the monolayer, while for thicker samples they report an interface of the MnSe<sub>2</sub> monolayer with bulk  $\alpha$ -MnSe(111). This phase of the material is non-magnetic, and yet the observed magnetic moments are of up to twice the value of those in the monolayer alone. In this work, we present a detailed analysis of the interactions at this interface between the two phases, using the Heyd-Scuseria-Ernzerhof hybrid functional. We have studied the effects on the electronic and magnetic structure of both phases of the material, and the dependence on the sample thickness. We study the role that strain plays at the interface, and how it affects the magnetic moments of the structure.

Supported by NSF-DMR 1508325, and Ohio Supercomputer Center .

11:40am **2D+EM+MI+MN+NS+QS-WeM12 Rotationally Controlled van der Waals Heterostructures of 2D Materials, Emanuel Tutuc, K. Kim, G.W. Burg, H.C.P. Movva**, The University of Texas at Austin

INVITED

Heterostructures of atomic layers such as graphene, hexagonal boron-nitride, and transition metal dichalcogenides (TMDs) can serve as testbed for novel quantum phenomena in two-dimensions, and potential device applications. A key ingredient that can add a new dimension to the atomic layer heterostructures palette is the rotational control, and alignment of different two-dimensional (2D) layers. We review here an experimental technique that enables rotationally controlled heterostructures with accurate alignment of the individual layer crystal axes [1]. We illustrate the applicability of this technique to the rotationally aligned double layers of graphene [2], or TMDs [3] separated by a tunnel barrier which display resonant, energy- and momentum-conserving tunneling in vertical transport, consistent with theoretical expectations. When two 2D layers are overlaid with a relative twist, the resulting heterostructure shows a new type of periodicity associated with the moiré superlattice, which are only beginning to be systematically investigated as platform for strongly correlated electron physics. We discuss the electron transport in tunable moiré patterns realized in twisted bilayer [4], and double bilayer graphene heterostructures.

Work done in collaboration with S. K. Banerjee, L. F. Register, B. J. LeRoy, A. H. MacDonald, T. Taniguchi, and K. Watanabe.

- [1] K. Kim *et al.*, *Nano Lett.* **16**, 1989 (2016);
- [2] G. W. Burg *et al.*, *Nano Lett.* **17**, 3919 (2017); G. W. Burg *et al.*, *Phys. Rev. Lett.* **120**, 177702 (2018).
- [3] K. Kim *et al.*, *Nano Lett.* **18**, 5967 (2018).
- [4] K. Kim *et al.*, *Proc. Natl. Acad. Sci. USA* **114**, 3364 (2017).

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## Electronic Materials and Photonics Division

### Room A214 - Session EM+2D+AS+MI+MN+NS+TF-WeM

#### Nanostructures and Nanocharacterization of Electronic and Photonic Devices

**Moderators:** Sang M. Han, University of New Mexico, Jason Kawasaki, University of Wisconsin - Madison

8:00am **EM+2D+AS+MI+MN+NS+TF-WeM1 Photonic Thermal Conduction in Semiconductor Nanowires**, *E.J. Tervo, M.E. Gustafson, Z.M. Zhang, B.A. Cola, Michael A. Filler*, Georgia Institute of Technology

We present a practical material system—chains of infrared plasmonic resonators situated along the length of semiconductor nanowires—where near-field electromagnetic coupling between neighboring resonators enables photonic thermal transport comparable to the electronic and phononic contributions. We model the thermal conductivity of Si and InAs nanowires as a function of nanowire diameter, resonator length, aspect ratio, and separation distance by combining discrete dipolar approximation calculations, to determine the relevant dispersion relations, with thermal kinetic theory. We show that photonic thermal conductivities exceeding  $1 \text{ W m}^{-1} \text{ K}^{-1}$  are possible for 10 nm diameter Si and InAs nanowires containing repeated resonators at 500 K, more than an order of magnitude higher than existing materials systems and on par with that possible with phonons and electrons. These results highlight the potential for photons in properly engineered solids to carry significant quantities of heat and suggest new ways to dynamic control thermal conductivity.

8:20am **EM+2D+AS+MI+MN+NS+TF-WeM2 Electric Field-Induced Defect Migration and Dielectric Breakdown in ZnO Nanowires**, *Hantian Gao, M. Haseman*, Department of Physics, The Ohio State University; *H. von Wenckstern, M. Grundmann*, Universität Leipzig, Felix-Bloch-Institut für Festkörperphysik; *L.J. Brillson*, The Ohio State University

Nanowires of the II-VI compound semiconductor ZnO have generated considerable interest for next generation opto- and microelectronics. Central to nanowire electronics is understanding and controlling native point defects, which can move<sup>1</sup> and lead to dielectric breakdown under applied electric fields. We used nanoscale lateral and depth-resolved cathodoluminescence spectroscopy (DRCLS) with hyperspectral imaging (HSI) in a scanning electron microscope (SEM) to observe defect migration and redistribution directly under applied electric fields and after dielectric breakdown. HSI maps represent lateral intensity distributions of specific features acquired pixel by pixel across SEM-scanned areas and normalized to near band edge (NBE) emissions. A pulsed layer deposited (PLD) ZnO microwire (3  $\mu\text{m}$  diameter) exhibited homogeneous distributions of common luminescence features at 2.0 eV ( $V_{\text{Zn}}$  cluster) and 2.35 eV ( $\text{Cu}_{\text{Zn}}$ ) as well as 2.7 and 2.9 eV ( $V_{\text{Zn}}$ ) peaks near the wire surface. With increasing electrical bias up to  $3 \times 10^5 \text{ V/cm}$  between two Pt contacts, these defects systematically redistribute, even at room temperature, moving toward and under one of the contacts, draining the “bulk” nanowire, especially its near-surface region. Since ionized  $V_{\text{Zn}}$ -related and  $\text{Cu}_{\text{Zn}}$  antisite defects are acceptors, their removal reduces the compensation of electron density in the typically n-type ZnO and thus its resistivity.

Besides HSI lateral maps, DRCLS vs. incident beam energy yields depth profiles radially of defects at specific locations along the nanowire. These exhibit high near-surface and wire core densities that biasing reduces. Current voltage measurements with increasing field gradients show a gradual resistivity decrease until an abrupt dielectric breakdown of the microwire at 300 kV/cm (150 V/5  $\mu\text{m}$ ). The acceptor removal between the contacts and their accumulation under one of the contacts can both contribute to this breakdown due to the decrease in resistivity and higher current conduction between the contacts and possible defect-assisted tunneling<sup>2</sup> across the increased defect density under the contact, respectively. These electric field-induced defect movements may be of more general significance in understanding dielectric breakdown mechanism not only in ZnO nanostructures but also bulk semiconductors in general.

FG, MH, and LJB gratefully acknowledge support from AFOSR Grant No. FA9550-18-1-0066 (A. Sayir). HVW and MG acknowledge Deutsche Forschungsgemeinschaft (Gr 1011/26-1).

1. G. M. Foster, et al., *Appl. Phys. Lett.* **111**, 101604 (2017).

2. J.W.Cox, et al., *Nano Lett.* **18**, 6974 (2018).

8:40am **EM+2D+AS+MI+MN+NS+TF-WeM3 Characterization of SiGe/Si Multilayer FIN Structures using X-Ray Diffraction Reciprocal Space Maps**, *Roopa Gowda, M. Korde*, SUNY Polytechnic Institute; *M. Warmington*, Jordan Valley Semiconductors Inc.; *A.C. Diebold, V. Mukundan*, SUNY Polytechnic Institute

Nanowire and Nanosheet FET's are potential replacements for FinFET's, mainly beyond sub-10nm CMOS technology nodes, as gate-all-around (GAA) FET device architecture provides improved electrostatics in higher on current ( $I_{\text{on}}$ ) and better subthreshold swing. As GAA is one of the best promising device for logic applications for future technology nodes, there is an increased need of characterization technique for such multilayer  $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$  complex structures. We studied  $\text{Si}_{1-x}\text{Ge}_x/\text{Si}/\text{Si}_{1-x}\text{Ge}_x/\text{Si}/\text{Si}_{1-x}\text{Ge}_x/\text{Si}$  Simultilayer FIN structures using X-Ray Diffraction Reciprocal Space Maps (RSM). RSM is one of the most popular technique to study epitaxial thin-films nanostructures due to straightforward analysis of the data. We found RSM simulations showing sensitivity of nanosheet fin structures dimensions such as pitch-walk (PW), Nanosheet thickness (NST), composition and shape. RSM's provide better means to interpret more complex diffraction measurements than real space constructions. RSMs of  $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$  multilayer structure has been simulated using Bruker JV-RADS v6.5.50/HRXRD software. 1D line profiles extracted from RSMs was also used for the analysis of nanostructures dimensions. We obtained multilayer structure dimensions from the published information. We studied the influence of nanostructure parameters PW, NST, Composition and shape on RSMs. Imperfect periodic structures impact the intensity modulation of the grating rods (GRs). We observed that satellite peaks intensity reduces and harmonics peaks intensity enhances as PW increases. Rate of intensity change in higher order peaks is much faster than the lower harmonic peaks. We observed that the spacing between adjacent interference fringes in RSMs is related to the thickness of the layers. The period of fringes is inversely proportional to the thickness of the layer, hence total FIN height can be determined. 1D line profiles along  $Q_z$  shows decreased angular width and increase in intensity of the layer peak and interference fringes as NST increases. Symmetric 004 longitudinal RSMs and their line profiles clearly show layer peak shift from substrate peak as composition increases due to increase of SiGe lattice spacing along the growth direction. Cross-shaped GR pattern in RSMs is observed which is due to trapezoidal surface grating caused by SWA. Line profiles indicate that fin shapes influence the modulation of the GRs as a function of  $Q_x$ . We demonstrate the characterization of complex  $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$  multilayers using RSMs and their line profiles which are relevant for lateral nanowire and nanosheet FETs. Above findings from RSM simulations clearly indicate the influence of variations in structural dimensions.

9:00am **EM+2D+AS+MI+MN+NS+TF-WeM4 Nanoscale Depth and Lithiation Dependence of  $\text{V}_2\text{O}_5$  Band Structure by Cathodoluminescence Spectroscopy**, *Mitchell Walker, N. Pronin*, The Ohio State University; *A. Jarry, J. Ballard, G.W. Rubloff*, University of Maryland, College Park; *L.J. Brillson*, The Ohio State University

Vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) has attracted considerable interest for its potential use as a cathode for solid state lithium ion batteries. While researchers have studied the  $\text{V}_2\text{O}_5$  lithiation charge/discharge cycle for over two decades, we are only now able to measure directly its electronic band structure from the surface to the thin film bulk and its changes with Li intercalation on a near-nanometer scale. We used depth-resolved cathodoluminescence spectroscopy (DRCLS) to monitor the changes in electronic structure from the free surface to the thin film bulk several hundred nm below. DRCLS measures optical transitions at 1.8-2, 3.1-3.2, 3.6-3.7, 4.0-4.1, and 4.6-4.7 eV between multiple conduction bands to the pristine ( $\alpha$ )  $\text{V}_2\text{O}_5$  valence band maximum in excellent agreement with  $V_{3d}t_{2g}$  conduction band densities of states (DOS) predicted by density functional theory (DFT).<sup>1</sup> Triplet conduction band states at 1.8, 1.9, and 2 eV correspond to predicted  $V 3d_{xy}-O_c 2p_x/2p_y$  hybridized states resulting from strong deviations of the unit cell  $\text{VO}_6$  octahedra from cubic coordination correspond to optical absorption edges along the 3 crystallographic axes. With excitation depth increasing from  $< 10$  to 125 nm calibrated by Monte Carlo simulations, the relative amplitudes and energies of these states change, signifying gradual changes in octahedral distortion. The band structure changes significantly with Li intercalation into  $\text{Li}_x\text{V}_2\text{O}_5$  for  $x = 0, 1$ , and 2. Lithiation gradually removes the hybridized band and introduces a 2.4-2.7 eV  $V_{3d} t_{2g}$  band extending 50 nm ( $x=1$ ) or 25 nm ( $x=2$ ) into the surface. Higher (4.0 and 4.4 eV) features possibly related to a secondary phase dominate the spectra deep inside all  $\text{V}_2\text{O}_5$  films near the battery electrode. Delithiation reintroduces the 1.8-2 eV split-off band although significantly narrowed by octahedral distortions. Overall, DRCLS shows that

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the lithiation cycle alters the  $V_2O_5$  band structure on a scale of 10-100's of nm with lithiation. The direct measure of  $V_2O_5$ 's electronic band structure as a function of lithiation level provided by DRCLS can help guide future battery engineering work as more efficient lithium ion batteries are developed. In particular, these unique electrode measurements may reveal in what ways lithiation changes  $V_2O_5$  irreversibly, as well as reveal methods to extend solid state battery life. MW and LJB acknowledge support from NSF grant DMR-18-00130. AJ and GR acknowledge Nanostructures for Electrical Energy Storage (NEES), a Department of Energy Office of Science Frontier Research Center.

1. V. Eyert and K.-H. Höck, "Electronic structure of  $V_2O_5$ : Role of octahedral deformation," *Phys. Rev. B* 57, 12727 (1998).

11:00am **EM+2D+AS+MI+MN+NS+TF-WeM10 Hot Electron Emission from Waveguide Integrated Graphene**, *Ragib Ahsan, F.R. Rezaeifar, H.U. Chae, R. Kapadia*, University of Southern California

From free electron laser sources to electronic structure measurements, electron emission devices play an important role in a wide range of areas. Photoemission is one of the basic processes exploited in modern electron emission devices. However, higher-order processes like multiphoton absorption or optical field induced emission are necessary for efficient photoemission from high workfunction metallic emitters. Our work demonstrates a graphene emitter integrated on a waveguide that can evanescently couple with the photons delivered from a CW laser (405 nm) and registers photoemission at a peak power that is orders of magnitude lower than previously published results based on multiphoton and optical field induced emission processes. Coupling FDTD analysis of the waveguide to a rigorous quantum mechanical study of the scattering mechanisms and the tunneling processes in graphene, we have been able to model the emission current from the graphene emitter with good agreement to the experimental data. Our investigation reveals that the photoexcited electrons can go through three mutually competitive processes: (i) electron-electron scattering (ii) electron-phonon scattering and (iii) directly emission into the vacuum. Absorption of a photon causes a reduction in the tunnel barrier seen by the electron and the emission rate increases exponentially. Integration of graphene to the waveguide enables evanescent coupling between electrons and the photons causing almost 100% absorption of the photons. Our integrated photonics approach demonstrates an emission efficiency that is three orders of magnitude greater than free space excitation. These results suggest that integrating photonic elements with low dimensional materials such as 2D materials, nanoparticles, quantum dots, etc. can provide a new domain of efficient electron emission devices and integrated photonics.

11:20am **EM+2D+AS+MI+MN+NS+TF-WeM11 Imaging Candidate Nanoelectronic Materials with Photoemission Electron Microscopy (PEEM)**, *Sujitra Pookpanratana, S.W. Robey*, National Institute of Standards and Technology (NIST); *T. Ohta*, Sandia National Laboratories

The drive to produce smaller and lower power electronic components for computing is pushing the semiconductor industry to consider novel nanoscale device structures, not based solely on crystalline silicon. Continued innovation and progress towards novel nanoelectronic materials and devices in turn requires metrologies sensitive to electronic properties at these length scales. Tip-based imaging techniques provide electronic contrast with sub-nanometer resolution, however it is a local, scanning-based technique. Photoemission (or photoelectron spectroscopy) is the dominant technique to provide detailed electronic band structure information- level energies, dispersion, polarization dependence, etc. – but typically requires materials with millimeter, or larger, length scales. Photoemission electron microscopy (PEEM) can be employed to allow access to this vital information, providing full-field imaging capabilities sensitive to a variety of electronic contrast mechanisms at 10's of nanometers length scales. Here, we will present our results on imaging the impact of molecular dopants on multilayer tungsten disulfide ( $WS_2$ ) employing the PEEM at the Center for Integrated Nanotechnologies within Sandia National Laboratories. We will also discuss the commissioning of a recently installed PEEM to perform complementary measurements at NIST-Gaithersburg.

Technological commercialization of transition metal dichalcogenides (TMDs) in nanoelectronics devices requires control of their electronic properties, such as charge carrier type and density, for specific device functionality. Conventional techniques for doping are problematic for atomically thin 2D materials. The sensitivity of mono- to few-layer (TMDs) to their local environment and interfaces can be employed *via* surface doping of molecules on TMDs to provide a promising route toward

controllable doping. Investigations of surface doping for one to few layer  $WS_2$  were performed using mechanically exfoliated  $WS_2$  on a  $SiO_2/Si$  substrate that was then exposed to tris(4-bromophenyl)ammoniumyl hexachloroantimonate, a p-dopant molecule. PEEM was performed before and after p-dopant exposure. After doping, we find that the contrast of the surface  $WS_2$  physical features change and valence band edge shifts about 0.8 eV away from the Fermi energy, consistent with p-doping. We will discuss the effects of molecular doping in terms of homogeneity and surface features across multiple  $WS_2$  flakes. Lastly, we will discuss commissioning of a new PEEM instrument installed at NIST in 2019, using results of graphene to demonstrate imaging capability and energy resolution of this instrument.

11:40am **EM+2D+AS+MI+MN+NS+TF-WeM12 Comparison of Features for Au and Ir Adsorbed on the Ge (110) Surface**, *Shirley Chiang*, University of California, Davis; *R.K. Xie, H.Z. Xing*, Donghua University, China; *T.S. Rahman*, University of Central Florida; *C.Y. Fong*, University of California, Davis

Two ad-atoms of Au and Ir adsorbed, respectively, on the Ge(110) surface are studied by a first-principles algorithm based on density functional theory. The surface is modeled by a slab consisting of 108 Ge atoms with a 10 Å vacuum region. Hydrogen atoms are used to saturate the dangling orbitals at the other side of the vacuum region. Two cases of Au adsorption and one case of Ir are reported. The case of Ir has a large binding energy because of its small atomic size compared with the Ge atom, and the partially filled d-states. The total energy for each case is given, as are the energies for removing one ad-atom at a time and also both ad-atoms. The binding energy of each case is obtained by simply taking the energy difference between these configurations; this method is more realistic because the experimental data measured by LEEM and STM indicate that the collective motions of the ad-atoms do not allow the surface to relax to its equilibrium state.[1] For a large separation in the case of two Au atoms, there is a smaller binding energy than for one ad-atom. This can relate to the fact that the collective motions seen experimentally do not happen at a full monolayer coverage of ad-atoms.[1] Additional comparisons will be made to an atomic model for Ir/Ge(111) from STM measurements.[2]

[1] B. H. Stenger et al., *Ultramicroscopy*, 183, 72 (2017).

[2] M. van Zijl et al., *Surf. Sci.* 666, 90, (2017).

Support from NSF DMR-1710748 (SC, CYF); NSF DMR-1710306 (TSR); National Natural Science Foundation of China Grants 61376102, 11174048 and computational support from Shanghai Supercomputer Center (RXX, HZX).

12:00pm **EM+2D+AS+MI+MN+NS+TF-WeM13 Reference Materials for Localization Microscopy**, *C.R. Copeland, R.G. Dixon, L.C.C. Elliott, B.R. Ilic*, National Institute for Science and Technology (NIST); *D. Kozak, K.-T. Liao*, FDA, National Institute for Science and Technology (NIST); *J.A. Liddle*, NIST Center for Nanoscale Science and Technology; *A.C. Madison*, National Institute for Science and Technology (NIST); *J.-H. Myung*, FDA; *A. Pintar, Samuel Stavis*, National Institute for Science and Technology (NIST)

As the diffraction limit fades away into the history of optical microscopy, new challenges are emerging in super-resolution measurements of diverse systems ranging from catalysts to therapeutics. In particular, due to common limitations of reference materials and microscope calibrations, many localization measurements are precise but not accurate. This can result in gross overconfidence in measurement results with statistical uncertainties that are apparently impressive but potentially meaningless, due to the unknown presence of systematic errors that are orders of magnitude larger. To solve this fundamental problem in measurement science, we are optimizing and applying nanofabrication processes to develop reference materials for localization microscopy, and demonstrating their use in quantitative methods of microscope calibration.

Our program consists of two complementary approaches. In the first, involving applied metrology, we are developing reference materials such as aperture arrays that can serve as standalone artifacts for widespread deployment. This approach will require the application of critical-dimension metrology to establish the traceability of master artifacts, and their use to calibrate a super-resolution microscope for high-throughput characterization of economical batches of reference materials. In the second approach, involving fundamental research, we are demonstrating the application of reference materials and calibration methods in our own experimental measurements. Most interestingly, achieving vertical integration of our two approaches and the unique capabilities that result, we are building reference materials into measurement devices for in situ calibration of localization measurements for nanoparticle characterization.

## Nanometer-scale Science and Technology Division

### Room A222 - Session NS-WeM

#### Optics and Scattering on the Nanoscale

**Moderators:** Alex Belianinov, Oak Ridge National Laboratory, Nancy Burnham, Worcester Polytechnic Institute

8:00am **NS-WeM1 Semiconductor Nanowires for Optoelectronics Applications**, *Chennupati Jagadish*<sup>1</sup>, Australian National University, Australia **INVITED**

Semiconductors have played an important role in the development of information and communications technology, solar cells, solid state lighting. Nanowires are considered as building blocks for the next generation electronics and optoelectronics. In this talk, I will introduce the importance of nanowires and their potential applications and discuss about how these nanowires can be synthesized and how the shape, size and composition of the nanowires influence their structural and optical properties. I will present results on axial and radial heterostructures and how one can engineer the optical properties to obtain high performance lasers, THz detectors and solar cells. Future prospects of the semiconductor nanowires will be discussed.

8:40am **NS-WeM3 Photonic-Plasmonic Fiber Probe for Nanoscale Chemical Imaging**, *B. Birmingham, K. Minn, B. Ko, H. Lee, Zhenrong Zhang*, Baylor University

Probing light-matter interaction in nanoscale regime requires the efficient delivery and collection of electromagnetic energy to and from the nanoscale region of interest. Metallic plasmonic nano-probes can efficiently excite and detect the near-field at nanoscale for near-field imaging and sensing applications such as tip-enhanced Raman spectroscopy (TERS). We have studied the interaction of molecules with bulk MoS<sub>2</sub>, a semiconductor, using TERS. MoS<sub>2</sub> has attracted tremendous attention due to promising applications in electronics, photonics, and catalysis. Here we have compared the difference in the interaction of sub-monolayer copper phthalocyanine (CuPc) molecules with MoS<sub>2</sub> and Au. The relative Raman peak ratio and Raman peak position shift from spatial TERS mapping show the difference in the adsorbates-adsorbates interaction and the adsorbates-substrates interaction on Au and MoS<sub>2</sub> substrates.

We also propose a photonic-plasmonic probe for nanoscale confinement of light. In our device, light in a fiber couples with the surface plasmons of a nano-antenna. The coupled plasmonic mode then propagates down the conical waveguide to the narrow apex where it gets localized and strongly focused, exhibiting immense field enhancement. By changing the structures at the fiber-antenna interface, the linearly polarized fiber mode is converted to radial surface plasmon polaritons (SPPs) through asymmetric coupling. The probe can be implemented into TERS setup to obtain spectroscopic information at the nanoscale.

9:00am **NS-WeM4 Nanoscale Infrared Confinement Using Surface Phonon Polaritons**, *Vanessa Breslin, A.B. Grafton*, National Research Council Postdoctoral Fellow; *D.C. Ratchford, A.J. Giles, K.P. Fears, C.R. So, D.S. Katzer, C.T. Ellis, J.G. Tischler*, U.S. Naval Research Laboratory; *J.D. Caldwell*, Vanderbilt University; *A.D. Dunkelberger, J.C. Owrutsky*, U.S. Naval Research Laboratory

Plasmonic materials can be used for surface enhanced infrared absorption, a particularly useful technique for chemical sensing applications, but these materials typically suffer from high optical loss due to the fast scattering of electrons, which results in broad optical resonances. In contrast, surface phonon polaritons (SPPs) have much lower losses because of the slower scattering rates of phonons, resulting in narrower resonance bands. In particular, our group is investigating polar dielectric inorganic crystals that have mid-IR Reststrahlen bands, frequency ranges where the crystals' optical constants resemble metals and can support SPP resonances. Currently, our efforts are focused on studying the optical properties of W(CO)<sub>6</sub> and calcite (CaCO<sub>3</sub>) crystals in the mid-IR. We are also experimenting with using a helium ion microscope, a gallium focused ion beam, and other lithographic techniques to nanostructure the surface of these polar dielectric materials in order to generate SPPs for sub-diffraction optical confinement of mid-IR incident light. The results of these studies will allow us to better understand how to tune SPPs in a broader

spectral range with different inorganic materials and provide a basis for exploring how these resonances interact with other chemical systems through enhanced spectroscopies and energy transfer.

9:20am **NS-WeM5 Actuating and Probing a Single-molecule Switch at Femtosecond Timescales**, *D. Peller, L.Z. Kastner, T. Buchner, C. Roelcke, F. Albrecht, R. Huber, Jascha Repp*, University of Regensburg, Germany **INVITED**

Accessing ultra-fast non-equilibrium phenomena is enabled by terahertz (THz) scanning tunneling microscopy [1] (THz-STM) through combining STM with lightwave electronics. In THz-STM, the electric field of a phase-stable single-cycle THz waveform acts as a transient bias voltage across an STM junction. These voltage transients may result in a net current that can be detected by time-integrating electronics. The recent development of this lightwave STM has enabled the combined femtosecond and sub-angstrom resolution in observing matter [2].

We now demonstrate the first combined femtosecond and sub-angstrom access in the control of matter. Ultrafast localized electric fields in lightwave STM enable exerting atom-scale femtosecond forces to selected atoms. By shaping atomic forces on the intrinsic timescale of molecules, coherent atomic motion can now be excited. Utilizing this coherent structural dynamics, we can modulate the quantum transitions of a single-molecule switch by up to 39%. We directly visualize the coherent excitation of the switch in the first femtosecond single-molecule movie [3].

To resolve the impact of coherent control of the single-molecule switch, alongside, we introduce single-shot action spectroscopy in lightwave STM as the first concept resolving individual path-selective reaction events of a single molecule in space and time. With this novel concept, we detect the outcome of every single laser shot and further separate the statistics of the two inverse reaction paths.

Our results open a new chapter in the control and observation of reactions of individual molecules directly on the relevant ultrafast and ultrasmlal scales.

References:

- [1] T. L. Cocker et al., Nature Photon. 7, 620 (2013).
- [2] T. L. Cocker et al., Nature 539, 263 (2016).
- [3] D. Peller et al., in preparation.

11:00am **NS-WeM10 Nanoscale Structural Imaging through Bragg Diffraction Microscopy**, *Martin Holt*, Argonne National Laboratory **INVITED**

The development of x-ray nanobeam instrumentation at synchrotron x-ray light sources has created a wide range of opportunities in understanding nanoscale phenomena in materials science, chemistry, and condensed matter physics. Such instruments, including the Center for Nanoscale Materials/Advanced Photon Source Hard X-ray Nanoprobe (HXN) employ highly brilliant x-ray beams with focal spot sizes on the order of tens of nanometers and sufficient phase-coherent intensity to produce high-dynamic range scattering patterns from individual nanoscale objects. The far higher brilliance resulting from the APS Upgrade project promises to enable new classes of nanodiffraction experiment and to bring new challenges in the management and predictive analytic interpretation of large coherent scattering datasets. The scientific use of these instruments has required the creation of advanced x-ray analysis techniques based on combinations of coherent diffraction and ptychography with the unique optical conditions of tightly focused x-ray beams enabling correlation of structural and chemical mapping. The classes of scientific questions that are addressable by these techniques and the potential impact of diffraction limited storage rings such as the APS-Upgrade project will be explored within the context of recent results.

11:40am **NS-WeM12 First Launch of XTIP - The World's First User Program for the Combination of Scanning Tunneling Microscopy with Synchrotron Radiation**, *Volker Rose, N. Shirato, D. Rosenmann, M. Fisher, S-W. Hla*, Argonne National Laboratory

The combination of the ultimate spatial resolution of scanning probe microscopy with the chemical and magnetic sensitivity of synchrotron x-rays has opened the prospect for an entirely new way of nanoscale materials' characterization. Over the last couple of years, Argonne National Laboratory has pioneered the development of synchrotron x-ray scanning tunneling microscopy (SX-STM). The technique has demonstrated imaging with direct elemental contrast down to the level of single atom height as well as imaging of nanoscale magnetic domains of thin films.

In order to open up this new capability to the entire science community, and to fully exploit the special capabilities of the technique, XTIP, a

<sup>1</sup> NSTD Recognition Award

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dedicated beamline for SX-STM has been construction at Argonne's Advanced Photon Source. To meet the scientific objective of the nanoscience and nanomagnetism communities most effectively, XTIP offers full polarization control over the 500-1600 eV photon energy range. The dedicated XTIP beamline, inaugurated in the summer of 2019, provides researchers access to a one-of-a-kind instrument. Among the potential breakthroughs are "designer" materials created from controlled assemblies of atoms and molecules, and the emergence of entirely new phenomena in chemistry and physics. The easy process for obtaining access to the XTIP beamline will also be covered.

This work was performed at the Advanced Photon Source and the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility under Contract No. DE-AC02-06CH11357.

**12:00pm NS-WeM13 Application of Scanning Tunneling Microscopy and Tip-Enhanced Raman Spectroscopy to the Study of Intermolecular and Molecule-Substrate Interactions, Jeremy Schultz<sup>1</sup>, N. Jiang, University of Illinois at Chicago**

Molecular self-assembly on surfaces is defined by the unique set of circumstances that arise from the complicated interplay of molecule-molecule and molecule-substrate interactions. These interactions are defined by their highly localized chemical environments. As a result, it becomes necessary to apply spatially resolved techniques. In this work we have applied two primary techniques to the study of intermolecular and molecule-substrate interactions. Scanning tunneling microscopy (STM) reveals local electronic effects and structure, while tip-enhanced Raman spectroscopy (TERS) defines the vibrational fingerprint of a molecule which is highly sensitive to localized chemical effects. In combination with gas phase Density Function Theory (DFT) calculations it is possible to define the effects of molecule-substrate interactions on the molecules' vibrations. Three different systems involving organic molecules on single crystals have been examined: boron subphthalocyanine, 3,6-dibromo-9,10-phenanthrenequinone, and rubrene. Through the tandem technique of STM-TERS, intermolecular interactions that result in self-assembly, specifically hydrogen bonds, halogen bonds, and van der Waals interactions have been characterized. Similarly, molecule-substrate effects on molecular configuration and binding strength have been considered through comparison with DFT simulated Raman spectra to obtain a detailed description. Ultimately, the application of complementary techniques results in highly descriptive vibrational fingerprints with spatial resolution.

## Materials and Processes for Quantum Information, Computing and Science Focus Topic Room B231-232 - Session QS+2D+EM+MN+NS+VT-WeM

### Material Systems and Applications for Quantum Sciences

**Moderators:** Mena Gadalla, Harvard University, Kai Xiao, Oak Ridge National Laboratory

**8:00am QS+2D+EM+MN+NS+VT-WeM1 Quantum Information at the Molecular Foundry - An Overview of New Toolsets for QIS Research, Adam Schwartzberg, S. Cabrini, D.F. Ogletree, A. Weber-Bargioni, Lawrence Berkeley National Laboratory (LBNL)**

The fundamental unit of quantum computation and sensing is the qubit, and many physical systems have been investigated for practical realization. These include superconducting Josephson junction circuits, color centers, and isolated cold atoms or ions. Superconducting qubit circuits (SCQBs) being one of the most promising avenues to quantum computation. However, there are limitations to their practical application due to noise sources which shorten their functional lifetime.

In this talk I will introduce a suite of integrated, high-fidelity fabrication instrumentation that will allow new communities of users to investigate the fundamental limits of state-of-the-art quantum systems at the Molecular Foundry. We will enable users to understand existing systems and design new ones by creating a quantum fabrication toolset for directed growth of conventional and novel materials, advanced lithography and pattern transfer paired with in- and ex-situ surface characterization.

Three key QIS fabrication capabilities at the Molecular Foundry:

A robotic fabrication cluster system with materials deposition, including atomic layer and physical vapor depositions, plasma etching, and analytical characterization instrumentation, all automated by and contained within a vacuum sample handling robot.

A high resolution electron beam writing system will allow quantum device patterning with complete flexibility in feature shape, density and size, enabling nanoscale feature control.

A low temperature transport measurement system will allow for the investigation of novel materials for superconductors and dielectrics and "close the loop" between design and fabrication, proxy measurements such as interface characterization, and actual performance of quantum computation and sensing elements.

This instrumentation suite will enable the elucidation of chemical composition, structure, location, and size of microscopic noise sources in a superconducting quantum system, understanding the fabrication steps that introduced such noise sources, and developing fabrication approaches that minimize their presence.

I will also discuss ongoing and new research directions at the Molecular Foundry through internal staff and external user research.

**8:20am QS+2D+EM+MN+NS+VT-WeM2 Quantum Vacuum Metrology to Advance Quantum Science Capabilities, Jay Hendricks, J.E. Ricker, K.O. Douglass, National Institute of Standards and Technology (NIST); J.A. Fedchak, J. Scherschligt, National Institute of Standards and Technology (NIST)**

NIST is developing a series of next generation pressure and vacuum standards that will serve as a basis for key vacuum technology platforms required for emerging quantum science applications. The production of quantum sensors and devices is anticipated to require extremely demanding process control with exact knowledge of background residual gas, process chamber pressure, and accurate measurement of gas pressure feedstocks.

In 2019, National Metrology Institutes around the world worked to redefine the international system of units, the SI, such that the base units are now based on fundamental constants.

Moving forward, the next generation of pressure and standards will provide a new route of SI traceability for the pascal. By taking advantage of both the properties of light interacting with a gas and that the pressure dependent refractive index of helium can be precisely predicted from fundamental, first-principles quantum-chemistry calculations, a new route of realizing the pascal has been demonstrated. This talk will briefly cover the classical methods of realizing pressure that have served the metrology community well for the past 375 years. And then will take a deeper dive into the next generation of light-based pressure standards that will enable the elimination of mercury manometers, replacing them with a smaller, lighter, faster, and higher precision standards. From a metrology stand point, the new quantum-based SI pascal will move us from the classical force/area definition, to an energy density (joules per unit volume) definition. Should the technique be further miniaturized, it will lead to a revolution in pressure metrology, enabling a photonics-based device that serves both a gas pressure sensor and a portable gas pressure standard all in one.

NOTE: this topic is appropriate for VT sessions as well but thought it would be interesting to the broader audience that is interested in emerging quantum-based technologies that are needed to advance the field of quantum science.

**8:40am QS+2D+EM+MN+NS+VT-WeM3 Quantum Control of Spins in Silicon Carbide with Photons and Phonons, D. Awschalom, S.J. Whiteley, G. Wolfowicz, K.C. Miao, Christopher Anderson, University of Chicago INVITED**

There are numerous efforts to embrace solid-state defects and construct quantum systems to enable new information technologies based on the quantum nature of the electron. Current studies include semiconductors with incorporated point defects, whose quantum mechanical spin properties allow a fundamentally different means to process information. In particular, interfacing solid-state defect electron spins to other quantum systems is an ongoing challenge. Here we demonstrate electrically driven coherent quantum interference in the optical transition of single divacancies, enabling new control of the spin-photon interface [1]. By applying microwave frequency electric fields, we coherently drive the

<sup>1</sup> NSTD Graduate Student Award Finalist  
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excited-state orbitals and induce Landau-Zener-Stückelberg interference fringes in the resonant optical absorption spectrum. Furthermore, we develop a stroboscopic X-ray diffraction imaging technique that provides direct imaging and quantitative measurement of local strain at the nanometer scale. In conjunction with the fabrication of surface acoustic wave resonators, we mechanically drive coherent Rabi oscillations between arbitrary ground-state spin levels, including magnetically forbidden spin transitions, allowing for acoustic quantum control of local spins in silicon carbide and the exploration of spin-phonon coupling in the solid state [2]. These properties establish divacancies as strong candidates for quantum communication and hybrid system applications, where simultaneous control over optical and spin degrees of freedom is paramount.

[1] K. C. Miao *et al.*, arxiv: 1905.12780

[2] S. J. Whiteley *et al.*, Nature Phys. **15**, 490 (2019)

9:20am **QS+2D+EM+MN+NS+VT-WeM5 Tunable Control over InSb(110) Surface Conductance Utilizing Charged Defects**, **Robert Walko**, S.M. Mueller, S. Gant, J.J. Repicky, S.J. Tjung, E. Lang, E. Fuller, K. Werner, The Ohio State University; F. Bergmann, Bergmann Messgeraete Entwicklung; E. Chowdhury, J.A. Gupta, The Ohio State University

In this work we present a scanning tunneling microscopy (STM) study of tip-induced switching of charge states in individual indium adatoms on the InSb(110) surface. These adatoms are deposited onto the surface by controlled voltage pulses between the STM tip and the surface. We observe them in two distinct charge states: positive and neutral. Adatom-induced band bending from the positively charged state has been observed to induce a tenfold increase in surface conductance relative to the charge neutral state, the effect of which can be observed >100nm away from the indium adatom. When the STM tip is brought sufficiently close to the defect, electrons can tunnel from the tip to the defect and cause the charge state to switch from positive to neutral. During imaging, this switching leads to a “crater” feature around the defect due to the lower conductance of the charge neutral state. The spatial extent of the crater can be tuned via the applied bias voltage, the tunneling set-point current, and photoillumination of the surface. We explain this phenomenon using a model of competing rates between the filling and emptying of the defect state, similar to dangling bonds on the Si(111) surface.

This work acknowledges funding from the DOE (# DE-SC0016379)

9:40am **QS+2D+EM+MN+NS+VT-WeM6 Quantum Calligraphy: Writing Single-Photon Emitters in a Two-Dimensional Materials Platform**, **Matthew R. Rosenberger**, U.S. Naval Research Laboratory; C.K. Dass, Air Force Research Laboratory; H.-J. Chuang, S.V. Sivaram, K.M. McCreary, U.S. Naval Research Laboratory; J.R. Hendrickson, Air Force Research Laboratory; B.T. Jonker, U.S. Naval Research Laboratory

We present a paradigm for encoding strain into two dimensional materials (2DM) to create and deterministically place single photon emitters (SPEs) in arbitrary locations with nanometer-scale precision. Our material platform consists of a 2DM placed on top of a deformable polymer film. Upon application of sufficient mechanical stress using an atomic force microscope tip, the 2DM/polymer composite deforms, resulting in formation of highly localized strain fields with excellent control and repeatability. We show that SPEs are created and localized at these nanoindentations, and exhibit single photon emission up to 60K. This **quantum calligraphy** allows deterministic placement and real time design of arbitrary patterns of SPEs for facile coupling with photonic waveguides, cavities and plasmonic structures. In addition to enabling versatile placement of SPEs, these results present a general methodology for imparting strain into 2DM with nanometer-scale precision, providing an invaluable tool for further investigations and future applications of strain engineering of 2DM and 2DM devices.

Reference: Rosenberger *et al.*, “Quantum Calligraphy: Writing Single-Photon Emitters in a Two-Dimensional Materials Platform,” *ACS Nano*, 2019, <https://pubs.acs.org/doi/10.1021/acsnano.8b08730>

11:00am **QS+2D+EM+MN+NS+VT-WeM10 Challenges in Topological and Quantum Materials**, **David Alan Tennant**, Oak Ridge National Laboratory  
**INVITED**

Quantum materials are rapidly advancing but still present great challenges. Topological quantum

materials in particular are receiving great attention as they provide potentially robust routes to

quantum information processing that are protected against decoherence processes. Among key

challenges are the prediction and realization of magnetic materials in the form of magnetic Weyl

semimetals and quantum spin liquids as ways of realizing exotic quasiparticles such as Majorana fermions

that can be used for application. These materials present new experimental challenges in terms of identifying their

quasiparticles and demonstrating quantum coherence in their ground states. Here I will

show how we are using the integrated application of machine learning along with experiment and synthesis

to advance the discovery and understanding of these materials.

11:40am **QS+2D+EM+MN+NS+VT-WeM12 Rare Earth Silicon Photonics Engineering for Quantum Applications**, **Arindam Nandi**, X. Jiang, D. Pak, Purdue University; D.N. Perry, E.S. Bielejec, Sandia National Laboratories; Y. Xuan, M. Hosseini, Purdue University

Controlling intermodal coupling between multiple excitations within a photonic material may enable the design of novel quantum photonic metamaterials exhibiting anomalous effects. Understanding the complex mode dynamics towards the engineering of system Hamiltonian has been the subject of intensive research in recent years. Here, we design an atomic lattice composed of nearly 1000 rare earth ion segments deterministically engineered in silicon photonic structures to modify the emission properties of erbium in silicon. We observe anomalous photon emission at the telecommunication wavelength from atoms geometrically arranged to reduce the propagation loss. Moreover, we map asymmetric emission lineshapes led by intermodal Fano-type interference of the atomic and photonic resonance modes. Our observation paves the way for designing active metamaterials and novel topological photonics with engineered linear and nonlinear interactions for broad applications in quantum information. Moreover, I will result for direct integration of rare earth crystals with silicon photonic chip for implementation of quantum optical memories. The approach can impact the fields of quantum communication and computation through, for example, developing superradiant single photon sources, the study of non-equilibrium many-body quantum dynamics, and engineering quantum transport in a scalable solid-state platform.



## 2D Materials

### Room A216 - Session 2D+EM+MN+NS-WeA

#### 2D Device Physics and Applications

Moderator: Ivan Oleynik, University of South Florida

2:20pm **2D+EM+MN+NS-WeA1 Monolayer Electronics and Optoelectronics - Advances, Opportunities and Challenges, Ali Javey, University of California at Berkeley** **INVITED**

Two-dimensional semiconductors exhibit excellent device characteristics, as well as novel optical, electrical, and optoelectronic characteristics. In this talk, I will present our recent advancements in surface passivation, contact engineering, surface charge transfer doping, and heterostructure devices of layered chalcogenides. We have developed a passivation technique that allows for observation of near-unity photoluminescence quantum yield in monolayer semiconductors. I will discuss the mechanism by which non-radiative recombination can be fully removed in monolayers. The work presents the first demonstration of an optoelectronically perfect monolayer, and highlights one of their unique properties. Finally, I will discuss an AC carrier injection mechanism to enable bright light emitting devices using monolayers, overcoming the problem of Schottky contacts.

3:00pm **2D+EM+MN+NS-WeA3 Investigation on Graphene Band-gap Engineering for Graphene Transistors Applications, Benfdila Arezki, University M. Mammeri Tizi-Ouzou, Algeria**

Graphene transistors are considered to be the successor's basic element for the next generation of advanced integrated circuits. However, graphene material suffers from the absence of bandgap to behave as semiconductor. The present paper deals with the investigation on the bandgap engineering approach aiming an increase of the switching characteristics of the graphene transistors.

The main obstacle for graphene transistor is the material zero bandgap that worsens the switching characteristics of the GFETs. Several techniques have been proposed to open a bandgap in graphene, among these engineering techniques, we can cite the Substrate induced bandgap, Bandgap engineering using h-BN/Ni (111). It is known that in theory a maximum of 0.50 to 0.53 eV can be obtained. Such bandgaps are observed on Graphene Bi-Layer (GBL) sheets grown on silicon carbide (SiC).

Other methods are the substitutional doping (SD), Nitrogen doping (NB). In any case graphene engineering should be considered in chemistry and physics view points. A high selective hydrogenation of graphene grown by lithography under the form of nanoruban showed a very interesting result of 0.7 eV. This process is part of selective chemical graphene functionalization techniques (SCGF).

In this paper we will deal with the graphene nanoruban and the opening of a bandgap capable of inducing an appreciable switching current ratio of at least  $I_{ON}/I_{OFF} > 10^6$ .

The Graphene Nano Ribbon (GNR) structure used in the form of GNR/FET for logic circuits and RF devices combines the high field, high mobility and the possibility of opening a bandgap. The higher carrier mobility of graphene is the basis of all electrical characteristics of graphene transistors.

In this paper we have used a semi-classical device model including the band to band tunneling that is described in Ref<sup>6</sup> to emphasize on the bandgap engineering. Device performances are studied based on the current-voltage characteristics with respective bandgap width variations.  $I_{OFF}$  current estimated and the performance ratio deduced.

3:20pm **2D+EM+MN+NS-WeA4 Fully Inkjet Printed, High Photo-responsive, 2D WSe<sub>2</sub>-Graphene Based Flexible Photodetector, R.F. Hossain, A.B. Kaul, Avra Bandyopadhyay, University of North Texas**

Tungsten di-selenide (WSe<sub>2</sub>), a classic representative of two dimensional (2D) layered materials has recently drawn much attention due to its unique optoelectronic properties, offering a potential platform to construct hetero-structure photodetector (PD) for ultrafast optoelectronic devices on low-cost, flexible substrates [1,2]. As WSe<sub>2</sub> exhibits a weak van der Waals interlayer bonding, one of the approaches to obtain 2D WSe<sub>2</sub> is through top-down liquid phase exfoliation (LPE), where the bulk crystal is dispersed in a solvent through appropriate sonication and centrifugation conditions [1]. In this work, we report on the synthesis of WSe<sub>2</sub> via LPE and the first-ever assembly of an all inkjet printed WSe<sub>2</sub>-graphene hetero-structure PD on flexible polyimide film, where the WSe<sub>2</sub> acted as a photo-active semiconductor and graphene was the carrier collector. The inkjet printed PD was photo-responsive to broadband incoming radiation in the visible regime, and exhibited a high photoresponsivity  $R \sim 0.70$  A/W, and

detectivity  $D \sim 3 \times 10^{10}$  Jones. The strain-dependent measurements were conducted with bending for different curvatures, indicating the feasibility of such devices for large format arrays printed on flexible substrates. The capacitance-frequency ( $C-f$ ) measurements were performed to investigate the trap states. In conclusion, this unique all inkjet printed 2D hetero-junction photodetector formed on flexible and conformable substrate was successfully shown to be highly photo-responsive to a wide range of light intensities and strain levels, making it a promising prospect for scalable flexible electronic and optoelectronic devices and circuitry.

#### References:

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[2] Pradhan, N. R., Ludwig, J., Lu, Z., Rhodes, D., Bishop, M. M., Thirunavukkuarasu, K., ... & Balicas, L. (2015). High photoresponsivity and short photoresponse times in few-layered WSe<sub>2</sub> transistors. *ACS applied materials & interfaces*, 7(22), 12080-12088.

4:20pm **2D+EM+MN+NS-WeA7 Chemical Vapor Sensing with Transition Metal Dichalcogenides via Photoluminescence Modulation, Aubrey T. Hanbicki, P.M. Campbell, S.V. Sivaram, U.S. Naval Research Laboratory; A.J. Kusterbeck, Nova Research, Inc.; V.K. Nguyen, R.A. McGill, K.M. McCreary, B.T. Jonker, E.D. Cobas, F.K. Perkins, U.S. Naval Research Laboratory; A.L. Friedman, Laboratory for Physical Sciences**

Two-dimensional transition metal dichalcogenides (TMDs) such as MoS<sub>2</sub> and MoSe<sub>2</sub> are promising materials for chemical vapor sensing applications. Their potential includes straightforward fabrication, readily available materials, and good selectivity, sensitivity, and speed of response. We previously showed [1] that monolayer TMDs are sensitive to and selective for vapors of strong electron donors and/or strong electron acceptors in concentrations as low as 1 part per million (ppm). Another attractive aspect is that TMDs have been shown to detect chemical vapors and gases in several ways, for instance via changes in electrical conductance or photoluminescence (PL) [2]. Sensors commonly have been fabricated based on the chemiresistive device properties, but here we will discuss our recent studies implementing TMD sensors using the PL as the core element of the sensor. We show that the PL intensity of monolayer CVD-grown WS<sub>2</sub> can rapidly (<< 1sec) detect triethylamine (TEA), a decomposition byproduct of the VX series of nerve agents, in concentrations <<1 ppm. The optical response is similar to the electrical response of other TMDs previously shown [1]. We shall discuss the mechanisms determining the size and shape of the optical responses. We envision suites of different TMDs using both optical and conductance sensing to rapidly and selectively detect chemical agents.

This research was performed while S.V.S held a National Research Council fellowship at NRL. This work was supported by core programs at NRL.

#### References

[1] A.L. Friedman et al., *Sci. Reports* 7, 3836 (2017)

[2] P.M. Campbell et al., *Appl. Phys. Lett.* 113, 163106 (2018)

4:40pm **2D+EM+MN+NS-WeA8 Effective and Robust Graphene Immunological Sensors Functionalized through Non-covalent Ninding of Antibody-Conjugated Tripodal Compound, A. Hugo, CEA-LETI, France; C. Sun, Northwestern University; M. Kumar, CEA-LETI, France; R. Othmen, J. Renard, V. Bouchiat, CNRS-Institut Néel, France; J. Mann, Northwestern University; J.M. Parpia, H.G. Craighead, Cornell University; P. Mailley, CEA-LETI, France; W.R. Dichtel, Northwestern University; T. ALAVA, Sebastian Hentz, CEA-LETI, France**

Electrical detection is a very robust technique to transduce the adsorption of charged protein to a biological selective layer (i.e. biosensing). Electrolyte gated field effect transistors (EGFET) integrating graphene monolayers as the transducing element have shown outstanding electrical sensitivity in liquid compared to silicon and diamond based EGFET. In order to build graphene EGFET as effective biosensing unit it is important to attach at its surface a functional layers of biological molecules that will carry the task of enforcing specific detection of compound. Protein are widely used as specific bioreceptor for sensor biological functionalization yet it has been shown that protein lose their function when simply adsorbed on graphene. Covalent binding being out of the way for 2D dimensional crystals such as graphene (for the inherent deterioration of mechanical and electrical properties) we have shown that custom made tripodal compound attaching the graphene basal plane through Pi-stacking of aromatic moieties could be used to attach specific biomolecules to graphene while maintaining their biological function hence their specificity.

In this report we present an optimized fabrication process for graphene EGFET that includes patterning and passivation of electrical contact. The devices reproducibly show state of the art electrical performances. We demonstrate that the process can be simply transferred to different host substrates to integrate graphene EGFET ubiquitously on Silicon, glass or printed circuit board with similar performances. Finally, we implemented biological functionalization of the sensors by attaching streptavidin to the sensor thanks to the non-covalent tripodal compound. We report consistent changes in the Dirac peak of graphene due to the adsorption of tripodal compound and streptavidin as well as the binding of biotin, specifically bound to streptavidin. We show the detection to be specific and reproducible.

5:00pm **2D+EM+MN+NS-WeA9 Electronic Properties of Ultra-Thin Na<sub>3</sub>Bi: A Platform for a Topological Transistor**, *Mark Edmonds*, Monash University, Australia **INVITED**

Na<sub>3</sub>Bi in bulk form represents a zero-bandgap topological Dirac semimetal (TDS), but when confined to few-layers is predicted to be a quantum spin Hall insulator with bulk bandgap of 300 meV.<sup>1</sup> Furthermore, application of an electric field to few-layer Na<sub>3</sub>Bi has been predicted to induce a topological phase transition from conventional to topological insulator.<sup>2</sup>

I will discuss our efforts to grow epitaxial few-layer Na<sub>3</sub>Bi via molecular beam epitaxy, and probe its electronic structure and response to an electric field using scanning probe microscopy/spectroscopy and angle-resolved photoelectron spectroscopy. We demonstrate that monolayer and bilayer Na<sub>3</sub>Bi are wide bandgap quantum spin Hall insulators ( $E_g > 300$  meV) that can be tuned with an electric field to semi-metallic, and at higher electric fields re-opened as a conventional insulator.<sup>3</sup> This is the first experimental demonstration of such an electric field tuned topological phase transition in any material. Finally, I will discuss our most recent efforts to perform transport measurements on few-layer Na<sub>3</sub>Bi at doping levels corresponding to bulk conduction and edge conduction, with and without an applied magnetic field.

## References

- [1] C. Niu et al., Phys. Rev. B (2017) 95, 075404
- [2] H. Pan et al., Scientific Reports (2015) 5, 14639
- [3] J. Collins et al., Nature 564, 390 (2018)

6:00pm **2D+EM+MN+NS-WeA12 Negative Fermi-level Pinning Effect Induced by Graphene Interlayer in Metal/Graphene/Semiconductor Junction**, *H.H. Yoon, W. Song*, Ulsan National Institute of Science and Technology (UNIST), Republic of Korea; *S. Jung*, SK Hynix, Republic of Korea; *J. Kim*, Ulsan National Institute of Science and Technology (UNIST); *K. Mo, G. Choi, H.Y. Jeong, J.H. Lee, Kibog Park*, Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

We report the direct observation revealing that the electric dipole layer originating from the off-centric distribution of interacting electrons at metal/graphene interface can induce the negative Fermi-level pinning effect in metal/graphene/semiconductor junction made on a semiconductor substrate containing regions with low interface-trap density. The graphene interlayer takes a role of diffusion barrier preventing the atomic intermixing at interface and preserving the low interface-trap density region. The change of electrostatic potential across the metal/graphene interface due to the interaction dipole layer and the doping of graphene is found to cause the negative Fermi-level pinning effect, supported by the Schottky barrier decreasing as metal work-function increasing. In case of metal/graphene/GaAs junction, the local small patches with very thin or no native oxide layer are considered to be responsible for the negative Fermi-level pinning. In the prevailing region with normal native oxides surrounding the small patches, the Fermi-level pinning appears to be strong. Meanwhile, the negative Fermi-level pinning is found to occur globally in metal/graphene/SiC junction where the SiC substrate is known to produce a low density of interface traps. This work provides an experimental method to form Schottky and Ohmic-like contacts simultaneously on a semiconductor substrate covered partially with graphene by using identical metal electrodes.

## Chemical Analysis and Imaging Interfaces Focus Topic

Room A120-121 - Session CA+NS+SS+VT-WeA

### Chemical Analysis and Imaging of Liquid/Vapor/Solid Interfaces I

**Moderators:** Juan Yao, Pacific Northwest National Laboratory, Andrei Kolmakov, National Institute of Standards and Technology (NIST)

2:20pm **CA+NS+SS+VT-WeA1 Chemical Analysis and Imaging of Environmental Interfaces**, *Vicki Grassian*, University of California at San Diego **INVITED**

Environmental interfaces, defined as any surface in equilibrium with its surrounding environment, are ubiquitous. From this broad definition, there are a myriad of different types of environmental interfaces that include atmospheric aerosols, nanomaterials and indoor surfaces. This talk will focus on the use of different molecular probes including various spectroscopic and imaging techniques to investigate interfaces relevant to outdoor and indoor environments.

3:00pm **CA+NS+SS+VT-WeA3 Liquid/Vapor Interfaces Investigated with Photoelectron Spectroscopy**, *Hendrik Bluhm*, Fritz Haber Institute of the MPG, Germany **INVITED**

Aqueous solution/vapor interfaces govern important phenomena in the environment and atmosphere, including the uptake and release of trace gases by aerosols and CO<sub>2</sub> sequestration by the oceans.[1] A detailed understanding of these processes requires the investigation of liquid/vapor interfaces with chemical sensitivity and interface specificity under ambient conditions, *i.e.*, temperatures above 200 K and water vapour pressures in the millibar to tens of millibar pressure range. This talk will discuss opportunities and challenges for investigations of liquid/vapor interfaces using X-ray photoelectron spectroscopy and describe some recent experiments that have focused on the propensity of certain ions and the role of surfactants at the liquid/vapor interface.

[1] O. Björneholm et al., Chem. Rev. **116**, 7698 (2016).

4:20pm **CA+NS+SS+VT-WeA7 Methanol Hydration Studied by Liquid  $\mu$ -jet XPS and DFT Simulations**, *Jordi Fraxedas*, Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Spain; *E. Pellegrin, V. Perez-Dieste, C. Escudero*, CELLS-ALBA, Spain; *P. Rejmak*, Institute of Physics PAS, Poland; *N. Gonzalez, A. Fontseré, J. Prat, S. Ferrer*, CELLS-ALBA, Spain

The advent of liquid  $\mu$ -jet setups, in conjunction with X-ray Photoemission Spectroscopy (XPS), has opened up a plethora of experimental possibilities in the field of atomic and molecular physics [1]. Here, we present a combined experimental and theoretical study of the hydration of methanol at the aqueous solution/vapor interface. These are first experimental results obtained from the new liquid  $\mu$ -jet setup at the Near Ambient Pressure Photoemission (NAPP) endstation of the CIRCE helical undulator beamline (100–2000 eV photon energy range) at the CELLS-ALBA synchrotron light source, using a differentially pumped SPECS PHOIBOS 150 hemispherical electron energy analyzer [2]. The experimental results are compared with simulations from density functional theory (DFT) regarding the electronic structure of single molecules and cluster configurations as well as with previous experimental studies.

Methanol is the simplest amphiphilic molecule capable of hydrogen bonding due to its apolar methyl and polar hydroxyl groups. The results obtained from pure water at 600 eV photon energy emphasize the short range tetrahedral distribution as previously observed for crystalline and amorphous ice. We also find indications for ordering phenomena in water/methanol mixtures by the reduced O1s XPS liquid line width (as compared to pure water), which could be ascribed to the amphiphilic character of the methanol molecule. Regarding the C1s XPS lines, the vapor/liquid peak ratios allow for a quantitative determination of the methanol volume concentrations in both the vapor as well as in the liquid phase, that are corroborated by an analogue analysis of the valence band (VB) spectra. A detailed quantitative analysis of the water/methanol liquid VB XPS spectrum accounting for the photon energy dependence of photoemission cross sections confirms the atomic/orbital characteristics of the methanol molecular orbitals involved in the transitions and their pertinent intensities. From the decomposition of the liquid VB spectrum of the water/methanol mixture together with finite XPS probing depth we derive a methanol volume fraction of 43% for the outer liquid layers as compared to the nominal bulk liquid value of 37.5%. Finally, from the different binding energy (BE) shifts of the water/methanol liquid VB spectrum with respect to that of pure methanol, we develop a CH<sub>3</sub>OH-

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(H<sub>2</sub>O)<sub>3</sub> cluster-based model that relates these different BE shifts to the different MO hybridizations within that cluster.

[1] B. Winter, M. Faubel, Chem. Rev. 106 (2006) 1176.

[2] V. Pérez-Dieste, L. Aballe, S. Ferrer, J. Nicolàs, C. Escudero, A. Milán, E. Pellegrin, J. Phys. Conf. Ser. 425 (2013) 072023.

4:40pm **CA+NS+SS+VT-WeA8 Survey of Ionic Liquid Interfaces under Vacuum and Ambient Conditions: An XPS Perspective**, *Yehia Khalifa*, Ohio State University; *A. Broderick, J.T. Newberg*, University of Delaware; *Y. Zhang, E. Maginn*, University of Notre Dame

Properties and behavior of Ionic Liquid interfaces tend to behave differently from their bulk counterparts. In this study the preferential enhancement of the lower molar concentration anion [TFSI] in a mixture of [C2MIM][OAc] and [C2MIM][TFSI] is shown in the top 17 Å via angle-resolved X-ray photoemission spectroscopy under ultra high vacuum conditions. This is supported by molecular simulations where a quantitative relationship is also established between the two techniques. This interfacial enhancement is not only unique to mixtures but is also displayed in a pure ionic liquid with a hydrophilic anion such as [HMIM][Cl] studied via ambient pressure X-ray photoemission spectroscopy. The surface of [HMIM][Cl] under vacuum and increasing pressures of water vapor was evaluated (maximum of 5 Torr, 27% relative humidity). Our quantitative results indicate a significantly larger mole fraction of water at the interface compared to the bulk with increasing pressures when compared to previously published tandem differential mobility analysis results on [HMIM][Cl] nanodroplets. Furthermore the reverse isotherms has shown that the water uptake on the interface is a reversible process. These results highlight the unique behavior of ionic liquid interfaces that can be exploited for smart materials design and application.

5:00pm **CA+NS+SS+VT-WeA9 Ambient Pressure XPS Study of Gallium-Indium Eutectic (EGaln) Surface under Oxygen and Water Vapor**, *Meng Jia, J.T. Newberg*, University of Delaware

Liquid metals (LMs) have a combination of high thermal/electrical conductivity and excellent deformability. The application of LMs in the field of electronics has identified many opportunities for their use as stretchable electronics, self-healing conductors and interconnects. Gallium-Indium eutectic (EGaln) is one of the leading alternatives to toxic liquid mercury because of its low vapor pressure, low viscosity, low toxicity and high conductivity. A surface oxide layer is known to form when EGaln is exposed to ambient conditions. However, surface sensitive measurements of this chemistry occurring under ambient conditions are strongly lacking. Herein we present results from the interaction of oxygen and water vapor with the liquid-gas interface of an EGaln droplet deposited on an W foil using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). EGaln was examined up to a maximum of 1 Torr pressure at 550 K. Results reveal that under ambient conditions both oxygen and water vapor form a Ga(3+) oxide (Ga<sub>2</sub>O<sub>3</sub>) as an outer layer, while a thin layer of Ga(1+) oxide (Ga<sub>2</sub>O) resides between metallic EGaln and the outer Ga(3+) oxide. Both gases were unreactive towards Indium under our experimental conditions. The oxidation kinetics in the presence of water vapor were much faster compared oxygen. Proposed reaction mechanisms will be discussed.

5:20pm **CA+NS+SS+VT-WeA10 Laboratory-based Hard X-ray Photoelectron System for the study of Interfaces**, *S. Eriksson*, Scienta Omicron; *Henrik Bergersen*, Scienta Omicron, Sweden

Hard X-ray photoelectron spectroscopy (HAXPES) has traditionally found its application in the core topics of condensed matter physics, but the slowly growing number of beamlines worldwide has widened its appeal to other interest groups. HAXPES uses X-rays in the 2-10 keV range to excite photoelectrons, which are used to non-destructively study the chemical environment and electronic structure of materials.

In contrast to the very surface-sensitive XPS, HAXPES is much more bulk sensitive. This makes it applicable to bulk materials and structured samples, e.g. layered samples and heterostructures. In addition, its bulk sensitivity means that realistic samples can be investigated without the need of prior surface preparation. However, the number of existing HAXPES systems is very small and they are predominantly located at synchrotrons (approx. 20 beamlines worldwide) due to low photoionization cross sections necessitating high X-ray intensities, limiting their availability to users and applications.

This work presents a new laboratory-based instrument capable of delivering monochromated hard X-rays with an energy of 9.25 keV and a focused 30x45 μm<sup>2</sup> X-ray spot, giving excellent energy resolution of <0.5 eV. Systematic reference measurements are presented outlining the

systems capability as well as the latest results from various application fields including energy related materials such as batteries.

Ultimately, this spectrometer presents an alternative to synchrotron-based endstations and will help to expand the number and range of HAXPES experiments performed in the future. HAXPES is a cutting edge characterisation method and the advancement of this technique will tremendously increase the potential to study an ever increasing range of inorganic materials and beyond.

## Electronic Materials and Photonics Division Room A214 - Session EM+2D+NS+TF-WeA

### THEME Session: Electronics and Photonics for a Low-Carbon Future

**Moderators:** Michael A. Filler, Georgia Institute of Technology, Stephen McDonnell, University of Virginia

2:20pm **EM+2D+NS+TF-WeA1 Uncovering the Materials Paradigm for Solar Absorbers through In situ Imaging and Characterization**, *Mariana Bertoni*, Arizona State University **INVITED**

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

We will show that the high penetration of hard X-rays combined with the high sensitivity to elemental distribution, structure, and spatial resolution offers a unique avenue for highly correlative studies at the nanoscale. We will present results on CdTe and Cu(In,Ga)Se<sub>2</sub> where carrier collection is directly correlated to the compositional and structural properties of the material under a large variety of synthesis and operating conditions. The segregation of copper at the grain boundaries of both solar absorbers will be discussed in detail as well as the defects impact to carrier collection efficiency. Furthermore, the kinetics of copper segregation during growth and processing will be presented.

3:00pm **EM+2D+NS+TF-WeA3 Atomic Layer Deposition's Potential in Sustainability**, *Karen Buechler*, ALD NanoSolutions **INVITED**

Atomic layer deposition (ALD) is an exciting thin film deposition technique which holds the promise to permit enormous material innovations. These material innovations are currently enabling advanced catalysts, high capacity energy storage, advanced manufacturing technologies and many other products. Many of these products work towards reducing energy needs. This talk will highlight several examples of advanced material development through ALD which lead to advanced products which in turn are reducing the carbon footprint of consumers and manufacturers.

4:20pm **EM+2D+NS+TF-WeA7 Challenges in Materials and Processing to Implementation of Energy Efficient SiC Technology**, *Mei-Chien Lu*, Monte Rosa Technology

Energy and sustainability have been the main driving forces for the implementation of silicon carbide technology for efficient energy conversion in recent applications in electrical vehicles, hybrid electrical vehicles, data center power management, and photovoltaic and wind power. The decades-long research and development efforts are attributed to the complexity of polytypes of crystal structures of silicon carbide. Reducing these inherent defects from crystal growth and epitaxial layer growth are crucial and continuing tasks. Device architectures are found to be more efficient along selected crystal planes. Innovative processing technologies have to be developed to make these devices built by compound semiconductors with strong covalent bonding manufacturable. Fundamental challenges in materials, devices, and processing technologies will first be briefed. A patent landscape analysis is then conducted herein to reveal the past trends to pave the paths for future research and development. Implementations of silicon carbide devices are in its infancy with some full SiC inverter adopted by a commercial electrical vehicle manufacturer. Market shares and momentum of silicon carbide power electronics as well as the expectations from perspectives of department of energy and industry major players will be discussed. The continuous efforts

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to address the challenges in materials and processing are encouraged to support the full scale implementation of energy efficient silicon carbide technology.

**4:40pm EM+2D+NS+TF-WeA8 High Efficiency of Hot Electron Transfer at a Metal-Insulator-Semiconductor to Electrolyte Interface, Hyun Uk Chae, R. Ahsan, Q. Lin, R. Kapadia, University of Southern California**

Hot electrons generated from metal has drawn considerable interest in recent years due to the potential for lowering the high-barrier chemical reactions. The majority of hot electron controlling strategy at present have been plasmonic devices using localized surface plasmon resonance (LSPR). Several works have been done using plasmons to induce the hot electron generation to use as catalysts for chemical reactions like hydrogen evolution reaction (HER). However, the efficiency of those devices is extremely low and the mechanism behind it is quite complicated and remain unclear until now. To take advantage of hot electrons efficiently, properly and simply designed devices are required. Here, we demonstrate the different mechanisms of hot electron transfer in a thin gold film in an Au-Al<sub>2</sub>O<sub>3</sub>-Si metal-insulator-semiconductor (MIS) junction by modulating Au film thickness, the applied voltage between Au-Si junction. Hot electron injection contributes to modifying the electron distribution inside the Au electrode, which enables HER to be driven more at same overpotential in solution. This work present that the injection of non-equilibrium electrons can shift the onset voltage of HER by ~0.6 V on the gold film in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The efficiency of hot electron density efficiency shows ~85% at 2V of MIS junction bias and solution bias of -1.5 V vs Ag/AgCl is also presented. In addition to experimental results, we carried out the 2-D Monte Carlo simulation to track the injected hot electrons to study for the detail behaviors of thermalization mechanism inside the Au region which indicates the rate of HER. Since electrons quickly lose their energy within femtosecond by electron-electron or electron-phonon scattering, it is significant to see how they behave inside the injected medium to understand the reactions more precisely. The high-efficiency of hot electron usage reported here can be an opening towards the creation of practical hot-electron devices, which could be widely applied to the various fields.

**5:00pm EM+2D+NS+TF-WeA9 Integrated Photocathodes for Solar Driven Conversion of Carbon Dioxide to value-added Products, J.W. Ager, Lawrence Berkeley Lab, University of California, Berkeley; Guru Gurudayal, PPG**

INVITED

If renewable power sources such as solar and wind could be used to produce chemical precursors and/or fuels, it would provide an alternative to mankind's unsustainable use of fossil fuels and slow the rate of CO<sub>2</sub> emission into the atmosphere [1,2]. Solar to chemical energy conversion by photoelectrochemical processes is a promising approach to address this challenge. Analogous to photovoltaics [3], driving the uphill redox reactions required for net solar to chemical energy conversion necessitates directional charge transport [4]. Additionally, in order to convert carbon dioxide to hydrocarbons, one must manage multi-electron transfer reactions (e.g. 12 in the case of ethylene and ethanol), and minimize potential losses in all parts of the system [5].

Charge selective contacts can be used to steer direct photo-generated carriers to catalytic sites that perform CO<sub>2</sub> reduction in an integrated photocathode. In contrast to conventional photocathode designs which employ p-type absorbers, we used a back illumination geometry with an n-type Si absorber to permit the use of absorbing metallic catalysts which would otherwise block the light. Back and front interfaces were configured by ion implantation and by surface passivation to achieve carrier selectivity. Surface texturing of the Si was used to optimize light absorption on the illuminated side and increase the surface area available for catalysis on the electrolyte side. Selectivity to C-C coupled products was achieved by using hierarchical Au-Ag-Cu nanostructures as electrocatalysts [6].

The photovoltage, 550- 600 mV under simulated 1-sun illumination, confirms the carrier selectivity and passivation of the front and back interfaces. Compared to planar controls, textured photocathodes generate higher current densities, exceeding 30 mA cm<sup>-2</sup>. Under simulated diurnal illumination conditions, over 60% faradaic efficiency to C<sub>2+</sub> hydrocarbon and oxygenate products (mainly ethylene, ethanol, propanol) is maintained for several days. By coupling photocathodes to series-connected semi-transparent halide perovskite solar cells, we demonstrated stand-alone, CO<sub>2</sub> reduction with a 1.5% conversion efficiency to hydrocarbons and oxygenates [7].

1. Graves, C.; Ebbesen, S. D.; Mogensen, M.; Lackner, K. S. *Renew. Sustain. Energy Rev.* **2011**, *15*, 1–23.

2. Chu, S.; Cui, Y.; Liu, N. *Nat. Mater.* **2016**, *16*, 16–22.

3. Wurfel, U.; Cuevas, A.; Wurfel, P. *IEEE J. Photovoltaics* **2015**, *5*, 461–469.

4. Osterloh, F. E. *ACS Energy Lett.* **2017**, *2*, 445–453.

5. Gurudayal et al. *Energy Environ. Sci.* **2017**, *10*, 2222–2230.

6. Lum, Y.; Ager, J. W. *Energy Environ. Sci.* **2018**, *11*, 2935–2944.

7. Gurudayal et al. *Energy Environ. Sci.* **2019**, *12*, 1068–1077.

**5:40pm EM+2D+NS+TF-WeA11 Modeling of Optical Scattering in White Beetle Scales, Seung Ho Lee, S.M. Han, S.E. Han, University of New Mexico**

Keywords: Light Scattering; Diffusion Approximation

Abstract: Extremely thin “super-white” coatings that reject solar spectrum but radiate through the transparent atmospheric window in mid-infrared have broad implications in heat management and energy savings for diverse sectors, including building construction, ship manufacturing, and space vehicle operation. In our previous work, we were able to create paint-format “super-white” coatings from microsphere-based materials.<sup>1,2</sup> In this work, however, we borrow our inspiration from white beetles in nature that reveal structural ingenuity at the nanometer scale to achieve such white film. White beetle scales display exceptionally strong light scattering power from a thin anisotropic random biopolymer network. While previous studies have revealed that the anisotropy plays an important role in strong light scattering, the physics of anisotropic light propagation remains less than fully understood. In particular, the studies have shown that light scattering in anisotropic random media may deviate significantly from the anisotropic diffusion approximation. This uncertainty in diffusion approximation led to a study interrogating the scale structures by fully solving Maxwell's equations. These calculations yet left questions on their accuracy, as the structural dimensions in perpendicular direction to the incident light were significantly greater than optical wavelengths. In this work, we systematically reduce the structural size in our simulations, using Fourier analysis of the white beetle scale structures. The size reduction enables fast, accurate calculations of light scattering in the biological structures. From these simulations, we find that the diffusion approximation is valid in describing light propagation in the white beetle scales. Further, we derive a light diffusion equation for anisotropic media from the radiative transfer equation and show that the equation for anisotropic diffusion derived in the past studies is inaccurate. We discuss how our newly derived equation can be used for accurate numerical calculations of light scattering and characterizing anisotropic light diffusion.

<sup>1</sup> S. Atiganyanun, J. Plumley, S. J. Han, K. Hsu, J. Cytrynbaum, T. L. Peng, S. M. Han, and S. E. Han, "Effective Radiative Cooling by Paint-Format Microsphere-Based Photonic Random Media," *ACS Photon.* **5**, 1181-1187 (2018).

<sup>2</sup> J. D. Alden, S. Atiganyanun, R. Vanderburg, S. H. Lee, J. B. Plumley, O. K. Abudayyeh, S. M. Han, and S. E. Han, "Radiative Cooling by Silicone-Based Coating with Randomly Distributed Microbubble Inclusions," *J. Photon. Energy* **9**, 032705-1:10 (2019).

## Nanometer-scale Science and Technology Division

### Room A222 - Session NS+2D+AS-WeA

#### Probing and Modifying Surface and Interfacial Chemistry at the Nanoscale

**Moderators:** Phillip First, Georgia Institute of Technology, Adina Luican-Mayer, University of Ottawa, Canada

**2:20pm NS+2D+AS-WeA1 Bitumen's Microstructures are Correlated with its Bulk Thermal and Rheological Properties, x. Yu, Worcester Polytechnic Institute; S. Granados-Focil, Clark University; M. Tao, Nancy Burnham, Worcester Polytechnic Institute**

Understanding of how the chemistry of asphalt binders (i.e., bitumens) affects their bulk properties is critical for development of structure-related mechanical models and performance-based specifications for asphalt binders, including mitigation of potholes and improved recycling of this non-renewable material. However, establishing the chemical-mechanical relationships that govern asphalt binders' properties remains a challenge due to binders' complex chemical makeup [1] and the intriguing dynamic molecular interactions among binders' various chemical constituents. [2] Here, we investigate the effect of chemical composition on binders' microstructure and thermal and rheological behavior. Two virgin binders from different crude oil origins were chosen and a series of derivative binders was made by remixing different weight ratios of the asphaltenes

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and the maltenes obtained from the two source binders. Thermal and rheological properties of all binders were measured using modulated differential scanning calorimetry and dynamic shear rheometry, respectively. Binders' microscopic characteristics (e.g., nano- and micro-structures and their contrast in phase images) were evaluated using atomic force microscopy. In bitumens with more miscibility between the asphaltenes and maltenes, the samples appear to undergo a sol-gel transition as the asphaltene concentration increases above 25%. In less miscible bitumens, micro-scale phase segregation is readily apparent at the surface. Our results show that bitumens' characteristic microstructures, as a result of the complex molecular interactions among their various chemical components, are correlated with their bulk thermal and mechanical properties. Notably, the asphaltene/maltene ratio alone cannot predict a bitumen's bulk properties. Instead, a bitumen's distinctive microstructures and its colloidal miscibility index provide meaningful insights into the effect of chemical composition on glass transition, phase stability, and rheological properties of the bitumen, which may in turn help improve the sustainability and design of roads. [3]

1. X. Yu et al., *Adv. Colloid Interface Sci.* 218, 17-33 (2015).
2. X. Yu et al., *Energy & Fuels* 32, 67-80 (2018).
3. X. Yu et al., submitted

**2:40pm NS+2D+AS-WeA2 Energetics and Statistical Mechanical Analysis of Complexation on Metal Surfaces**, J. Lee, J.W. Evans, T.L. Windus, P.A. Thiel, Da-Jiang Liu, Ames Laboratory and Iowa State University

Stabilities of metal-ligand complexes on surfaces are crucial for the process of self assembly of 2D structures. We provide a comprehensive theoretical assessment at the level of Density Functional Theory (DFT) of the stability of various coinage metal-sulfur complexes,  $M_mS_n$ , with  $M=Cu, Ag, \text{ and } Au$ , both in the gas-phase and also for these complexes adsorbed on the (111) and (100) surfaces of the same coinage metal. An early influential theoretical study on  $S/Cu(111)$  proposed that the  $Cu_3S_3$  complex being the most stable copper containing species. Later combined low temperature STM and DFT studies suggest that a heart-shaped  $Cu_2S_3$  and its concatenations being more stable. Larger and even more complex  $Ag-S$  complexes have been observed for  $S/Ag(111)$ . No complexation have been observed for  $S/Cu(100)$  and  $S/Ag(100)$ . On the other hand, a  $Au_4S_5$  complex and its fragmentations have been observed for  $S/Au(100)$ , but no complexation is observed for  $S/Au(111)$  at low S coverage. We select a set of nine types of complexes, chosen for their proposed existences, intrinsic stabilities, and affinities for adsorption on metal surfaces. For the adsorbed species, we calculate various aspects of their energetics including their formation energy from sulfur adsorbed on terraces and from metal atoms that are in thermal equilibrium with the substrate. From this perspective, our DFT analysis shows that  $Ag_2S_3$ ,  $Ag_3S_3$  and many larger complexes on  $Ag(111)$  are strongly stable,  $Cu_2S_3$  is stable and some larger complexes are marginally stable on  $Cu(111)$ , but only  $Au_4S_4$  on  $Au(111)$  is stable. In contrast, no complex is stable on  $Cu(100)$  and  $Ag(100)$ , but a group of complex is stable on  $Au(100)$ , with  $Au_4S_5$ . DFT results are consistent with experiments with the apparent exception of  $Au(111)$ . This comprehensive assessment of energetics provides key input for statistical mechanical analysis of S adlayer ordering in the absence of complexation, and of the kinetics of complex formation and associated enhanced mass transport and surface dynamics.

**3:00pm NS+2D+AS-WeA3 Adding the Chemical Dimension to Lithography at All Scales: Enabling Cellular Therapies & Other Adventures in Biology and Medicine**, Paul S. Weiss<sup>1</sup>, University of California, Los Angeles **INVITED**

By controlling the exposed chemical functionality of materials from the submolecular through the centimeter scales, we have enabled new capabilities in biology, medicine, and other areas. I will discuss current and upcoming advances and will pose the challenges that lie ahead in creating, developing, and applying new tools using these capabilities. These advances include using biomolecular recognition in sensor arrays to probe dynamic chemistry in the brain and microbiome systems. In other areas, we introduce biomolecular payloads into cells for gene editing at high throughput for off-the-shelf solutions targeting hemoglobinopathies, immune diseases, and cancers. These methods use specific chemical functionalization and control of surface contact and adhesion in microfluidic channels.

**4:20pm NS+2D+AS-WeA7 STM Directed Synthesis of Armchair Graphene Nanoribbons and Their Oxidation**, C. Ma, Oak Ridge National Laboratory; Z. Xiao, North Carolina State University; A.A. Puzos, Arthur Baddorf, Oak Ridge National Laboratory; W. Lu, North Carolina State University; K. Hong, Oak Ridge National Laboratory; J. Bernholc, North Carolina State University; A.-P. Li, Oak Ridge National Laboratory

Highly controlled synthesis of graphene nanoribbons (GNRs) can be performed on a surface by polymerization of a selected precursor. Typically, this polymerization involves surface-assisted cyclodehydrogenations during thermal activation on catalytic metal surfaces. We have shown that armchair edge GNRs can be synthesized with 7, 14, and 21 carbon atom widths by absorbing 10,10'-dibromo-9,9'-bianthryl (DBBA) precursor molecules on  $Au(111)$ .<sup>1</sup> Synthesis follows a two-step process of which the first step is polymerization at 470 K. The second step, cyclodehydrogenation, can be promoted globally by annealing to 670 K, or locally following hole injection using a scanning tunneling microscope (STM) tip.<sup>2</sup> Wider 14 or 21-aGNRs were formed when two or three 7-wide GNRs were conjugated side-by-side via inter-ribbon cyclodehydrogenation at the edge sites. Scanning Tunneling Spectroscopy (STS) reveals an electronic band gap dependent on the ribbon width. Bandgaps of  $\sim 2.6$ ,  $\sim 0.3$ , and  $\sim 0.7$  eV are measured for 7, 14, and 21 GNRs respectively, consistent with expectations of simple models.

For practical applications, understanding the stability of GNRs to oxidation is important. We have examined the thermal stability of 7-aGNRs after exposure to air.<sup>2</sup> Combining STM, Raman spectroscopy, x-ray photoemission spectroscopy, and first-principles theory calculations, the armchair GNRs are found to oxidize first at the zigzag ends while the edges remain stable. Oxygen attaches to the zigzag ends at temperatures as low as 180°C. Armchair edges are stable up to 430°C and become oxidized only above 520°C. Two oxygen species are identified, one a hydroxyl (OH) and the second atomic oxygen bridging two carbons, both of which are common in oxidized graphitic lattices. The bandgap is significantly reduced from 2.6 eV to 2.3 eV in the vicinity of the hydroxyl and to 1.9 eV near bridging O. These results suggest that the oxidation will significantly affect the transport properties of GNRs and provide parameters useful for maintaining integrity of GNRs during processing for devices.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

1. C. Ma, et al., *Nano Letters* 17, 6241 (2017).
2. C. Ma, et al., *Nature Communications* 8, 14815 (2017).
3. C. Ma, et al., *Physical Review Materials* 2, 014006 (2018).

**4:40pm NS+2D+AS-WeA8 Carbon-based Two-dimensional Materials from Surface-catalyzed Reactions of Small Molecules**, M. Wolf, C.R. Gerber, Rebecca Quardokus, University of Connecticut

Aryl halides undergo an Ullmann-like coupling reaction on surfaces to yield a carbon-based two-dimensional material. 1,2-dibromobenzene couples to  $Au(111)$  lifting the gold herringbone reconstruction. The reaction intermediates and coupled gold atoms are mobile on the surface at 4 K. The FCC and HCP sections of the underlying gold substrate shift to new positions. Annealing the dibromobenzene on  $Au(111)$  decouples the intermediates from the gold. The gold herringbone reconstruction returns and a covalently-bonded carbon-based network forms on the  $Au(111)$  surface.

**5:00pm NS+2D+AS-WeA9 Bottom-up Fabrication of 2D Molecular Networks via On-surface Reactions**, Sabine Maier, University of Erlangen-Nürnberg, Germany **INVITED**

On-surface synthesis has attracted significant attention in recent years due to its potential to fabricate novel low-dimensional nanomaterials with atomic precision. In order to understand and control the synthesis of high-quality low-dimensional nanostructures, many efforts have been made to steer the reaction pathway by the design of smart precursors and by applying templating effects from the substrate. One of the challenges is the fabrication of long-range ordered two-dimensional covalently-linked networks via on-surface reactions. In contrast to molecular self-assemblies that are constructed by non-covalent bonds, the irreversible nature of the covalent bonds limits the structural control, which results in small domains and defects.

In my presentation, I will focus on recent high-resolution scanning probe microscopy experiments in combination with density-functional theory about the bottom-up fabrication and electronic properties of atomically precise one- and two-dimensional molecular nanostructures on metals.[1-4] Thereby, the effect of the flexibility, the symmetry, and chirality of the

<sup>1</sup> NSTD Recognition Award

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precursor molecules on the structure formation of covalently-linked molecular structures will be discussed. In particular, I will outline how well-ordered nanoporous 1D and 2D covalent molecular structures can be fabricated by use of debromination coupling reactions. We demonstrate the narrowing of the electronic band gap by increasing the  $\pi$ -system in covalently-linked structures and also show delocalized electronic states in surface-supported organometallic networks. Finally, I will conclude with a comparison of the structure formation of molecular nanostructures on bulk insulators and metal surfaces.

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5:40pm **NS+2D+AS-WeA11 Determining the Jahn-Teller Stabilization Energy of Surface Vacancies on Si(111)- $\sqrt{3} \times \sqrt{3}$ :B**, *Daejin Eom*, Korea Research Institute of Standards and Science, Republic of Korea; *C.-Y. Moon*, Korea Research Institute of Standards and Science; *J.-Y. Koo*, Korea Research Institute of Standards and Science, Republic of Korea

The vacancy defect on the Si surface becomes increasingly important with the device scaling because it works as the charge trapping and scattering center with varying ionization states. Yet its characteristics have not been addressed as comprehensively as the bulk vacancy in Si. In fact, its behavior would be affected by the gap state evolution and the Fermi level pinning on the Si surface. On the other hand, the (111)-surfaces of Si come to have the  $\sqrt{3} \times \sqrt{3}$  reconstruction instead of the  $7 \times 7$  one when they are heavily B-doped [1,2]. This  $\sqrt{3} \times \sqrt{3}$  surface does not evolve any energy state within the band gap, being contrary to the  $7 \times 7$  one [2]. Also, the Fermi level is shifted to the valence band maximum on the  $\sqrt{3} \times \sqrt{3}$  surface whereas it is pinned in the middle of the gap on the  $7 \times 7$  surface [2]. Hence the vacancy defects on the two surfaces may have dissimilar characteristics from each other. Here, we generate the vacancy defects on the  $\sqrt{3} \times \sqrt{3}$  surface via the atom manipulation technique and measure their structural and electronic properties by using the scanning tunneling microscopy and spectroscopy. We find that, unlike the  $7 \times 7$  surface, the vacancy defects on the  $\sqrt{3} \times \sqrt{3}$  surface are Jahn-Teller distorted in the ground state, but undergo the symmetry-restoring transition when gated by the external bias. We also determine the energy gain or stabilization energy of the Jahn-Teller transition quantitatively. These findings would extend our knowledge on the surface vacancies on Si and eventually contribute to the fabrication of better-performing nanometer-scale devices.

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6:00pm **NS+2D+AS-WeA12 Influence of the Substrate on Self-Assembly: Terphenyl Monolayers investigated by NC-AFM and FM-KPFM**, *Niklas Biere*<sup>1</sup>, Experimental Biophysics & Applied Nanoscience, University of Bielefeld, Germany; *S. Koch, P. Stohmann, Y. Yang, A. Götzhäuser*, Physics of Supramolecular Systems and Surfaces, University of Bielefeld, Germany; *D. Anselmetti*, Experimental Biophysics & Applied Nanoscience, University of Bielefeld, Germany

Carbon Nano Membranes (CNM) are mechanical stable and homogeneous quasi-2D systems, which are formed by electron radiation induced, cross-linked self-assembled monolayers (SAM). Contrary to graphene, the CNM structural and functional properties can be tailored by the selection of precursors for the SAM formation [1]. CNMs show the capability to act as a molecular sieve to filter e.g. water molecules from impurities with extraordinary efficiency [2]. While this result promises remarkable applications, the actual process of CNM formation as well as their structure and the mechanism for water permeation is still in the focus of our investigations. Furthermore, the choice of substrate influences the self-assembly of our precursor molecules more than previously expected, even with isoelectronic surfaces like gold and silver. In this work, we will present data acquired by noncontact-AFM combined with FM-KPFM under ultra-high vacuum conditions to investigate and compare the morphology of in-situ prepared SAMs and CNMs of terphenylthiols on Au(111) and Ag(111).

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## 2D Materials

### Room A216 - Session 2D+EM+MI+NS+QS+SS-ThM

#### Dopants, Defects, and Interfaces in 2D Materials

Moderator: Evan Reed, Stanford University

8:00am **2D+EM+MI+NS+QS+SS-ThM1 Interfacial Engineering of Chemically Reactive Two-Dimensional Materials, Mark Hersam, Northwestern University** **INVITED**

Following the success of ambient-stable two-dimensional (2D) materials such as graphene and hexagonal boron nitride, new classes of chemically reactive layered solids are being explored since their unique properties hold promise for improved device performance [1]. For example, chemically reactive 2D semiconductors (e.g., black phosphorus (BP) and indium selenide (InSe)) have shown enhanced field-effect mobilities under controlled conditions that minimize ambient degradation [2]. In addition, 2D boron (i.e., borophene) is an anisotropic metal with a diverse range of theoretically predicted phenomena including confined plasmons, charge density waves, and superconductivity [3], although its high chemical reactivity has limited experimental studies to inert ultrahigh vacuum conditions [4-7]. Therefore, to fully study and exploit the vast majority of 2D materials, methods for mitigating or exploiting their relatively high chemical reactivity are required [8]. In particular, covalent organic functionalization of BP minimizes ambient degradation, provides charge transfer doping, and enhances field-effect mobility [9]. In contrast, noncovalent organic functionalization of borophene leads to the spontaneous formation of electronically abrupt lateral organic-borophene heterostructures [10]. By combining organic and inorganic encapsulation strategies, even highly chemically reactive 2D materials (e.g., InSe) can be studied and utilized in ambient conditions [11].

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8:40am **2D+EM+MI+NS+QS+SS-ThM3 Effects of Mn Doping on the Surface Electronic Band Structure and Bulk Magnetic Properties of ZnS and CdS Quantum Dot Thin Films, Thilini K. Ekanayaka<sup>1</sup>, G. Gurung, University of Nebraska-Lincoln; G. Rimal, Rutgers University; S. Horoz, Siirt University, Turkey; J. Tang, T. Chien, University of Wyoming; T. Paudel, A.J. Yost, University of Nebraska-Lincoln**

Semiconducting quantum dots (QDs) are desirable for solar cells due to the ability to tune the band gap by changing the QD size without changing the underlying material or synthesis technique. Doping QDs with a transition metal is one way of further tailoring the electronic band structure and magnetic properties of QDs in order to improve overall device performance. Understanding the mechanisms causing the change in the electronic band structure and magnetic properties due to transition metal doping is important to device-by-design schemes. In this study, we measure the effects of Mn dopants on the surface electronic band structure of ZnS and CdS QDs using scanning tunneling microscopy/spectroscopy and photoemission spectroscopy. In both the ZnS and CdS systems, a decrease in band gap upon introduction of Mn is observed. Additionally, a rigid band shift was observed in ZnS upon Mn doping. It is argued, using X-ray photoemission spectroscopy, that the rigid band shift is due to a hole-doping mechanism caused by the formation of Zn vacancies accompanied by a Mn<sup>3+</sup> oxidation state which leads to the reduction in total S vacancies as compared to the undoped ZnS system. No band shift was observed in CdS upon Mn doping, but a strong sp-d hybridization takes place which results in a significant band gap reduction. Furthermore, induced midgap states originating from the Mn dopant appear in the surface electronic band structure of Mn: CdS. Measurements of the magnetization of Mn doped and undoped ZnS and CdS confirms the

presence of d<sup>0</sup> ferromagnetism. The magnetization is reduced and the coercive field is increased post Mn doping which suggests the anti-ferromagnetic alignment of Mn dopant atoms. Density Functional Theory calculations support the Mn anti-ferromagnetic alignment hypothesis and a ground state with Mn in the 3<sup>+</sup> valence. This study provides important information on the role of dopants and vacancies in dilute magnetic semiconductor quantum dot materials for applications in photovoltaics and spintronics.

9:00am **2D+EM+MI+NS+QS+SS-ThM4 Interaction of Molecular O<sub>2</sub> with Organolead Halide Nanorods by Single-Particle Fluorescence Microscopy, Juvinch Vicente, J. Chen, Ohio University**

The photoluminescence (PL) of organolead halide perovskites (OHPs) is sensitive to its surface conditions, especially surface defect states, making the PL of small OHP crystals an effective way to report their surface states. At the ensemble level, when averaging a lot of nanocrystals, the photoexcitation of OHP nanorods under inert nitrogen (N<sub>2</sub>) atmosphere leads to PL decline, while subsequent exposure to oxygen (O<sub>2</sub>) results to reversible PL recovery. At the single-particle level, individual OHP nanorods photoblinks, whose probability is dependent on both the excitation intensity and the O<sub>2</sub> concentration. Combining the two sets of information, we are able to quantitatively evaluate the interaction between a single surface defect and a single O<sub>2</sub> molecule using a kinetic model. This model provides fundamental insights that could help reconcile the contradicting views on the interactions of molecular O<sub>2</sub> with OHP materials and help design a suitable OHP interface for a variety of applications in photovoltaics and optoelectronics.

9:20am **2D+EM+MI+NS+QS+SS-ThM5 Complementary Growth of 2D Transition Metal Dichalcogenide Semiconductors on Metal Oxide Interfaces, T.E. Wickramasinghe, Gregory Jensen, R. Thorat, Nanoscale and Quantum Phenomena Institute; S.H. Aleithan, Nanoscale and Quantum Phenomena Institute, Saudi Arabia; S. Khadka, E. Stinaff, Nanoscale and Quantum Phenomena Institute**

A chemical vapor deposition (CVD) growth model will be presented for a technique resulting in naturally formed 2D transition metal dichalcogenide (TMD) based metal-oxide-semiconductor structures. The process is based on a standard CVD reaction involving a chalcogen and transition metal oxide-based precursor. Here however, a thin metal oxide layer, formed on lithographically defined regions of a pure bulk transition metal, serves as the precursor. X-ray diffraction and cross-sectional SEM studies show insight into the type and thickness of the metal oxide created during optimal growth conditions. The chalcogen reacts with the metal oxide, forming TMD material which migrates outward along the substrate, leading to lateral growth of highly-crystalline, mono-to-few layer, films. In addition to displaying strong luminescence, monolayer Raman signatures, and relatively large crystal domains, the material grows deterministically and selectively over large regions and remains connected to the bulk metallic patterns, offering a scalable path for producing as-grown two-dimensional materials-based devices.

9:40am **2D+EM+MI+NS+QS+SS-ThM6 Kagome-type Lattice Instability and Insulator-metal Transition in an Alkali-doped Mott Insulator on Si(111), Tyler Smith, H. Weitering, University of Tennessee Knoxville**

The 1/3 ML monolayer (ML) 'alpha phase' of Sn on Si(111) is a remarkable platform for the study of strong correlations in a spin 1/2 triangular adatom lattice. In this work, we employ an adatom doping scheme by depositing potassium onto the triangular Sn lattice. The K-atoms destabilize the parent Mott insulating phase and produce a charge-ordered insulator, revealing a rare Kagome lattice at the surface. Scanning Tunneling Microscopy and Spectroscopy reveal a phase transition from an insulating kagome lattice to a metallic triangular lattice at about 200 K. DFT band structure calculations for this kagome system [J. Ortega et al., unpublished] reveal the presence of a flat-band just below the Fermi level, making this novel system a compelling platform for hole-doping studies of magnetic and/or superconducting instabilities.

11:00am **2D+EM+MI+NS+QS+SS-ThM10 Chemical Migration and Dipole Formation at TMD/TI Interfaces, Brenton Noesges, T. Zhu, The Ohio State University; D. O'Hara, University of California, Riverside; R. Kawakami, L.J. Brillson, The Ohio State University**

Proximity effects at the interface between two materials can induce physical properties not present in either material alone. Topological insulators (TIs) such as Bi<sub>2</sub>Se<sub>3</sub> with non-trivial surface states are sensitive to interface proximity effects where overlayers and adsorbates can act as a dopant source, chemically interact with the TI surface, or couple across the

<sup>1</sup> National Student Award Finalist

Tl surface states leading to novel quantum phases. Transition metal dichalcogenides (TMDs), a class of 2D van der Waals materials, are a promising candidate to control this interface given the shared general hexagonal symmetry and wide range of TMD properties. However, the interface between TMDs and Bi<sub>2</sub>Se<sub>3</sub> can be more complex than the ideal van der Waals interface. Chemical species exchange like metal cation exchange and selenium migration from substrate to growing film can impact the structure and properties of either layer. Self-assembly mechanisms have also been observed where complete metal monolayers form inside the Bi<sub>2</sub>Se<sub>3</sub> quintuple layer [1]. We used x-ray photoelectron spectroscopy (XPS) connected in vacuo via UHV suitcase to a molecular beam epitaxy (MBE) system to investigate chemical interaction at the interface between selenide TMDs and Bi<sub>2</sub>Se<sub>3</sub>. Air-free transferring is crucial to minimize contamination at the interface and prevent oxidation in the air-sensitive TMDs. We compare the effects of ultrathin pure Mn metal overlayers and monolayer MnSe<sub>x</sub> on Bi<sub>2</sub>Se<sub>3</sub> to pristine Bi<sub>2</sub>Se<sub>3</sub>. In the case of pure Mn metal on Bi<sub>2</sub>Se<sub>3</sub>, Bi core levels exhibit a 1.7 eV shift toward lower binding energies while the Mn core levels also show signs of Mn-Se bonding. These core level changes indicate that, in the absence of excess Se during growth, Mn pulls Se from the substrate leaving behind Bi<sub>2</sub> bilayers near the surface. Depositing a monolayer of MnSe<sub>x</sub> produces very different results than the pure metal case. Bi<sub>2</sub>Se<sub>3</sub> core levels measured below the monolayer MnSe<sub>x</sub> film exhibit a rigid 0.8 eV chemical shift toward higher binding energies indicative of surface/interface dipole formation. The presence of this dipole is likely due to growth of primarily α-MnSe instead of the 1T-MnSe<sub>2</sub> 2D phase [2]. Scanning tunneling microscopy (STM) height maps and spectroscopy data provide further evidence of majority α-MnSe formation. XPS core level analysis combined with controlled depositions, air-free transfers and surface analysis can provide a consistent explanation of chemical diffusion and dipole formation at a TMD/Tl interface. This work is supported by NSF MRSEC under award number DMR-1420451.

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[2] D.J. O'Hara et al. *Nano Lett.*, 18(5), 3125-3131 (2018).

11:20am **2D+EM+MI+NS+QS+SS-ThM11 Atomically Resolved Electronic Properties of Defects in the in-plane Anisotropic Lattice of ReS<sub>2</sub>**, *Adina Luican-Mayer*, University of Ottawa, Canada

Among the layered transition metal dichalcogenides, the compounds that exhibit in-plane anisotropy are of particular interest as they offer an additional tuning knob for their novel properties. In this talk, we present experimental evidence of the lattice structure and properties of semiconducting ReS<sub>2</sub> by using scanning tunneling microscopy and spectroscopy (STM/STS). We demonstrate that rhenium atoms form diamond-shaped clusters, organized in disjointed chains and characterize the semiconducting electronic band gap by STS. When imaging the surface of ReS<sub>2</sub>, we encounter "bright" or "dark" regions indicating the presence of charged defects that will electrostatically interact with their environment. By spatially mapping the local density of states around these defects, we explore their origin and electrostatic nature. Experimental results are compared with ab-initio theory.

12:00pm **2D+EM+MI+NS+QS+SS-ThM13 Size-independent "Squeezed" Shape of Metal Clusters Embedded Beneath Layered Materials**, *A. Lii-Rosales*, Ames Laboratory and Iowa State University; *S. Julien, K.-T. Wan*, Northeastern University; *Y. Han*, Ames Laboratory and Iowa State University; *K.C. Lai*, Iowa State University; *M.C. Tringides, J.W. Evans, Patricia A. Thiel*, Ames Laboratory and Iowa State University

We have developed a continuum elasticity model for metals embedded beneath the surfaces of layered materials. The model predicts that the equilibrated cluster shape is invariant with size, manifest both by constant side slope and by constant aspect ratio (width:height ratio). This prediction is rationalized by dimensional analysis of the relevant energetic contributions. The model is consistent with experimental data for Cu and Fe clusters embedded in graphite, especially in the limit of large clusters. For comparison, we have performed a Winterbottom analysis of the equilibrium shape of an uncovered Cu cluster supported on top of graphite. The aspect ratio of the embedded cluster is about an order of magnitude higher than that of the supported cluster. Analysis of key energetics indicates that this is due to the strain energy (resistance to deformation) of the top graphene membrane, which effectively squeezes the metal cluster and forces it to adopt a relatively low, flattened shape. These insights may be useful for developing components such as metallic heat sinks or electrodes in electronic devices that use two-dimensional or layered materials.

**Chemical Analysis and Imaging Interfaces Focus Topic**

**Room A120-121 - Session CA+2D+AS+BI+NS-ThM**

**Chemical Analysis and Imaging of Liquid/Vapor/Solid Interfaces II**

**Moderators:** Utkur Mirsaidov, National University of Singapore, Xiao-Ying Yu, Pacific Northwest National Laboratory

8:00am **CA+2D+AS+BI+NS-ThM1 From Surfaces to Solid-Gas and Solid-liquid Interfaces: Ambient Pressure XPS and Beyond**, *Miquel B. Salmeron*, Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

The rapidly increasing field of surfaces under ambient conditions of temperature and pressure, in gas and liquid environments, reflects the importance of understanding surface properties in conditions closer to practical situations. A lot of progress has been made in the last two decades, enabled by the emergence of a number of new techniques, both spectroscopy and microscopy, that can deliver atomic scale information with the required surface/interface sensitivity. I will present recent advances with examples that illustrate the novel understanding derived from the use of new techniques. One in the gas-solid interface where two important barriers have been bridged: the pressure gap, and the temperature gap. These gaps are very important when dealing with weakly bound molecules, where only in the presence of gas at a suitable pressure, or at low temperatures, a non-negligible coverage of adsorbed molecules can be achieved. The temperature gap manifests also in the removal of kinetic barriers. By bridging these two gaps a host of new interface structures have been unveiled that bring new understanding to catalytic phenomena. This will be illustrated with the examples of Cu and CuCo alloys in the presence of CO. In the case of solid-liquid interfaces, the introduction of new methods using well established x-ray spectroscopies is opening the way to the study of the important electrical double layer structure as a function of applied bias, as I will illustrate with the application of X-Ray absorption and IR to sulfuric acid-Pt and Ammonium Sulfate-graphene interfaces.

8:40am **CA+2D+AS+BI+NS-ThM3 Probing Solid-liquid Interfaces with Tender X-rays**, *Zbynek Novotny, N. Comini, B. Tobler*, University of Zuerich, Switzerland; *D. Aegerter, E. Fabbri*, Paul Scherrer Institute, Switzerland; *U. Maier*, Ferrovac GmbH, Switzerland; *L. Artiglia, J. Raabe, T. Huthwelker*, Paul Scherrer Institute, Switzerland; *J. Osterwalder*, University of Zuerich, Switzerland

Many important chemical and biological processes occur at the interface between a solid and a liquid, which is difficult to access for chemical analysis. The large inelastic scattering cross section of electrons in the condensed matter makes X-ray photoelectron spectroscopy (XPS) highly surface sensitive but less sensitive to buried interfaces. This limitation can be overcome by stabilizing an ultrathin layer of liquid with a thickness in the order of a few tens of nanometres and by employing tender X-rays (photon energy ranging between 2-8 keV) that can be used to probe the buried solid-liquid interface. We have recently built and commissioned a new instrument at the Swiss Light Source that combines ambient-pressure XPS with in-situ electrochemistry. With this new setup, we can stabilize a thin liquid layer on a solid surface by a dip&pull method [1], and by using tender X-rays (2-8 keV) from the Phoenix beamline, we can probe the properties and chemistry at the solid-liquid and liquid-gas interface while having a potential control over the ultrathin electrolyte film. The capabilities of this new instrument were demonstrated during the first commissioning beamtime, where we stabilized a thin electrolyte layer (0.1 M KOH) over the Ir(001) electrode. The dip&pull technique was used for the first time using well-defined single-crystalline surfaces (see Supplementary document). Core-level binding energy shifts following the applied potential were observed for species located within the electrolyte film. This included the oxygen 1s level from liquid water, potassium, and, interestingly, also an adventitious carbon species, while the interface was carbon-free. We will present the results from the first commissioning beamtime and outline the future directions we are going to pursue using this new instrument.

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# Thursday Morning, October 24, 2019

9:00am **CA+2D+AS+BI+NS-ThM4 X-ray Photoelectron Spectroscopy Insight into X-ray Induced Radiolysis at Heterogeneous Liquid Electrolyte Interface**, *Christopher Arble*, National Institute of Standards and Technology (NIST); *H. Guo*, Southeast University, China; *E. Strelcov*, *B. Hoskins*, National Institute of Standards and Technology (NIST); *M. Amati*, *P. Zeller*, *L. Gregoratti*, Elettra-Sincrotrone Trieste, Italy; *A. Kolmakov*, National Institute of Standards and Technology (NIST)

Assessing chemical processes of electrolyte interfaces under operando conditions is an aspirational goal of great importance to many industrial applications<sup>1</sup> that remains technically challenging to investigate. XPS is a powerful characterization tool that can probe elemental and chemical information of atoms with nanoscale depth sensitivity but has traditionally been restricted to UHV conditions. There has been a concerted effort to enable quantitative in-situ measurements of gas and liquid interfaces under realistic environments.<sup>2-4</sup> Recently, advances in 2D materials, i.e., graphene, have been utilized to probe heterogeneous interfaces through molecularly impermeable, electron transparent membranes to maintain UHV pressure in the analysis chamber.<sup>5</sup>

Herein we apply photoemission spectromicroscopy to study the electrochemical dynamics of an array of several thousand individual electrolyte cells encapsulated with electron transparent bilayer graphene.<sup>6</sup> We monitored the chemical speciation at the electrode- aqueous CuSO<sub>4</sub> electrolyte interface as a function of potential. During the electrochemical experiments, the effects of irradiation upon the solution were observed to influence the system, and spectral deconvolution identified oxidized species of copper and oxygen as well as reduced states of sulfur that were connected to reaction pathways tied with radiolysis. Corresponding SEM images and subsequent EDS spectral maps display spatially confined irradiated byproducts which can be associated with the species observed in with XPS.

Observations of XPS spectroscopic regions in the system were taken at varied X-ray dosages to probe the impacts of radiolysis on the liquid solution concerning the spectroscopic observation of electrochemical deposition of Cu. This experimental methodology imparts a greater understanding of the influence of X-ray induced water radiolysis processes towards the quantification of the electrode/electrolyte interfaces and the underlying dosages necessary for artifact-free data acquisition in condensed media.

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9:20am **CA+2D+AS+BI+NS-ThM5 Theoretical Investigation of Reactivity at Complex Solid-Liquid Interfaces**, *R. Rousseau*, *Manh Nguyen*, Pacific Northwest National Laboratory **INVITED**

Contrary to solid/gas interfaces, in solid/liquid interfaces the molecules in the liquid can be organized such that those near the surface are appreciably different from the bulk. This can be impacted by: the composition of the liquid phase, the size shape and loading of nanoparticles and the hydro/lipophilicity of the support. In this talk we will outline the findings from our ongoing studies of both thermal and electrochemically driven hydrogenation of organic molecules. We will present both classical and ab initio molecular dynamics calculations that simulate the structure and composition within the double both at the support as well as on surface of catalytic nanoparticles. The calculations explicitly identify the different roles of entropy and binding energy on the activity and selectivity of solution phase hydrogenation. A first example [1] shows how phenol/water mixtures behave on hydrophilic and lipophilic surfaces, and provides a possible explanation as to why a higher phenol hydrogenation conversion is observed [2] on Pd catalysts on hydrophilic surfaces than on lipophilic surfaces. We show how reaction rates can be manipulated by changing the concentration of phenol adjacent to the catalysts through modification of the degree of support hydrophilicity, size and loading of nanoparticles, and temperature. In a second example [3], we simulate the speciation on a Au and graphitic carbon cathodic surface of a complex solvent mixture containing organics, salts, acids, as a function of cathode charge and temperature. Here we show that the ability to transfer an electron to the organic is governed by the amount of organic in the double layer as well as its orientation with respect to the electrode

surface. While both examples included have been drawn from the upgrading of bio-oil ex pyrolysis, the principles shown are relevant to any application in heterogeneous catalysis with condensed reaction media.

References

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11:00am **CA+2D+AS+BI+NS-ThM10 In-situ/Operando Soft X-ray Spectroscopy for Interfacial Characterization of Energy Materials and Devices**, *Y.-S. Liu*, *X. Feng*, *Jinghua Guo*, Lawrence Berkeley National Laboratory

In-situ/operando soft x-ray spectroscopy offers unique characterization in many important energy materials of energy conversion, energy storage and catalysis in regards to the functionality, complexity of material architecture, chemistry and interactions among constituents within.

It has been found that the microstructure and composition of materials as well as the microstructure evolution process have a great influence on performances in a variety of fields, e.g., energy conversion and energy storage materials, chemical and catalytic processes. In-situ/operando x-ray spectra characterization technique offers an opportunity to uncover the phase conversion, chemical environment of elements and other critical information of solid/liquid interfaces in real time. We will present soft x-ray spectroscopy characterization techniques, e.g. soft x-ray absorption spectroscopy (XAS) and resonant inelastic soft x-ray scattering (RIXS), and the development of in situ/operando capabilities for the characterization of interfacial phenomena in energy materials and devices.

A number of the experimental studies, which revealed the catalytic and electrochemical reactions in real time, will be presented, e.g. solid (metal film)/liquid (water) electrochemical interface, Mg-ion batteries, and Li-S batteries [1-5]. The experimental results demonstrate that in-situ/operando soft x-ray spectroscopy characterization provides the unique information for understanding the real reaction mechanism.

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11:20am **CA+2D+AS+BI+NS-ThM11 The Importance of Amino Acid Adsorption on Polymer Surfaces in *P. Aeruginosa* Biofilm Formation**, *Olutoba Sanni*, University of Nottingham, UK

High throughput materials discovery screens have revealed polymers that reduce bacterial surface colonization which have progressed to currently ongoing clinical trials [Hook *et al.* *Nature Biotech* 2012]. These novel poly(meth)acrylate coatings reduced biofilm formation by *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Escherichia coli* in laboratory cultures *in vitro* and *in vivo* in a mouse foreign body infection model. These coatings are known to function by preventing biofilm formation, however why the bacterial cells respond in this way to these polymers has yet to be elucidated. The initial interaction between bacteria and surfaces has been identified as a key determining factor when bacteria decide to either irreversibly attach and colonise a surface or not.

The exposure of most materials to biological milieu is accompanied by adsorption of biomolecules. In protein containing media there is a strong relationship between the adsorbed protein layer formed on materials and mammalian cell attachment. However, in protein-free media such as used

by Hook et al., this cannot be a contributor to early bacterial cell attachment. Consequently, here we carry out careful surface chemical analysis on two polymers known to exhibit drastically different biofilm formation in a standard protein-free, amino acid containing bacterial culture medium (RPMI).

Time of flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) analysis determined that high amino acid adsorption correlates with the surface exhibiting low *P. aeruginosa* colonisation. A total of 10 peaks characteristic of specific amino acids were identified by ToF-SIMS to be adsorbed on polymer. We successfully fitted the Freundlich and Langmuir adsorption isotherm models from which we determined adsorption capacity of polymers, calculated the on/off rate of amino acid adsorption on both anti-biofilm and pro-biofilm surfaces. With XPS, the overlayer coverage of amino acids on the polymer surface was established to be approximately 0.2 nm.

The study was extended to quantify in high throughput manner the adsorption of amino acids from RPMI media onto surfaces of 288 polymer materials printed onto a microarray. Ion fragments generated from ToF-SIMS were used to produce a regression model from which we identified polymers with cyclic moieties as major promoters of amino acid adsorption.

This is the first report suggesting adsorbed amino acids or other adsorbed nutrients may correlate with the biofilm formation tendency of materials.

## Electronic Materials and Photonics Division Room A214 - Session EM+AP+MS+NS+TF-ThM

### Advanced Processes for Interconnects and Devices

**Moderators:** Andy Antonelli, Nanometrics, Bryan Wiggins, Intel Corporation

**8:00am EM+AP+MS+NS+TF-ThM1 High-density Plasma for Soft Etching of Noble Metals, Gerhard Franz, V. Sushkov, Munich University of Applied Sciences, Germany; W. Oberhausen, R. Meyer, Technische Universität München, Germany**

During our research to define a contact which can be serve as thin hard mask in III/V semiconductor processing, we focused on the Bell contact which consists of Ti/Pt(Mo)/Au and chlorine-based plasmas generated by electron cyclotron resonance. For platinum, we identified  $\text{PF}_3$  as main component which acts comparable to CO [1]. This fact triggered our search for suited etchants for gold and copper. For Au, the best ambient is a mixture of  $\text{CH}_4$ ,  $\text{Cl}_2$ , and  $\text{O}_2$  which is stabilized by Ar [2]. This mixture generates residual-free etching of metal films which are clearly free of "fencing" and "hear's ears."

The etching process has been established up to thicknesses of half a micron which is the typical thickness of metal films on the p-side of laser devices. With the aid of optical emission spectroscopy, the generation of CO could be proven [3]. This reagent seems to be the main component for real etching without residual fencing.

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[3] G. Franz, W. Oberhausen, R. Meyer, and M.-C. Amann, *AIP Advances* **8**, 075026 (2018)

**8:20am EM+AP+MS+NS+TF-ThM2 Crystalline InP Growth and Device Fabrication Directly on Amorphous Dielectrics at Temperatures below 400°C for Future 3D Integrated Circuits, Debarghya Sarkar, Y. Xu, S. Weng, R. Kapadia, University of Southern California**

A fundamental requirement to realize 3D integrated circuits is the ability to integrate single crystal semiconductor devices on the back-end of functional layers within a thermal budget of  $\sim 400^\circ\text{C}$ . Present state-of-the-art methods involve wafer bonding or epitaxial growth and transfer, since directly growing on amorphous materials by traditional epitaxial growth processes like MOCVD and MBE would give polycrystalline films with submicron-scale grains. To that end, a newly introduced and actively developing growth method called Templated Liquid Phase (TLP) has demonstrated the ability to achieve single crystal compound semiconductor mesas of areal dimension  $\sim 10\mu\text{m}$  diameter on diverse amorphous substrates. While previous demonstrations of TLP growth were at temperatures around  $500\text{--}600^\circ\text{C}$ , in this presentation we would discuss some of the recent material characteristics and device results achieved and insights obtained, for crystalline InP mesas grown on amorphous dielectrics  
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at temperatures below  $400^\circ\text{C}$ . InP nucleation and growth was obtained for temperatures  $360^\circ\text{C}$  down to  $200^\circ\text{C}$ . Morphological variations of the grown crystals observed under different growth conditions (temperature, pressure, precursor flux) and strategies to obtain compact macro-defect free crystal growth would be presented. Contrary to general expectation of poor optoelectronic quality at these lower temperatures, the room temperature steady-state photoluminescence shows peak position and full width at half maximum comparable to that of commercial InP wafer. External quantum efficiency is within an order of magnitude of single crystal commercial wafer at optimal growth conditions. Back-gated phototransistor was fabricated using low temperature InP grown directly on the amorphous gate oxide, and with all processing steps below the thermal budget of  $400^\circ\text{C}$ . A typical device showed reasonable ON-OFF ratio of about 3 orders of magnitude, with peak responsivity of 20 A/W at  $V_{\text{gs}}=3.2\text{V}$  and  $V_{\text{ds}}=2.1\text{V}$  under an irradiance of  $4\text{ mW/cm}^2$  of broadband light. In summary, this technology could potentially open up a viable avenue to realize 3D integrated circuits by enabling integration of high performance electronic and optoelectronic devices on the back-end of functional layers within the acceptable thermal budget of  $400^\circ\text{C}$ .

**8:40am EM+AP+MS+NS+TF-ThM3 The Role and Requirements of Selective Deposition in Advanced Patterning, Charles Wallace, Intel Corporation**  
INVITED

The edge placement error (EPE) margin on features patterned at tight pitches presents a difficult integrated challenge. Area selective deposition, chemically selective etches and the design of thin films for selectivity have risen to the top priorities in advanced patterning. The EPE control requirement creates a complex interaction between many integrated modules such as thin film deposition, etch (wet and dry), chemical-mechanical polish and lithography. The introduction of EUV lithography into the semiconductor patterning process has enabled some simplification of process architecture; however, has not decreased EPE margin enough to keep up with the pitch scaling requirements. Chemical selectivity is the most effective way to avoid EPE-caused failures on devices which lead to poor yield. Some of the limits to achieving selective growth solutions include development of self-assembled monolayers (SAMs), selective ALD/CVD growth and the metrology required to prove success. The development of manufacturable deposition chambers by the industry is a key requirement in order to adequately test the capability of these new process options.

**9:20am EM+AP+MS+NS+TF-ThM5 Graphene-Template Assisted Selective Epitaxy (G-TASE) of Group IV Semiconductors, M. Arslan Shehzad, A. T. Mohabir, M.A. Filler, Georgia Institute of Technology**

As conventional 2-D transistor scaling approaches its limits, 3-D architectures promise to increase the number of devices and reduce interconnect congestion. A process able to monolithically integrate single-crystalline group IV materials into the back-end-of-line (BEOL) may enable such designs. Here, we demonstrate the graphene-template assisted selective epitaxy (G-TASE) of single-crystal Ge on amorphous substrates at temperatures as low as  $250^\circ\text{C}$ . This work represents a significant step forward for TASE methods, which have been largely limited to III-V and II-VI materials, bulk crystal templates, as well as higher temperatures. We specifically grow Ge nanostructures on graphene-on-oxide at the bottom of nanometer-scale oxide trenches by leveraging differences in group IV atom sticking probability between graphene and oxide surfaces. Raman mapping confirms the single crystallinity of as-grown Ge crystals. Time-dependent studies show a linear increase in Ge crystal height even after emerging from the oxide trench, indicating Ge atoms preferentially adsorb to the top facet under our growth conditions. Our studies also reveal that G-TASE is sensitive to the plasma process used to expose graphene in the oxide trenches. This work extends TASE to a new, technologically-relevant materials system and provides fundamental insight into the underlying physicochemistry.

**KEY WORDS:** silicon, germanium, epitaxy, graphene, selective deposition

**9:40am EM+AP+MS+NS+TF-ThM6 Resistivity and Surface Scattering Specularity at (0001) Ru/dielectric Interfaces, S.S. Ezzat, University of Central Florida; P.D. Mani, View Dynamic Glass, Inc.; A. Khaniya, W.E. Kaden, University of Central Florida; D. Gall, Rensselaer Polytechnic Institute; K. Barmak, Columbia University; Kevin Coffey, University of Central Florida**

In this work we report the variation of resistivity with film thickness and with changes in surface characteristics for ex-situ annealed single crystal (0001) Ru thin films grown on c-axis sapphire single crystal substrates. The room temperature deposition of  $\text{SiO}_2$  on the Ru surface increased the

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resistivity of the annealed films and is interpreted as an increase in diffuse scattering of the upper surface from a primarily specular previous condition in the context of the Fuchs-Sondheimer model of surface scattering. The characterization of the films and upper Ru surface by low energy electron diffraction (prior to SiO<sub>2</sub> deposition), x-ray reflectivity, x-ray diffraction, and sheet resistance measurements is reported. The film resistivity and specularly of the Ru/SiO<sub>2</sub> interface is observed to reversibly transition between high resistivity (low specularly) and low resistivity (high specularly) states.

11:00am **EM+AP+MS+NS+TF-ThM10 Electrochemical Atomic Layer Deposition and Etching of Metals for Atomically-Precise Fabrication of Semiconductor Interconnects**, *Y. Gong, K. Venkatraman, Rohan Akolkar*, Case Western Reserve University **INVITED**

Moore's law drives continued device miniaturization in nano-electronics circuits. As critical dimensions are approaching the single nanometer length scale, the semiconductor industry is seeking novel technologies for precisely tailoring materials and structures at the atomic scale. While vapor-phase, plasma-assisted techniques of atomic layer deposition (ALD) and etching (ALE) are capable of providing nano-scale control over metal deposition and etching, these processes may not provide the requisite atomic-scale precision. Additionally, ALD precursors are unstable and often expensive. Thus, alternative solution-phase electrochemical processes are being developed in our laboratory. In our electrochemical ALD (e-ALD) approach, a sacrificial monolayer of zinc is first deposited on the noble substrate via underpotential deposition (UPD). The zinc adlayer then undergoes spontaneous surface-limited redox replacement (SLRR) by the desired metal such as Cu or Co. Sequential UPD and SLRR steps enable fabrication of multi-layered deposits in a layer-by-layer fashion. An analogous approach for electrochemical ALE (e-ALE) is also being developed. In electrochemical ALE of Cu, surface-limited sulfidization of Cu forms a cuprous sulfide (Cu<sub>2</sub>S) monolayer. The sulfidized Cu monolayer is then selectively removed through spontaneous complexation of the Cu<sup>+1</sup> in a chloride-containing etchant medium. The sequence can be repeated to etch bulk metal films one atomic layer at a time. This talk will highlight numerous advantages and fundamental characteristics of e-ALD and e-ALE processes and describe opportunities for integrating them in wafer-scale metallization applications.

12:00pm **EM+AP+MS+NS+TF-ThM13 Wafer-Scale Fabrication of Carbon-Based Electronic Devices**, *Zhigang Xiao, J. Kimbrough, J. Cooper, K. Hartage, Q. Yuan*, Alabama A&M University

In this research, we report the wafer-scale fabrication of carbon nanotube or graphene-based electronic device such as field-effect transistors (FETs). Carbon nanotube-based devices were fabricated with the alternating electric field-directed dielectrophoresis (DEP) method, and the graphene-based devices were fabricated with the carbon films grown with plasma-enhanced atomic layer deposition (PEALD) or e-beam evaporation. Semiconducting carbon nanotubes were dispersed ultrasonically in solutions, and were deposited and aligned onto a pair of gold electrodes in the fabrication of carbon nanotube-based electronic devices using the dielectrophoresis method. The DEP-aligned tubes were further fabricated into carbon nanotube field-transistors (CNTFETs) and CNTFET-based electronic devices such as CNT-based inverters and ring oscillators using the microfabrication techniques. The fabricated devices were imaged using the scanning electron microscope (SEM) and high-resolution transmission electron microscope (HRTEM), and the electrical properties were measured from the fabricated devices using the semiconductor analyzer. The semiconducting CNTs achieved higher yield in the device fabrication, and the fabricated devices demonstrated excellent electrical properties.

## Advanced Ion Microscopy and Ion Beam Nano-engineering

### Focus Topic

Room B231-232 - Session HI+NS-ThM

### Novel Beam Induced Material Engineering and Nano-Patterning

**Moderators:** Olga S. Ovchinnikova, Oak Ridge National Laboratory, Shinichi Ogawa, National Institute of Advanced Industrial Science and Technology (AIST)

8:00am **HI+NS-ThM1 Tuning out-of-plane Piezoelectricity in 2D Materials using Ion Beams**, *Yunseok Kim*, Sungkyunkwan University, Republic of Korea **INVITED**

Two-dimensional (2D) transition metal dichalcogenides (TMDs) have been extensively studied owing to their ultra-thin nature as well as superior material properties. In particular, after the experimental observation of intrinsic in-plane piezoelectricity in the 2D MoS<sub>2</sub>, fundamental studies on the piezoelectricity as well as piezoelectric device applications of the 2D TMDs have attracted significant interest. However, their applications are strongly limited due to the fact that crystallographically only in-plane piezoelectricity exists in the 2D TMDs. In this presentation, I will summarize our recent effect on the realization of tunable out-of-plane piezoelectricity in the 2D TMDs using He ion beams. Among various 2D TMDs, we have chosen MoTe<sub>2</sub> because it is very sensitive to the external stimuli such as strain. We first examined the realization of the out-of-plane piezoelectricity by local asymmetry breaking based on the surface corrugation to check its feasibility. Then, He ion irradiation as a function of dose were performed onto the MoTe<sub>2</sub> surface. It was found that the out-of-plane piezoelectricity was indeed induced by He ion beams and, further, the magnitude of the induced out-of-plane piezoelectricity was dependent on the dose level. The proposed strategy for modulation of tunable out-of-plane piezoelectricity can be easily applied to a broader class of 2D TMD materials that have not been used for applications with out-of-plane piezoelectricity. Accordingly, it can stimulate the expansion of practical energy device applications with 2D TMDs.

8:40am **HI+NS-ThM3 Defect Engineering of Ferroelectric Thin Films – Leveraging Ion Beams for Improved Function**, *Lane Martin*, University of California at Berkeley **INVITED**

Modern approaches to epitaxial thin-film growth have enabled unprecedented control of ferroelectric materials including the realization of enhanced polarization and ordering temperatures, production of ordered-domain structures, and improved properties. Today we are looking beyond simple lattice mismatch control for new ways to manipulate and control ferroic response and to produce unexpected or emergent effects. In this talk, we will investigate a number of observations of such emergent or unexpected properties in epitaxial thin films made possible via innovative synthesis and processing methodologies. In particular, we will explore recent examples of how synthesis, defects, and epitaxial constraint can be combined to produce exotic effects in ferroic systems. Primary focus will be given to the *ex situ* production of defects with ion bombardment to control defect-induced electronic states that can drive dramatic changes in leakage currents and impact ferroelectric response in materials like BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, BiFeO<sub>3</sub>, and others. For example, we will explore how high-energy-ion beams (>3 MeV beams of helium ions) can induce nonequilibrium densities of intrinsic point and defect clusters that have unintended positive effects – including reducing leakage in films by as much as 3-4 orders of magnitude, tuning coercive fields for switching, and much more. At the same time, leveraging focused-helium-ion bombardment, it is possible to create nanoscale patterns of defect-engineered material where emergent function, such as multi-state switching, is accomplished. Finally, we will explore how ion-bombardment procedures can also provide a knob to tune local energy competition in materials like relaxor ferroelectrics to gain new insight into material physics. All told, we will highlight specifics about the routes to produce defect-engineered ferroelectric thin films, will explore approaches to characterize and study the nature of defects that are produced – including application of techniques like deep-level transient spectroscopy, and will examine the implication of such defect structures for dielectric and ferroelectric properties – including studies of defect-based effects on switching processes and kinetics. We will end with an exploration of what further growth of defect-engineering approaches might enable in the way of novel function and applications in these materials.

9:20am **HI+NS-ThM5 Exploring Proximity Effects and Large Depth of Field in Helium Ion Beam Lithography: Large-area Dense Patterns and Tilted Surface Exposure**, *Ranveig Flatbø*, Univeristy of Bergen, Norway; *A. Agarwal*, Massachusetts Institute of Technology; *R. Hobbs*, Trinity College Dublin; *M. M. Greve*, Univeristy of Bergen; *B. Holst*, Univeristy of Bergen, Norway; *K.K. Berggren*, Massachusetts Institute of Technology

Helium ion beam lithography (HIL) is an emerging nanofabrication technique. It benefits from a reduced interaction volume compared to that of an electron beam of similar energy, and hence reduced long-range scattering (proximity effect), higher resist sensitivity and potentially higher resolution. Furthermore, the small angular spread of the helium ion beam gives rise to a large depth of field. This should enable patterning on tilted and curved surfaces without the need of any additional adjustments, such as laser-auto focus. So far, most work on HIL has been focused on exploiting the reduced proximity effect to reach single-digit nanometer resolution, and has thus been concentrated on single-pixel exposures over small areas. Here we explore two new areas of application. Firstly, we investigate the proximity effect in large-area exposures and demonstrate HIL's capabilities in fabricating precise high-density gratings on large planar surfaces (100  $\mu\text{m} \times 100 \mu\text{m}$ , with pitch down to 35nm) using an area dose for exposure. Secondly, we exploit the large depth of field by making the first HIL patterns on tilted surfaces (sample stage tilted 45°). We demonstrate a depth of field greater than 100  $\mu\text{m}$  for an estimated resolution of 20 nm.

9:40am **HI+NS-ThM6 Fabrication of Plasmonic Nanostructures by Helium-Ion Milling**, *André Beyer*, *M. Westphal*, Bielefeld University, Germany; *S. Stephan*, Oldenburg University, Germany; *D. Emmrich*, *H. Vieker*, Bielefeld University, Germany; *K. Chen*, Jinan University, Guangzhou, China; *G. Razinskas*, *H. Gross*, *B. Hecht*, Würzburg University, Germany; *M. Silies*, Oldenburg University, Germany; *A. Götzhäuser*, Bielefeld University, Germany

Plasmonic nanostructures are essential for controlling and directing light on the nanoscale. While fabrication techniques like standard electron beam lithography (EBL) methods or focused ion beam (FIB) milling with Ga<sup>+</sup> ions are approaching their limit in the 10-nm-regime, ion beam milling with He<sup>+</sup> ions is capable of milling features below 6 nm [1,2]. In this contribution, we give two specific examples of helium-ion milled plasmonic nanostructures: (i) gold bowtie antennas milled from 100 nm thick polycrystalline gold films on mica substrates and (ii) nanoslit cavities in chemically-synthesized 40 nm thick single-crystalline gold flakes [2]. Both examples benefit from a combined approach using a Ga<sup>+</sup> FIB for milling large features and employing the fine resolution of the helium ion microscope (HIM) for milling small features. We will discuss different patterning strategies to optimize the writing speed and minimize substrate swelling. In addition, our approach to quantify the sizes of milled gaps will be shown. It is based on low dose imaging in combination with substantial line-profile averaging which we applied to few-hundred-nanometer-long homogeneous helium-ion milled lines.

[1] H. Kollmann et al., *Nano Letters* 14, 4778 (2014).

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11:00am **HI+NS-ThM10 Towards Atomically Precise Carbon Quantum Electronic Devices**, *J.L. Swett*, University of Oxford, UK; *O. Dyck*, *S. Jesse*, Oak Ridge National Laboratory; *Jan Mol*, Queen Mary University of London, UK

## Towards Atomically Precise Carbon Quantum Electronic Devices

Jacob L. Swett<sup>a</sup>, Ondrej Dyck<sup>b</sup>, Stephen Jesse<sup>b</sup>, Jan A. Mol<sup>a,c</sup>

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Graphene exhibits many unique properties that can be further enhanced through nanostructuring and atomic manipulation. Such nanostructured devices have potential applications as molecular junctions [1], spin qubits [2], heat engines [3], and sensors [4], providing substantial motivation for their realization. Electron and ion beams provide unique and complementary tools for realizing some of these structures due to their ability to modify the graphene with atomic and nanoscale precision, respectively. Modification may take the form of direct-write patterning [5], defect production [6], dopant introduction [7], and dopant manipulation [8]. Although much progress has been realized in these areas, transport measurements of top-down fabricated atomically precise carbon

nanostructures have yet to be realized. Here we present lessons learned and key findings for this emerging direction of research leveraged from years of fabrication and transport measurements of single molecules via non-covalent bonding to graphene nanoelectrodes [9]. We will present a broad overview of the challenges and progress in understanding and controlling the transport through atomic-scale devices and discuss how these lessons inform and translate to current experiments on introducing dopants and manipulating atoms on the atomic scale with electron and ion beams in graphene and other 2D materials. Finally, practical strategies for realization of these devices will be discussed, including contamination control, fabrication strategies, and transport measurements.

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11:40am **HI+NS-ThM12 Fabrication of High-Q nanofiber Bragg Cavity Using a Helium Ion Microscope**, *Hideaki Takashima*, Kyoto university, Japan; *A. Fukuda*, *H. Maruya*, *T. Tashima*, Kyoto University, Japan; *A. Schell*, Central European Institute of Technology, Czech Republic; *S. Takeuchi*, Kyoto University, Japan

Efficient coupling between single light emitters and photons propagating in single mode fibers has been attractive attention recently for the realization of photonic quantum information devices, such as single photon sources, and quantum phase gates. Toward the realization of these devices, we have developed nanofiber Bragg cavity (NFBC), which is an optical nanofiber embedded in a microcavity in it, using a gallium focused ion beam (FIB) milling system. The NFBC has small mode volume of wavelength size, ultra-wide tunability of the resonant wavelength, and high coupling efficiency (>80%). However, experimentally achieved quality (Q) factors have been still a few hundreds. Here, we report the development of the NFBC using a helium ion microscope (ZEISS "ORION NanoFab").

Nanofibers are fabricated by heating a single-mode fiber with a ceramic heater and stretching the end of the fiber. The diameter of the nanofibers is reduced to about 300 nm. The helium ion beam is periodically irradiated from the top side of the nanofiber to fabricate Bragg grating. The period at the center of the grating is modified for introducing a defect to be worked as a microcavity.

In order to evaluate the Q factor of the NFBC, we measure a transmission spectrum. The light of a halogen lamp is connected to the one end of the NFBC and the transmitted light is observed with a spectrometer with the resolution of 0.17 nm.

When we measure the transmission spectrum of the NFBC with the grooves of 320, a sharp resonant peak with the linewidth of 0.54 nm was observed in the center of the stop band. This agrees with the Q factor of 1260, which is more than 4 times larger than the NFBC fabricated with the Ga FIB system (Q ~ 300). Taking into account of the resolution of the spectrometer, it is expected that the real Q factor would be higher than this value.

In conclusion, we reported the fabrication of NFBC using the helium microscope. When the number of the grooves is 320, the Q factor is 1260, which is more than 4 times larger than the NFBC fabricated by the Ga FIB system.

Besides this result, we will discuss the NFBC when the number of the grooves is changed and the comparison with finite-difference time-domain (FDTD) simulation.

We acknowledge financial support of the JSPS-KAKENHI (Nos. 21101007, 26220712, 23244079, 25620001, 23740228, 26706007, 26610077, and 16K04918); JST-CREST (JPMJCR1674); and Q-LEAP. A part of this work was supported by "Nanotechnology Platform Project (Nanotechnology Open Facilities in Osaka University)" of Ministry of Education, Culture, Sports, Science and Technology, Japan [F-18-OS-0029].

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12:00pm **HI+NS-ThM13 Time of Flight Secondary Ion Mass Spectrometry in the Helium Ion Microscope for Battery Materials and Other Nanoscale Problems**, *N. Klingner*, Helmholtz Zentrum Dresden-Rossendorf, Germany; *Gregor Hlawacek*, Helmholtz-Zentrum Dresden Rossendorf, Germany; *L.J. Wheatcroft*, *B.J. Inkson*, University of Sheffield, UK; *R. Heller*, Helmholtz Zentrum Dresden-Rossendorf, Germany

Helium Ion Microscopy (HIM) has become a wide spread imaging and nanofabrication technology. However, existing HIM users can currently not perform elemental analysis in an easy and cost efficient way. We present results obtained using a light weight retrofitable Time of Flight Secondary Ion Mass Spectrometer (TOF-SIMS). I will briefly give an overview on new developments in our TOF-SIMS setup which allows to obtain information on the elemental composition of the sample. The lateral resolution for the presented TOF-SIMS add-on has been measured to be 8 nm. A particular advantage of the presented TOF-SIMS implementation is that it allows for charge compensation during data acquisition and thus the elemental analysis of insulators or poorly conducting materials. In addition delayed extraction can be realized which will allow a field free application of the primary beam which reduces aberrations and the setup time. While not a dedicated high mass resolution instrument it allows to answer many scientific questions by combining the high lateral resolution of the HIM with elemental information. The examples include but are not limited to battery materials and corrosion protection of steel.

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Stefan Facsko. Nanometer scale elemental analysis in the helium ion microscope using time of flight

spectrometry. *Ultramicroscopy*, 162:91–97, 2016.

## Nanometer-scale Science and Technology Division Room A222 - Session NS+2D+QS-ThM

### Direct Atomic Fabrication by Electron and Particle Beams & Flash Session

**Moderators:** Canhui Wang, National Institute of Standards and Technology (NIST), Xiaolong Liu, Northwestern University

8:00am **NS+2D+QS-ThM1 Multiprobe Scanning Tunneling Microscopy and Spectroscopy: Atomic-level Understanding of Quantum Transport in Functional Systems**, *Marek Kolmer*<sup>1</sup>, *W. Ko*, *A.-P. Li*, Oak Ridge National Laboratory

Techniques based on multiprobe scanning tunneling microscopy (MP-STM) allow determination of charge and spin transport in variety of systems supported on surfaces of solid materials. In classical 2- and 4-probe methods STM tips are navigated by scanning electron microscope or high-resolution optical microscope typically in micrometer scales down to hundreds of nanometers. These MP-STM methods are currently regarded as universal tools for in-situ characterization of mesoscopic transport phenomena [1,2].

Such a mesoscopic experimental paradigm has recently been changed by downscaling of 2-probe STM experiments towards the atomic level [3,4]. In this case current source and drain probes are positioned in atomically defined locations with respect to the characterized nanosystems. Our experiments rely on fully STM-based tip positioning protocol with probe-to-probe separation distances reaching tens of nm [3,4]. Such probe-to-probe lateral positioning precision is combined with about pm vertical sensitivity in probe-to-system contacts. These two factors enable realization of two-probe scanning tunneling spectroscopy (2P-STS) experiments, where transport properties can be characterized by macroscopic probes kept in atomically defined tunneling conditions [4].

Here, we will apply 2P-STS methodology to probe quantum transport properties in functional systems: graphene nanoribbons (GNRs) epitaxially grown on the sidewalls of silicon carbide (SiC) mesa structures. These GNRs display ballistic transport channels with exceptionally long mean free paths and spin-polarized transport properties as proven by mesoscopic

multiprobe transport experiments [5-7]. Interestingly, the nature of these ballistic channels remains an open question. We will show that 2P-STS experiments give new insight into quantum origin of the transport behaviors.

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This work was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility.

8:20am **NS+2D+QS-ThM2 Light and Heavy Ions from New Non-classical Liquid Metal Ion Sources for Advanced Nanofabrication**, *Paul Mazarov*, RAITH GmbH, Germany; *T. Richter*, *L. Bruchhaus*, *R. Jede*, Raith GmbH; *Y. Yu*, *J.E. Sanabria*, Raith America; *L. Bischoff*, Helmholtz Zentrum Dresden-Rossendorf, Germany; *J. Gierak*, CNRS—Université Paris-Sud, France

### INVITED

Nanofabrication requirements for FIB technologies are specifically demanding in terms of patterning resolution, stability and the support of new processing techniques. Moreover the type of ion defines the nature of the interaction mechanism with the sample and thus has significant consequences on the resulting nanostructures [1]. Therefore, we have extended the technology towards the stable delivery of multiple ion species selectable into a nanometer scale focused ion beam by employing a liquid metal alloy ion source (LMAIS) [2]. This provides single and multiple charged species of different masses, resulting in significantly different interaction mechanisms. Nearly half of the elements of the periodic table are made available in the FIB technology as a result of continuous research in this area [3]. This range of ion species with different mass or charge can be beneficial for various nanofabrication applications. Recent developments could make these sources to an alternative technology feasible for nanopatterning challenges. In this contribution the operation principle, the preparation and testing process as well as prospective domains for modern FIB applications will be presented. As example we will introduce a GaBiLi LMAIS [4]. It enables high resolution imaging with light Li ions and sample modification with Ga or heavy polyatomic Bi clusters, all coming from one ion source. For sub-10 nm focused ion beam nanofabrication and microscopy, the GaBiLi-FIB or the AuSiGe-FIB could benefit of providing additional ion species in a mass separated FIB without changing the ion source.

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9:00am **NS+2D+QS-ThM4 Visualizing the Interplay between Spatial and Magnetic Confinement in Graphene Quantum Dots**, *Joseph Strosio*, National Institute of Standards and Technology (NIST)

### INVITED

At the heart of the wave nature of quantum mechanics is the quantization of energy due to quantum confinement, taking place when the particle's de Broglie wavelength becomes comparable to the system's length scale. In a quantum dot (QD), electrons are confined in all lateral dimensions using geometric constraints or a combination of electric and magnetic fields. Being a tunable quantum workbench, QDs have found a ubiquity of applications. Behaving as artificial atoms they have found extensive use as qubits in quantum information technologies, and tools for emulating basic models of condensed-matter physics. QDs offer an ideal platform for studying the interplay between quantum confinement, caused by spatial constraints or by large magnetic fields via cyclotron motion, and interaction effects. Recently, the ability to apply local nanometer scale gate potentials in graphene heterostructures has enabled the creation of QDs for Dirac

<sup>1</sup> NSTD Early Career Award Finalist

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quasiparticles. Graphene QDs are formed inside circular p-n junctions, where one has detailed control of electron orbits by means of local gate potentials and magnetic fields. We study the interplay between spatial and magnetic confinement using scanning tunneling spectroscopy measurements of the energy spectrum of graphene QDs as a function of energy, spatial position, and magnetic field. In zero field, the Dirac quasiparticles are confined by Klein scattering at large incident angle at the p-n junction boundary. The confined carriers give rise to an intricate eigenstate spectrum, effectively creating a multi-electron artificial atom. Applying a weak magnetic field results in a sudden and giant increase in energy for certain angular momentum states of the QD, creating a discontinuity in the energy spectrum as a function of magnetic field. This behavior results from a  $\pi$ -Berry phase associated with the topological properties of Dirac fermions in graphene, which can be turned on and off with magnetic field. With increased applied magnetic field, the QD states are observed to condense into Landau levels, providing a direct visualization of the transition from spatial to magnetic confinement in these artificial graphene atoms. With further increase in magnetic fields, an intricate interplay between Coulomb charging of compressible Landau levels separated by incompressible rings emerges, which we map as a function of energy, spatial position, and magnetic field utilizing the exceptional capabilities of scanning tunneling spectroscopy.

**9:40am NS+2D+QS-ThM6 Using Controlled Manipulation of Molecules to Trace Potential Energy Surfaces of Adsorbed Molecules, O.E. Dagdeviren, C. Zhou, Yale University; M. Todorovic, Aalto University, Finland; Eric Altman, U.D. Schwarz, Yale University**

The development of scanning probe microscopy techniques has enabled the manipulation of single molecules. More recently it has been demonstrated that the forces and energy barriers encountered along the manipulation path can be quantified using non-contact atomic force microscopy (AFM). To explore the practicality of using this novel approach to experimentally measure the energy barriers an adsorbed molecule encounters as it moves across a surface decorated by other molecules including potential reaction partners, we have been studying benzene molecules on Cu (100) as a model system. We first choose a specific manipulation path and then move the tip repeatedly along this path as the tip-sample distance is reduced while recording the AFM cantilever oscillation amplitude and phase. To preserve the accuracy of the recovered tip-sample interaction potentials and forces, we use oscillation amplitudes significantly larger than the decay length of the tip-sample interaction potential are used. Operating the microscopy in the tuned-oscillator mode and analyzing the resulting cantilever oscillation amplitude and phase as functions of the spatial coordinates allows recovery of the potential energy of the interaction between the tip and the sample, the force on the tip normal to the surface, and the lateral force acting on the tip along the manipulation path, all as functions of tip vertical and lateral position with 0.01 Å resolution. In over 50 distinct manipulation events, the molecules were either pushed, pulled, jumped to the tip, or did not move depending on the chemical environment surrounding the molecule and the chemical identity of the tip. For further insight, we have compared the experimentally measured energy landscapes and manipulation outcomes with computational results obtained using a Bayesian Optimization Structure Search protocol.

**11:00am NS+2D+QS-ThM10 Direct Writing of Functional Heterostructures in Atomically Precise Single Graphene Nanoribbons, Chuanxu Ma, Oak Ridge National Laboratory; Z. Xiao, North Carolina State University; J. Huang, L. Liang, Oak Ridge National Laboratory; W. Lu, North Carolina State University; K. Hong, B.G. Sumpter, Oak Ridge National Laboratory; J. Bernholc, North Carolina State University; A.-P. Li, Oak Ridge National Laboratory**

Precision control of interfacial structures and electronic properties is the key to the realization of functional heterostructures. Here, utilizing the scanning tunneling microscope (STM) both as a manipulation and characterization tool, we demonstrate the fabrication of a heterostructure in a single atomically precise graphene nanoribbon (GNR) and report its electronic properties<sup>1</sup>. The heterostructure is made of a seven-carbon-wide armchair GNR (7-aGNR) and a lower band gap intermediate ribbon synthesized bottom-up from a molecular precursor on an Au substrate. The short GNR segments are directly written in the ribbon with an STM tip to form atomic precision intraribbon heterostructures. Based on STM studies combined with density functional theory calculations, we show that the heterostructure has a type-I band alignment, with manifestations of quantum confinement and orbital hybridization. We further investigate the negative differential resistance (NDR) devices using the GNR

heterostructure based double-barrier models<sup>2</sup>. Our computational results indicate that nanoscale engineering for NDR needs to consider atomic size effect in design and atomic precision in fabrication. This combined theoretical-experimental approach opens a new avenue for the design and fabrication of nanoscale devices with atomic precision.

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**11:20am NS+2D+QS-ThM11 Effects of Helium and Neon Processing on 2D Material Properties, Alex Belianinov, Oak Ridge National Laboratory; S. Kim, Pusan National University, South Korea; V. Iberi, S. Jesse, O.S. Ovchinnikova, Oak Ridge National Laboratory**

Recent advances in CVD-growth consistently yield high quality 2D materials for large(er) scale fabrication. Monolayers of molybdenum and tungsten diselenide and selenide, graphene, and other exotic 2D materials are becoming routine in fabrication of functional electronic and optoelectronic devices. In order to attain novel functionalities, it is critical to tune and engineer defects in 2D materials directly with nanometer precision. Advances in ion beam-based imaging and nanofabrication techniques have offered a pathway to precisely manipulate 2D materials and offer a roadmap to create junctions, amorphized areas, and introduce dopants for new types of electronic devices. Here, we demonstrate the use of a focused helium and neon ion beams in a scanning helium ion microscope (HIM) in tailoring material functionality in MoSe<sub>2</sub>, WSe<sub>2</sub>, CuInP<sub>2</sub>S<sub>6</sub> and graphene.

The helium ion microscope can “direct-write” capabilities, capable of both imaging and nanofabrication with Helium and Neon gases, thus making it an excellent candidate for processing a wide range of 2D, and conventional materials. We explore milling by the helium and neon ion beams of suspended and supported samples in order to control material’s electronic and mechanical properties. We validate the results with other chemical imaging techniques such as Scanning Transmission Electron Microscopy, correlated band excitation (BE) scanning probe microscopy, and photoluminescence (PL) spectroscopy.

## Acknowledgement

This work was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy (DOE) Office of Science User Facility.

**11:40am NS+2D+QS-ThM12 Operating Molecular Propeller in Quantum Regime with Directional Control, Y. Zhang, Tolulope Ajayi, Ohio University; J.P. Calupitan, Université de Toulouse, France; R. Tumbleson, Ohio University; G. Erbland, C. Kammerer, CEMES-CNRS, France; S. Wang, Ohio University; L. Curtiss, A. Ngo, Argonne National Laboratory; G. Rapenne, NAIST, Japan; S.-W. Hla, Ohio University**

Synthetic molecular machines are fascinating and have a great promise to revolutionize a large scientific and technology fields. The immense interest to this research area is evident by the 2016 Nobel Prize in Chemistry awarded for the design and synthesis of molecular machines. Unlike biological molecular machines, which typically have the sizes of a few microns, artificial machines operating at the nanometer scale are in the quantum regime. Here, we have developed a robust multi-component molecular propeller that enables unidirectional rotations on a materials surface when they are energized. Our propeller system is composed of a stator having a ratchet-shaped molecular gear designed to anchor on a gold surface and a rotator with three molecular blades. By means of scanning tunneling microscope imaging and manipulation, the rotation steps of individual molecular propellers are directly visualized, which confirms the unidirectional rotations of both left and right handed molecular propellers into clockwise and counterclockwise directions, respectively. Moreover, the mechanical manipulation of the molecular with the scanning probe tip further reveal detailed rotation mechanism, thereby opening a new research direction to investigate mechanical properties of the molecular machines with an atomic level precision.

## Thin Films Division

Room A122-123 - Session TF+EM+NS+SS-ThM

### Thin Films for Energy Harvesting and Conversion

**Moderators:** Siamak Nejati, University of Nebraska-Lincoln, Xinwei Wang, Shenzhen Graduate School, Peking University

8:00am **TF+EM+NS+SS-ThM1 Redesigning Batteries into Efficient Energy Harvesters and Sensors for Wearable Applications, Cary Pint, Vanderbilt University** **INVITED**

Here I will discuss the research efforts of my team demonstrating how active materials utilized in batteries can be reconfigured into an electrochemical framework to harvest, rather than store, energy. This new functionality of battery materials arises from the fundamental coupling between mechanical stresses and electrochemistry that my group has demonstrated while investigating the "strain-engineering" of battery materials. By exploiting this coupling in a symmetric cell device configuration, we are able to construct devices that convert mechanical energy to electrical energy by mechanical modulation of the electrochemical reaction potential. I will discuss the development of this device platform from proof-of-concept device fabrication using 2D materials to our most recent demonstration of textile-integrated biocompatible fibers integrated into fabrics for harvesting/sensing of human motion. Most notably, I will discuss how the sluggish diffusion kinetics of ions between two electrodes – whereas a challenge for emerging battery applications, enables these devices to measure a continuous response from the whole broad range of frequencies associated with human motion. This allows these wearable harvesters to provide real-time sensing data that can be directly correlated with dynamic human motion models. This new approach leverages the efficient nature of electrochemistry, the wide range of materials selection and chemistries relevant for batteries, and without any of the safety concerns of batteries due to the symmetric electrode configuration.

8:40am **TF+EM+NS+SS-ThM3 Engineering Effective Back Contact Barrier by interfacial MoSe<sub>2</sub> defect states for CZTSe: nanolayer Ge solar cells., Sanghyun Lee, Indiana State University**

The steadily emerging Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTSSe) devices are alternative thin film solar cells with abundant elements in earth's crust for the past several years. Despite several advantages such as high absorption coefficient (>10<sup>4</sup> cm<sup>-1</sup>) and a tunable direct band gap energy (1 to 1.4 eV), the improvement and understanding have been stagnant in the past several years. Recently, CZTSe: nanolayer Ge solar cells have shown significantly improved pseudo-mono grain toward the depth direction.

Due to the improvement and the similarity between CZTSe and Cu(In,Ga)Se<sub>2</sub> (CIGS) thin film solar cells, the CZTSe/Molybdenum (Mo) back contact interface was often misinterpreted by expecting the similar back contact property to CIGS. However, unlike the stable CIGS (CuInSe<sub>2</sub>)/Mo interface, the CZTSe/Mo interface is thermodynamically unstable due to the higher oxidation states of Sn. Although the presence of an interfacial MoSe<sub>2</sub> layer at Mo/absorber is always confirmed, properties of the back contact-interface such as structure and electrical behaviors are convoluted.

Following our empirical results about the back contact barrier of CZTSe: nanolayer Ge devices, we perform analytical and numerical modeling to explain the back contact improvement theoretically. The device modeling are carried out with the simulator, developed at Indiana State University. The tool is run in MATLAB environment, connected to other external tools (Sentaurus TCAD). Based on our result, defects in MoSe<sub>2</sub> interfacial layer dominate the back contact property of CZTSe: nanolayer Ge devices by increasing of the effective back contact barrier, which consists of two different back contact barriers, thereby increasing series resistance as well. The reduction of MoSe<sub>2</sub> defect concentration from 1 x 10<sup>17</sup> to 1 x 10<sup>15</sup> cm<sup>-3</sup> decreases the effective barrier height by 51 meV, which results in approximately 34 % decrease in the series resistance (See supporting data). Conversely, as the defect concentration increases, the benefit from the back contact barrier lowering by the valence bands offset between MoSe<sub>2</sub> and CZTSe absorber is reduced and essentially eliminated. However, the back contact barrier between MoSe<sub>2</sub> and Mo metal contact remains the same even with increased MoSe<sub>2</sub> defect concentration. Incorporating thin Ge nanolayer at the interface between the absorber and MoSe<sub>2</sub> positively influences and possibly reduces the defect states, lowering the effective barrier. The exponential fitting of the effective barrier and series resistance agrees well with the experimental results. The improvement of the back contact barrier for CZTSe: nanolayer Ge devices is calculated as 23.8 meV than CZTSe without nanolayer Ge devices.

9:00am **TF+EM+NS+SS-ThM4 Development of Low-Cost, Crack-Tolerant Metallization Using Screen Printing for Increased Durability of Silicon Solar Cell Modules, O.K. Abudayyeh, Osazda Energy; A. Chavez, University of New Mexico; J. Chavez, Osazda Energy; Sang M. Han, University of New Mexico; F. Zimbardi, B. Rounsaville, V. Upadhyaya, A. Rohatgi, Georgia Institute of Technology; B. McDanold, T. Silverman, National Renewable Energy Laboratory**

One of the ways to reduce the cost of solar electricity to 3¢/kWh, thus reaching parity with fossil-fuel-based generation, is to reduce the degradation rate of solar modules and extend their lifetime well beyond 30 years. The extended module lifetime in turn can positively influence the financial model and the bankability of utility-scale PV projects. Today, the highest-risk-priority solar module degradation mechanism is what is known as hot spots, often induced by cell cracks. In order to address this degradation mechanism, we make use of low-cost, multi-walled carbon nanotubes embedded in commercial screen-printable silver pastes, also known as metal matrix composites. When the carbon nanotubes are properly functionalized and appropriately incorporated into commercial silver pastes, the resulting metal contacts on solar cells, after screen-printing and firing, show exceptional fracture toughness. These composite metal contacts possess increased ductility, electrical gap-bridging capability up to 50 μm, and "self-healing" to regain electrical continuity even after cycles of complete electrical failure under extreme strain [1]. Accelerated thermal cycling tests on mini-modules constructed from aluminum back surface field (Al-BSF) cells show a slower degradation rate for the cells integrated with the composite grid fingers and busbars for the front surface metallization compared to the cells with conventional metallization.

[1] O. K. Abudayyeh, A. Chavez, J. Chavez, S. M. Han, F. Zimbardi, B. Rounsaville, V. Upadhyaya, A. Rohatgi, B. McDanold, T. J. Silverman, and N. Bosco, in "Low-Cost Advanced Metallization to Reduce Cell-Crack-Induced Degradation for Increased Module Reliability," 2019 NREL PV Reliability Workshop, Lakewood, CO, 2019.

9:20am **TF+EM+NS+SS-ThM5 Fabrication of Optical Test Structures for Enhanced Absorption in Thin Multi-junction Solar Cells, Erin Cleveland, N.A. Kotulak, S. Tomasulo, P. Jenkins, U.S. Naval Research Laboratory; A. Mellor, P. Pearce, Imperial College London, UK; N.J. Ekins-Daukes, University of New South Wales, Australia; M.K. Yakes, U.S. Naval Research Laboratory**

In space applications, a key figure of merit is conversion efficiency at end-of-life, which combines both beginning-of-life efficiency with degradation due to radiation exposure on orbit. In currently used InGaP/GaAs/Ge triple junctions, the GaAs middle cell has the most pronounced degradation, which limits the total current generation at the end-of-life. Recently, we demonstrated that as the thickness of the GaAs cell decreases, the tolerance to radiation damage increases. [1] However, because the cell absorbs less light as the thickness of the active region is reduced, the beginning-of-life performance suffers as compared to optically thick cells. To realize the benefits of both structures, light trapping architectures may be used to increase absorption within the cell while still maintaining the increased radiation tolerance of the thinner geometry.

Designing a wavelength selective light trapping structure positioned interstitially between two of the subcells of a multi-junction device is a new challenge which prohibits many of the well-known light trapping techniques. Recently, we have proposed a structure which combines a distributed Bragg reflector (DBR) with a textured diffraction grating. [2] Such a structure would provide substantial absorption of light in the middle subcell of a multi-junction device, while still allowing enough low-energy light to pass through the structure so the bottom cell remains well current matched with the other junctions. This structure is proposed to have over an order of magnitude increase in overall radiation tolerance while maintaining comparable beginning of life performance to the current technology.

In this presentation, we present a first experimental demonstration of this structure. The design combines a diffraction grating fabricated via nanosphere natural lithography [3], a low-index transparent spacer layer, and a DBR, which synergistically traps light inside the targeted subcell. This presentation will highlight processing techniques and challenges associated with fabricating a textured ultra-thin solar cell, while illustrating the effectiveness of integrating light trapping structures within an ultra-thin solar cell as an effort towards realizing high efficiency ultra-thin photovoltaic devices.

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9:40am **TF+EM+NS+SS-ThM6 Phosphorus as a *p*-Dopant in Pyrite FeS<sub>2</sub>, a Potential Low-cost earth-abundant Thin Film Solar Absorber**, *Bryan Voigt*<sup>1</sup>, W. Moore, D. Ray, M. Manno, University of Minnesota, Minneapolis; J.D. Jeremiason, Gustavus Adolphus College; L. Gagliardi, E.S. Aydil, C. Leighton, University of Minnesota, Minneapolis

Pyrite FeS<sub>2</sub> has long been considered an ideal absorber material for low-cost and sustainable thin film solar cells because it is composed of earth-abundant, non-toxic, inexpensive elements, has a suitable band gap (0.95 eV), and absorbs light so strongly that a 100-nm-thick film absorbs >90% of photons with energies above the band gap. Lack of doping control, however, has presented a barrier to realization of the *p-n* pyrite homojunction, *i.e.*, the simplest route to a pyrite solar cell. *Heterojunction* pyrite solar cells have proven to have disappointingly low efficiencies (~3%), surface conduction and leaky surface inversion layers being implicated as the culprit. While mitigation of pyrite surface conduction remains a challenge, doping has begun to yield to understanding, renewing optimism for a *p-n* pyrite homojunction solar cell. In particular, we have shown that rigorously phase-pure pyrite single crystals and thin films are exclusively *n*-type, due to a common dopant. Most recently, we have identified sulfur vacancies as this unintentional *n*-dopant, enabling robust control over *n*-doping levels in single crystals grown by chemical vapor transport (CVT). Progressing towards a *p-n* pyrite homojunction, here we demonstrate effective *p*-type doping in crystals by introducing phosphorus in the vapor phase during CVT growth. Increasing the phosphorus concentration from <0.1 ppm to 30 ppm evolves electronic conduction from *n*-type to *p*-type, with a clear and reproducible majority carrier inversion for concentrations >10 ppm. Typical transport properties of phosphorus-doped, *p*-type pyrite crystals include a hole thermal activation energy, room temperature resistivity, hole density, and mobility of ~170 meV, 3 Ω cm,  $2 \times 10^{18}$  cm<sup>-3</sup>, and 1 cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup>, respectively. Density functional theory calculations confirm that phosphorus substituted on the S site is an acceptor, predicting a defect level at 200 meV above the valence band maximum, in good agreement with experiment. With both *n*- and *p*-type doping control achieved, attempts at *p-n* pyrite homojunction solar cells become possible.

This work was supported by the customers of Xcel Energy through a grant from the Renewables Development Fund and in part by the National Science Foundation through the University of Minnesota MRSEC under DMR-1420013.

11:00am **TF+EM+NS+SS-ThM10 Relaxor-ferroelectric Thin Films for Energy Harvesting from Low-grade Waste-heat**, *Amrit Sharma*, B. Xiao, S.K. Pradhan, M.J. Bahoura, Norfolk State University

The need for efficient energy utilization is driving research into ways to harvest waste-heat which is ubiquitous, abundant and free. Thermal harvesting is a promising method for capturing freely available heat and converting it to a more usable form, such as electrical energy. Thermal harvesting for low power electronic devices using ferroelectric materials is one of the emerging areas of research because they possess spontaneous polarization and exhibit excellent piezoelectric as well as excellent pyroelectric coefficients. These materials are unique as they only sense time-dependent temperature change to generate electric power. We have grown lead-free BaZr<sub>0.2</sub>Ti<sub>0.8</sub>O<sub>3</sub> (BZT)/Ba<sub>0.7</sub>Ca<sub>0.3</sub>TiO<sub>3</sub> (BCT) multilayer heterostructures and studied the structural, dielectric, ferroelectric, pyroelectric and energy density characteristics. The BZT/BCT multilayer epitaxial heterostructures were grown on SrRuO (SRO) buffered SrTiO (STO) single crystal substrate by optimized pulsed laser deposition technique. The large angle x-ray scans showed only diffraction peaks from the substrate and pseudocubic reflections (00 $l$ ) from the multilayer heterostructure, confirming that these films are phase pure and epitaxial in nature. The atomic force microscopy (AFM) studies indicate that the surface roughness is low and that film growth is of high quality. The ferroelectric phase transitions have been probed above room temperature with relaxor behavior. The polarization versus electric field (P-E) measurement exhibits well-saturated hysteresis loop with maximum and

remnant polarization of 138 and 64 μC/cm<sup>2</sup>, respectively. Solid-state, thin-film devices, that convert low-grade heat into electrical energy, are demonstrated using pyroelectric Ericsson cycles, and their performance is optimized by independently enhancing pyroelectric coefficient and suppressing dielectric permittivity in compositionally graded heterostructures. Our findings suggest that pyroelectric devices may be competitive with thermoelectric devices for low-grade thermal harvesting.

11:20am **TF+EM+NS+SS-ThM11 Thermal Treatment Effects on the Thermoelectric Devices from Sn/Sn+SnO<sub>2</sub> Thin Films**, *Satilmis Budak*, E. McGhee, Z. Xiao, E. Barnes, R. Norwood, Alabama A&M University

Approximately two-thirds of energy is lost as waste heat; the direct harvest of this waste heat using thermoelectric (TE) materials has attracted worldwide interest. TE materials can convert waste heat from industrial processes, furnaces, and engine exhaust streams into useful electricity by the Seebeck effect. The energy conversion efficiency is shown by the dimensionless figure of merit, ZT, and  $ZT=S^2\sigma T/K$ , where S is the Seebeck coefficient,  $\sigma$  is the electrical conductivity, K is the total thermal conductivity, and T is the absolute temperature. The numerator  $S^2\sigma$  defines the power factor (PF), which primarily relates to the electric properties [1]. When operating as an energy-generating device, the TE device is termed a thermoelectric generator (TEG). The source of thermal energy manifests itself as a temperature difference across the TEG. When operating in a cooling or heating mode the TE device is termed a thermoelectric cooler (TEC). Similarly, the TE device produces heating or cooling that takes the form a heat flux which then induces a temperature difference across the TEC. TE devices are solid-state mechanisms that are capable of producing these three effects without any intermediary fluids or processes. For power generation applications TE devices are used in automobiles as exhaust gas waste heat recovery devices where thermal energy is scavenged along the exhaust line of a vehicle and converted into useful electricity [2]. The TE devices from 50 alternating layers of Sn/Sn+SnO<sub>2</sub> thin films were prepared using DC/RF Magnetron Sputtering. They were heat treated at different temperatures to form nanostructures to increase the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. Seebeck coefficient, van der Pauw resistivity, and thermal conductivity were used for the characterization. SEM/EDS was used to characterize the surface morphology of the films.

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11:40am **TF+EM+NS+SS-ThM12 Thermoelectric Properties of Efficient Thermoelectric Devices from Sb/Sb+SnO<sub>2</sub> Thin Films**, *Eshirdanya McGhee*, S. Budak, Z. Xiao, N. Caver, B. McNeal, Alabama A&M University

The thermoelectric (TE) concept could be seen as a perfect solution for recovering waste heat from engine exhaust and converts in to electric energy. TE generators are all solid-state devices that convert heat into electricity. Unlike traditional dynamic heat engines, TE generators contain no moving parts and are completely silent. Such generators have been used reliably for over 30 years of maintenance-free operation in deep space probes such as the Voyager missions of NASA. TE systems can be easily designed to operate with small heat sources and small temperature differences [1]. An ideal TE material behaves like an electron crystal and phonon glass, allowing a large temperature gradient across it while conducting electricity efficiently to generate a TE voltage. Significant progress in the TE performance of materials has been made by exploring ultra low thermal conductivity at high temperature and reducing thermal conductivity by nano-structuring, as well as by resonant doping and energy-dependent scattering of electrons [2]. The figure of merit ZT describes material performance. ZT depends on the thermoelectric material properties of Seebeck coefficient S, electrical conductivity  $\sigma$ , and thermal conductivity K, and  $ZT=S^2\sigma T/K$  where T is the temperature of the material [3]. TE devices from 50 alternating layers of Sb/Sb+SnO<sub>2</sub> thin films were prepared by DC/RF Magnetron Sputtering. TE devices were annealed at

<sup>1</sup> TFD James Harper Award Finalist



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different temperatures to form nano-structures to increase the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. For the characterization, Seebeck coefficient, van der Pauw resistivity, and thermal conductivity were used. The surface morphology was characterized using SEM/EDS.

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12:00pm **TF+EM+NS+SS-ThM13 3D Printed Triboelectric Nanogenerator**, I. Fattah, E. Utterback, **Naga Srinivas Korivi**, V. Rangari, Tuskegee University

We report on the development of polymer nanocomposite layers made by 3D printing. The nanocomposite is composed of polydimethylsiloxane (PDMS), barium titanate nanoparticles, and multi-walled carbon nanotubes. Flexible layers of this composite have been 3D printed using a commercial 3D printer, and function as triboelectric energy generators. To the best of our knowledge, this is the first report of a PDMS based triboelectric nanogenerator fabricated by 3D printing. The nanogenerators have been evaluated in contact and separation mode and produce a maximum of 2.6 Volts under pressure from a human finger.

The fabrication procedure involves sonicating barium titanate (BaTiO<sub>3</sub>, Skyspring Nanomaterials) and multi walled carbon nanotubes (MWCNT, Skyspring Nanomaterials) together in ethyl alcohol. This is followed by removing the excess ethyl alcohol, and manually grinding the nanoparticle powder to break any clusters. This is followed by mechanically blending liquid PDMS pre-polymer and its curing agent (~10:1 ratio by weight) with the nanoparticle powder in one beaker. Finally, the blend is filled into a dual plastic syringe, which is loaded onto an extrusion printing head of a commercial 3D printer (Hydra 16A, Hyrel LLC, USA). The printer reads a software file that defines the pattern or shape to be printed and dispenses the material from the syringe accordingly onto a base plate. For printing this composite, the base plate temperature was maintained between 75 – 90 °C, to allow curing within a few minutes. Once cured, the solid composite layers (270 μm thickness) can be peeled off the base plate.

The 3D printed PDMS-BaTiO<sub>3</sub>-MWCNT layers have been evaluated as triboelectric energy generation. In one embodiment, the 3D printed functions as the negatively charged layer in a contact-separation scheme. A polyimide sheet is used as positively charged layer. Carbon tapes are used as current collectors on both positive and negative charged layers. When these two layers are brought in contact with some pressure applied by a human finger, and then released, characteristic negative and positive voltage spikes are respectively observed. Peak voltages as high as 2.6 Volts have been obtained with the present 3D printed PDMS-BaTiO<sub>3</sub>-MWCNT layers. These observations indicate the applicability of this 3D printed composite in triboelectric energy generation.

**Acknowledgments:** This research was supported by the National Science Foundation grant #1827690.

## 2D Materials

### Room A216 - Session 2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA

#### Surface Chemistry, Functionalization, Bio, Energy and Sensor Applications

Moderator: Mark Edmonds, Monash University, Australia

2:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA1 Molecular Layers on Nanoporous Gold Electrodes**, *Elizabeth Landis*, College of the Holy Cross  
Nanoporous gold presents a surface with high conductivity and surface area, which makes it an interesting platform for surface chemistry. However, the nanoporous gold surface lacks the functionality necessary for many applications including sensing. We have investigated self-assembled thiol-based monolayers and the electroreduction of diazonium-based salts to form aryl molecular layers on nanoporous gold. We use infrared spectroscopy and cyclic voltammetry to show that the molecular layer ordering and density depends on the functionalization method, and the underlying nanoporous surface impacts molecular ordering and electron transfer properties.

2:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA2 Thermotropic Liquid Crystal (5CB) on Two-dimensional Materials**, *Paul Brown*, American Society for Engineering Education; *S. Fischer, J. Kotacz, C.M. Spillmann, D. Gunlycke*, U.S. Naval Research Laboratory

Current means of redirecting light often rely on either bulky mechanical gimbals or non-mechanical diffractive elements. The former often suffer from wear and are susceptible to failure, while the latter may have significant optical power confined within side lobes. One promising non-mechanical approach that can overcome present limitations in beam redirection incorporates liquid crystal (LC) for continuous, refractive steering. Nematogens, the molecules comprising the LC in a nematic phase, support inherent anisotropic optical and dielectric properties that result from local ordering of single molecules. Recent research suggests the possibility of including two-dimensional materials to act as both an alignment layer and electrode to LC. This offers the possibility of further reducing device dimensions and device response time. Yet little research has focused on the ground state properties of a nematogen interfacing with the two-dimensional substrate. In this talk, we present density functional theory results of the electronic properties of a well-known nematogen (5CB) interacting with graphene, boron nitride, and phosphorene. We also discuss the influence of an introduced single vacancy on the electronic properties of the composite system. We find that 5CB on phosphorene offers the strongest binding of the considered nanosheets. Moreover, we observe qualitatively different band alignments, and focus in particular on type I, which prohibits free carrier transfer between the substrate and nematic LC. Lastly, we discuss the impact of single vacancies on the performance of two-dimensional materials to operate as both an alignment layer and electrode for LC-based applications.

*This work has been supported by the Office of Naval Research, directly and through the U.S. Naval Research Laboratory.*

3:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA3 Is it Possible to Achieve Intra-molecular Resolution with Ambient AFM?**, *Vladimir Korolkov*, Oxford Instruments-Asylum Research; *S.C. Chulikov, M. Watkins*, University of Lincoln, UK; *P.H. Beton*, The University of Nottingham, UK

Although achieving molecular resolution is now almost a routine across various SPM imaging modes, resolving the actual molecular structure at the atomic level has only been accomplished with NC-AFM in UHV often at low temperatures and with a functionalized probe. Of course, the ultimate goal in SPM is to resolve the chemical structure of a molecule identifying each atom.

In this work we are presenting an approach to achieve intra-molecular resolution on adsorbed molecules in the ambient at room temperatures with a standard AFM cantilever with unmodified tip. We have discovered that using a combination of higher eigenmodes and low oscillation amplitudes (~3-5Å) of a standard Si-cantilever routinely provides ultra-high resolution on adsorbed molecules on surfaces<sup>1,2</sup> and bulk polymers<sup>3</sup>.

With this approach we have been able to observe both intra-molecular features and inter-molecular contrast in thin films of coronene and melem molecules on the surface of hexagonal boron nitride (hBN). In case of coronene, all six benzene rings have been resolved as well as underlying atomic lattice of hBN. Unlike coronene, melem forms molecular assemblies with square symmetry stabilized with in-plane strong hydrogen bonds between amino groups. We have observed a strong inter-molecular

contrast where the hydrogen bonds are expected to be. Similar to coronene, the observed intra-molecular contrast was associated with three triazine rings. We have used Probe particle model<sup>4</sup> to simulate our experimental AFM images and found very good agreement between them. In fact, PPM allowed us a correct interpretation of melem square phase assembly.

Both systems were studied at room and elevated temperatures where we observed phase transitions leading to thermodynamically stable systems. The experimental results are in excellent agreement with density functional theory calculations.

We believe the proposed approach, yet still in its infancy, could potentially provide a pathway to unambiguous identification of molecules on surfaces in the ambient on standard AFM systems.

<sup>1</sup>Korolkov et al., Nat. Chem., 2017

<sup>2</sup>Korolkov et al., Nat. Comm., 2017

<sup>3</sup>Korolkov et al., Nat. Comm., 2019

<sup>4</sup>Hapala et al., Phys. Rev. B 90, 085421

3:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA4 Tailoring Surface Properties via Functionalized Hydrofluorinated Graphene Compounds**, *Jangyup Son*, University of Illinois at Urbana-Champaign; *N. Buzov*, University of California at Santa Barbara; *S. Chen*, University of Illinois at Urbana-Champaign; *D. Sung*, Sejong University, Republic of Korea; *H. Ryu*, Seoul National University, Republic of Korea; *J. Kwon*, Yonsei University, Republic of Korea; *S. Kim, J. Xu*, University of Illinois at Urbana-Champaign; *S. Hong*, Sejong University, Republic of Korea; *W. King*, University of Illinois at Urbana-Champaign; *G.H. Lee*, Seoul National University, Republic of Korea; *A.M. van der Zande*, University of Illinois at Urbana-Champaign

Mixing compounds or alloys is an important process to tailor or enhance the intrinsic properties of materials such as chemical reactivity, mechanical strength, and electronic structure. In nanosystems, such as two-dimensional (2D) materials like graphene, transition metal dichalcogenides (TMDCs), and hexagonal boron nitride (hBN), where there is no distinction between the surface and the bulk, mixing of elements is also an important tool for tailoring the interaction of the material with its environment. A successful strategy for manipulating the chemical structures of 2D materials is the chemical functionalization of graphene with single elements such as H, O, N, and F. Yet, an even wider parameter space is possible by combining these functionalization species to produce ternary functionalized graphene compounds.

Here we present a new strategy for producing functionalized graphene compounds through the systematic control of the ratio between adatoms. We demonstrate tailored hydrofluorinated graphene (HFG) compounds via the sequential exposure of graphene to low-energy hydrogen plasma and xenon difluoride (XeF<sub>2</sub>) gas. We demonstrate reversible switching of the surface between completely hydrogenated graphene (HG) and fluorinated graphene (FG) as well as the intermediate ratio between two extremes. Moreover, we demonstrate pattern the surface functionalization on a single chip into chemically distinct materials (graphene, FG, HG, and HFG compounds).

Finally, with these patterned structures, we demonstrated tailoring of the surface and electronic properties of the 2D materials. First, the patterned structures enable direct comparisons of the relative surface properties such as wettability and surface friction. Additionally, the electrical properties of functionalized graphene compounds showed unusual recovery of electrical conductance during the partial transformation of FG to HFG, due to initial removal of existing F adatoms when exposed to hydrogen plasma. This study opens a new class of 2D compound materials and innovative chemical patterning that can lead to atomically thin 2D circuits consisting of chemically/electrically modulated regions.

4:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA7 Towards Higher Alcohol Synthesis from Syngas on 2D material-based catalysts: A First-Principles Study\***, *Tao Jiang, D. Le, T.S. Rahman*, University of Central Florida

Synthesis of higher alcohol from syngas has been of great interest owing to the limited petroleum resources and environmental concerns. Rational designing of cheap and efficient catalyst material for such synthesis is in great demand because of diminishing supply of the current state-of-the-art catalysts. Two dimensional (2D) materials are emerging with far-reaching potential for technical and industrial applications thanks to their unique properties, recent developments and improvement of production technologies. In this talk, we will discuss our recent work, based on first

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principles calculations, towards the unitization of 2D materials as catalysts for higher alcohol synthesis. In particular, defect laden hexagonal boron nitride (*dh*-BN) with N vacancies is excellent catalyst for hydrogenation of CO<sub>2</sub> towards ethanol formation, in the reaction pathway of which the crucial step for forming C<sub>2</sub> bond, i.e. reaction of adsorbed species CH<sub>3</sub>\* and CO\* to form CH<sub>3</sub>CO\*, is exothermic with reasonably low activation barrier (0.68 eV). On the other hand, we also find single layer of MoS<sub>2</sub> functionalized with small Au nanoparticle to catalyze CO hydrogenation reaction towards ethanol formation. Among all the elementary reactions, the important steps are the reaction of an adsorbed CH<sub>3</sub>\* and a CO\* molecule and the hydrogenation of acetyl to acetaldehyde (both are exothermic with activation barriers of 0.69 and 0.47 eV, respectively) to form C<sub>2</sub> species.[1] The results suggest that 2D materials are suitable candidates for higher alcohol synthesis. Full reaction pathways will be discussed together with results of Kinetic Monte Carlo simulations to shed light on the selectivity of the catalysts. Contact will be made with experimental data that validate our theoretical predictions.

[1] K. Almeida, K. Chagoya, A. Felix, T. Jiang et al, "Towards Higher Alcohol Formation using a single-layer MoS<sub>2</sub> activated Au on Silica: Methanol Carbonylation to Acetaldehyde", submitted

\*Work supported in part by DOE Grant DE-FG02-07ER15842

4:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA8 Proton Conductivity Properties of Electrospun Chitosan Nanofibers, Woo-Kyung Lee, J.J. Pietron, D.A. Kidwell, J.T. Robinson, C.L. McGann, S.P. Mulvaney, U.S. Naval Research Laboratory**

A major challenge of the 21<sup>st</sup> century will be to establish meaningful two-way communication between biology and electronics. The study of protonics, devices that mimic electronics but pass protons instead of electrons, seeks to bridge this gap. Protonic conductive materials (PCMs) are essential elements of these devices and we have demonstrated significant improvement in conductivity for chitosan PCMs when deposited as electrospun nanofibers. The observed improvements stem from both enhanced molecular alignment and from chemical doping due to the electrospinning carrier fluid, trifluoroacetic acid (TFA). We deposited electrospun chitosan nanofibers over palladium protodes and then used the helium ion microscope to isolate single nanofibers for detailed study. We observed that single chitosan nanofibers are strongly doped by TFA with x-ray photoelectron spectroscopy demonstrating extensively protonated nitrogen functionality. With the isolated, single chitosan nanofibers we observed that water uptake, fiber/electrode contact area, and doping concentration are critical parameters of protonic device performance and lead to increased conductivity (*i.e.* low resistivity). The average resistivity of single chitosan nanofibers is  $6.2 \times 10^4 \Omega\text{-cm}$ , approximately two orders of magnitude lower than the resistivity of cast chitosan PCMs (cast from acetic acid solutions not TFA). We have observed excellent agreement between theoretical models and experiment results that explore each of the contributions to the improved conductivity. In addition, the fabrication and measurement of ionic field-effect transistor of single chitosan fiber using conductive atomic force microscope will be discussed.

5:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA9 Sensor for Breath and Skin Diagnostics, Pelagia I Gouma, The Ohio State University**  
Resistive gas sensors have received a bad reputation of being largely non-selective.

Our work has produced a crystallo-chemical model for selective gas sensing by polymorphic

metal oxides. The reaction-based and ferro-electric poling sensing mechanisms are discussed

in detail. Novel processing methods to produce the respective nano sensors are presented along

with the device fabrication for the non-invasive diagnosis of gaseous biomarkers in human

and animal breath or skin. This sensor technology is expected to revolutionize medical diagnostics.

5:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA10 Symmetry Controlled Adsorption of Diodobenzene on MoS<sub>2</sub>, Zahra Hooshmand, University of Central Florida; P. Evans, P.A. Dowben, University of Nebraska - Lincoln; T.S. Rahman, University of Central Florida**

In a joint experimental and theoretical study, we have uncovered evidence of the importance of symmetry in the adsorption of the isomers of diiodobenzene on MoS<sub>2</sub>(0001). The intensity ratio of iodine to molybdenum

measured, as a function of exposure for different isomers of the diiodobenzene, show that while for ortho (1,2-) and para (1,4-) diiodobenzene the rate of adsorption at 100 K is very low, that for meta (1,3-) diiodobenzene is considerably more facile. We have applied dispersion corrected density functional theory-based calculations to understand the subtleties in the electronic structure and geometry of adsorption of these diiodobenzene isomers on MoS<sub>2</sub>(0001). All three isomers are found to weakly chemisorb with the same binding strength as well as adopt similar configurations. The calculated electron affinity of the three molecules also do not show a specific trend that would verify experimental data. However, analysis of the frontier orbitals indicate that those of 1,3-diiodobenzene are strongly affected by interactions with MoS<sub>2</sub>, while that of the other two isomers remain unchanged. Our results show that symmetry is the identifying factor in these adsorption characteristics. The results of frontier orbitals analysis confirm that for adsorption of (1,2-) and (1,4-) diiodobenzene a reduction in the symmetry of the adsorbent is needed. To further validate our conclusions, we compare the above results with that of the adsorption of the diiodobenzene isomers on defect-laden MoS<sub>2</sub>(0001).

\* Work support in part by DOE grant DE-FG02-07ER15842

5:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA11 Mechanistic Understanding of the CO Hydrogenation Reaction on Defect Engineered 2D-TaS<sub>2</sub> and 2D-MoS<sub>2</sub> Catalysts, Mihai Vaida, University of Central Florida**

Due to global energy demands, investigation of catalytic reaction mechanisms on novel catalytic materials that can lead to efficient production of storable fuels from sustainable inputs is of central importance. In this contribution the adsorption of CO and H<sub>2</sub> molecules, as well as the CO hydrogenation reaction are investigated on defect engineered two dimensional (2D) TaS<sub>2</sub> and MoS<sub>2</sub>. Crystalline 2D-TaS<sub>2</sub> and 2D-MoS<sub>2</sub> with surface area of 1 cm<sup>2</sup> are synthesized via a multistep process based physical vapor deposition on Cu(111). The surface composition, morphology, and electronic structure are investigated via Auger electron spectroscopy, low energy electron diffraction, scanning tunneling microscopy, scanning tunneling spectroscopy, and photoemission spectroscopy. The interaction of the molecules with the surface and the catalytic reaction mechanisms are investigated via temperature programmed desorption/reaction. No catalytic reactions have been observed on crystalline 2D materials. However, an enhanced catalytic activity is observed after the generation of sulfur vacancies via Ar sputtering. The CO hydrogenation on TaS<sub>2</sub> occurs on low coordinated Ta atoms through the formation of formyl radical (HCO) and formaldehyde (HCOH). On 2D-MoS<sub>2</sub>, the CO hydrogenation also occurs on low coordinated Mo atoms. However, in this case the formyl radical splits to form methyldyne radical (CH), which subsequently react with other CH radical to produce acetylene (C<sub>2</sub>H<sub>2</sub>).

## Chemical Analysis and Imaging Interfaces Focus Topic Room A120-121 - Session CA+NS+SS+VT-ThA

### Progress in Instrumentation and Methods for Spectro-microscopy of Interfaces

**Moderators:** Jinghua Guo, Lawrence Berkeley National Laboratory, Andrei Kolmakov, National Institute of Standards and Technology (NIST)

2:20pm **CA+NS+SS+VT-ThA1 Helium and Neon Ion Beams for the Imaging and Analysis of Interfaces, John A. Notte, C. Guillermier, F. Khanom, B. Lewis, Carl Zeiss PCS, Inc.**

**INVITED**  
The recently developed ORION NanoFab instrument provides a single platform with He<sup>+</sup>, Ne<sup>+</sup>, and Ga<sup>+</sup> focused ion beams. The gallium beam is a conventional FIB and offers high currents and high sputter yields for material removal applications such as sample preparation or exposing sub-surface features. The He and Ne ion beams originate from a sub-nanometer ionization volume of the gas field ion source (GFIS) and because of this, can be focused to remarkable small probe sizes, 0.5 nm and 1.9 nm respectively. The He beam is now well established for high resolution imaging with surface sensitivity, long depth of focus, and the ability to image insulating surfaces without a conductive overcoating. The helium beam has also been used successfully in a variety of nanofabrication tasks such as lithographic exposure of resist, fine sputtering, beam chemistry, and precision modification of materials. The neon beam with its intermediate mass provides a higher sputtering yield, and with that, the ability to perform SIMS analysis with an unprecedented small focused probe size. A newly integrated magnetic spectrometer enables analytical

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capabilities on this same platform, with a lateral resolution limited only by the collision cascade. Features smaller than 15 nm have been detected. Together these complementary imaging modes can be combined to provide insights of morphology and composition at the smallest length scales.

In this talk the underlying technology of the NanoFab-SIMS will be introduced, as will the physics of the beam-sample interactions. The bulk of the presentation will provide a survey of results, both published and new, demonstrating how this instrument can serve in a variety of applications related to interfaces.

3:00pm **CA+NS+SS+VT-ThA3 Interfacial Studies using Ambient Pressure XPS**, *Paul Dietrich*, A. Thissen, SPECS Surface Nano Analysis GmbH, Germany **INVITED**

Over the last decades XPS under Near Ambient Pressure (NAP) conditions has demonstrated its promising potential in a wide variety of applications. Starting from operando studies of surface reactions in catalysis, the applications soon have been enhanced towards studies of processes at liquid surfaces, mainly using freezing/melting cycles, liquid jets or liquid films on rotation disks or wheels. Since more than 15 years, the need for basic studies of fundamental solid-liquid interface chemistry has attracted growing interest. Dip-and-pull experiments at synchrotron sources finally also demonstrated, that in-situ and operando XPS in electrochemical experiments can be realized, significantly contributing to the basic understanding of modern energy converting or storing devices, like batteries, fuel cells, etc.

The development of pure laboratory NAP-XPS systems with optimized sample environments, like special sample holders, Peltier coolers and operando liquid cells combined with full automation and process control provides possibilities for preparation and analysis of a multitude of liquid samples or solid-liquid interfaces on a reliable daily base.

Interfaces of semiconductors with organic solvents are important for production processes and device operation. The first example presented shows the simplicity of obtaining relevant results on Silicon in different organic solvents without the need of highly sophisticated set-ups or special excitation sources beyond Al K $\alpha$ .

Another example shows an operando study of metal corrosion in acetic acid. Moreover a versatile set-up is presented, allowing for studies of solid-electrolyte interfaces for example in Lithium ion batteries as a simple laboratory experiment.

Finally an outlook is given on the future perspective of applications and scientific contributions of routine operando XPS.

4:00pm **CA+NS+SS+VT-ThA6 Operando Spectroscopy and Microscopy of the Electrode-Electrolyte Interface in Batteries**, *Feng Wang*, Brookhaven National Laboratory **INVITED**

Real-time tracking structural/chemical changes of electrodes in batteries is crucial to understanding how they function and why they fail. However, in real battery systems electrochemical/chemical reaction occurs at varying length scales, leading to changes not only in the bulk but often locally at electrolyte/electrode interface. *In situ* X-ray techniques are typically employed for studying structural changes in the bulk electrodes and often limited by their poor spatial resolution in probing local changes at interface. Herein, we present our recent results from developing new operando spectroscopy and microscopy techniques, specialized for studying electrochemical/chemical reaction and structural modification of the solid-electrode surface and interface, *in the presence of the electrolyte and during battery operation*. Examples will be given to show how interfacial reaction during battery operation is visualized directly, allowing gaining insights into electrode/electrolyte design for practical use in batteries. New opportunities for combining *first principles* simulation and deep machine learning to complement and guide experiments will also be discussed.

4:40pm **CA+NS+SS+VT-ThA8 Ultrasensitive Combined Tip- and Antenna-Enhanced Infrared Nanoscopy of Protein Complexes**, *B.T. O'Callahan*, Pacific Northwest National Laboratory; *M. Hentschel*, University of Stuttgart, Germany; *M.B. Raschke*, University of Colorado Boulder; *P.Z. El-Khoury*, Pacific Northwest National Laboratory; *Scott Lea*, Pacific Northwest National Laboratory

Surface enhanced infrared absorption (SEIRA) using resonant plasmonic nanoantennas enables zeptomolar detection sensitivity of (bio)analytes, although with diffraction limited spatial resolution. In contrast, infrared scattering-scanning near-field optical microscopy (IR s-SNOM) allows simultaneous imaging and spectroscopy with nanometer spatial resolution

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through vibrational coupling to the antenna mode of a probe tip. In this presentation, we discuss our approach combining these two methods to image both continuous and sparse distributions of ferritin protein complexes adsorbed onto IR-resonant Au nanoantennas. The joint tip- and antenna-enhancement yields single protein complex sensitivity due to coupling with the vibrational modes of the bioanalytes. The coupling is revealed through IR s-SNOM spectra in the form of Fano lineshapes, which can be modelled using coupled harmonic oscillators. Through simulations of the recorded hyperspectral images, we extract the optical signatures of protein complex monolayers. This work paves the way for single protein identification and imaging through a combination of tip and antenna-enhanced IR nanoscopy.

5:00pm **CA+NS+SS+VT-ThA9 Imaging and Processing in Liquid Gel Solutions with Focused Electron and X-ray Beams**, *T. Gupta*, National Institute of Standards and Technology (NIST); *P. Zeller*, *M. Amati*, *L. Gregoratti*, Elettra - Sincrotrone Trieste, Trieste, Italy; *Andrei Kolmakov*, National Institute of Standards and Technology (NIST)

Gels are porous polymeric scaffolds that can retain high volume fraction of liquids, can be easily functionalized for a specific need, can be made biocompatible and therefore, found numerous applications in drugs delivery, tissue engineering, soft robotics, sensorics, energy storage, etc. We have recently proposed a technique for micro-patterning and high-resolution additive fabrication of 3D gel structures in natural liquid solutions using electron and soft X-ray scanning microscopes [1]. The core of the technology is the employment of ultrathin electron (X-ray) transparent molecularly impermeable membranes that separate high vacuum of the microscopes from a high-pressure fluidic sample. In this communication, we report on effects of the beam and exposure conditions on to the degree of crosslinking of pristine and composite PEGDA hydrogels. We found that cross-linking occurs at very low irradiation doses. The size of the crosslinked area saturates with the dose and bond scission occurs at elevated radiation doses what has been supported with O 1s and C 1s XPS spectra evolution and prior research [2]. These chemically modified regions can be selectively etched what enables an additional partnering option for the gelled features with a spatial resolution of ca 20 nm. Finally, we defined the imaging conditions for guest particles in composite hydrogels in its liquid state during the crosslinking process. We were able to observe the electrophoretic migration of sub 100 nm Au nanoparticles inside the gel matrix.

## References

[1] T. Gupta *et al.*, "Focused Electron and X-ray Beam Crosslinking in Liquids for Nanoscale Hydrogels 3D Printing and Encapsulation," *arXiv preprint arXiv:1904.01652*, 2019.

[2] N. Meyerbröcker and M. Zharnikov, "Modification and Patterning of Nanometer-Thin Poly (ethylene glycol) Films by Electron Irradiation," *ACS applied materials & interfaces*, vol. 5, no. 11, pp. 5129-5138, 2013.

5:20pm **CA+NS+SS+VT-ThA10 In Situ TEM Visualization of Solution-based Nanofabrication Processes: Chemical Wet-etching and Capillary Forces**, *Utkur Mirsaidov*, National University of Singapore, Singapore **INVITED**

Controlled fabrication of 3D nanoscale materials from semiconductors is important for many technologies. For example, scaling up the density of the transistors per chip requires the fabrication of smaller and smaller vertical nanowires as channel materials [1]. Two key processes essential to the fabrication of these devices is a precise etching of the nanostructures and the damage-free solution based cleaning (damage occurs during post-clean drying due to capillary forces). However, very little is known about both of these processes because it is extremely challenging to visualize etching and cleaning with solutions directly at the nanoscale. Here, using in situ liquid phase dynamic TEM imaging [2-4], we first describe the detailed mechanisms of etching of vertical Si nanopillars in alkaline solutions [5]. Our design of liquid cells includes a periodic array of patterned nanopillars at a density of  $1.2 \times 10^{10} \text{ cm}^{-2}$ . We show that the nanoscale chemical wet-etch of Si occurs in three stages: 1) intermediates generated during alkaline wet etching aggregate as nanoclusters on the Si surface, 2) then the intermediates detach from the surface before 3) dissolving in the etchant.

Next, we describe the capillary damage of these high-aspect-ratio Si nanopillars during drying after the solution-phase cleaning. Our results reveal that drying induced damage to nanopillars occurs in three distinct steps. First, as water evaporates from the surface patterned with nanopillars, water film thins down non-uniformly leaving small water nanodroplets trapped between the nanopillars. Second, the capillary forces induced by these droplets bend and bring the nanopillars into contact with each other at which point they bond together. Third, droplets trapped

between the nanopillars evaporate leaving the nanopillars bonded to each other. We show that even after the nanodroplets finally evaporate, interfacial water covering the nanopillars act as a glue and holds the pillars together.

Our findings highlight the importance of being able to visualize the processes relevant to nanofabrication in order to resolve the failure modes that will occur more frequently as the device sizes get even smaller in the future.

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[3] H. Zheng et al, *Science* 324 (2009), p. 1309.

[4] U. Mirsaidov et al, *Proc. Natl. Acad. Sci. U.S.A.* 109 (2012), p. 7187.

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## Advanced Ion Microscopy and Ion Beam Nano-engineering Focus Topic

Room B231-232 - Session HI+NS-ThA

### Emerging Ion Sources, Optics, and Applications

**Moderators:** Gregor Hlawacek, Helmholtz-Zentrum Dresden Rossendorf, Germany, Shida Tan, Intel Corporation

2:20pm **HI+NS-ThA1 Cold Atom Ion Sources, Jabez McClelland, J.R. Gardner, W.R. McGehee**, National Institute of Standards and Technology (NIST); *A. Schwarzkopf, B.J. Knuffman, A.V. Steele, zeroK NanoTech Corp.*

**INVITED**

Ionization of laser-cooled atoms has emerged as a new approach to creating high brightness ion sources for applications such as focused ion beam (FIB) microscopy, milling, and secondary-ion mass spectrometry (SIMS). Conventional sources, such as the Ga liquid metal ion source (LMIS) or the gas field ionization source (GFIS), attain brightness by emitting from a very sharp tip. In contrast, cold atom sources attain high brightness through reducing the transverse velocity spread of the ions. With the ultracold, microkelvin-range temperatures achievable with laser cooling, the corresponding velocity spread can lead to a brightness significantly higher than typical LMIS values. Moreover, the phase-space shape of the emittance of the source – narrow in velocity, wide in space – brings new opportunities for ion optical design. For example, high currents can be obtained without the high current density present in sharp tip sources. This can result in reduced Coulomb effects, such as increased emittance and broadened energy spread (Boersch effect). Other advantages of this type of source include insensitivity to contamination, access to new ionic species, inherent isotopic purity, and fine control over emission, down to the single ion level. To date, sources have been demonstrated with Cr,<sup>1</sup> Li,<sup>2</sup> Rb,<sup>3</sup> and Cs<sup>4,5</sup> ions, realizing novel species and nanometer-scale spot sizes. In this talk I will review progress in the field and discuss recent developments in Li ion sources and applications.

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3:00pm **HI+NS-ThA3 Silicon Lithiation by Direct-writing with a Focused Li<sup>+</sup> ion Beam, W.R. McGehee, Evgheni Strelcov, V. Oleshko, C. Soles, N.B. Zhitenev, J.J. McClelland**, National Institute of Standards and Technology (NIST)

Improving the performance of Li-ion batteries requires understanding and controlling nanoscale ion transport at the level of interfaces, grain boundaries and defects. While in the last decades a range of electron and

scanning probe microscopy techniques have been developed for probing local transport, no reliable method exists for quantitative and controllable nanoscale lithiation. Moreover, wet-cell electrochemical lithiation is significantly complicated by electrolyte decomposition, formation of solid-electrolyte interfacial (SEI) layer and parasitic reactions running in parallel to lithium insertion.

Building on our previous work,<sup>1</sup> here we introduce a new method of direct-write quantitative lithiation of battery-relevant materials in vacuo, in the absence of SEI or liquid electrolyte. To benchmark the technique, we use a focused, several keV Li<sup>+</sup>-ion beam to inject lithium into 35-nm thick crystalline Si membranes with a sub-micron lateral precision. The lithiated regions, undergoing morphological, structural, chemical and functional transformations, were characterized with a combination of electron and scanning probe microscopy techniques. We observed saturation of interstitial lithium in the silicon membrane at  $\approx 10\%$  dopant number density and spill-over of excess lithium onto the membrane's surface. The implanted Li<sup>+</sup> remains electrochemically active, and the spill-over effect can possibly be avoided by cooling the sample. The presented method is especially useful for probing non-equilibrium and low-concentration phases of lithiated materials that form because of incomplete lithium extraction or during initial states of pristine anode lithiation. Focused ion beam lithiation will enable controlled studies and improved understanding of Li<sup>+</sup> ion interaction with local defect structures and interfaces in electrode and solid-electrolyte materials.

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W.R.M. and E.S. contributed equally.

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3:20pm **HI+NS-ThA4 A New FIB for Deterministic Single Ion Implantation, Nathan Cassidy**, UK National Ion Beam Centre, University of Surrey, UK; *D. Cox*, Advanced Technology Institute, University of Surrey, UK; *R. Webb*, UK National Ion Beam Centre, University of Surrey, UK; *B. Murdin*, Advanced Technology Institute, University of Surrey, UK; *B. Blenkinsopp, I. Brown*, Ionoptika Ltd., UK; *R. Curry*, The Photon Science Institute, University of Manchester, UK

Single isolated dopant atoms implanted into solid state devices have been shown to be a viable architecture for quantum technologies. Ion implantation provides many advantages as a manufacturing method for such devices, such as speed and scalability, however controlling the number of implanted ions with single-ion precision poses a significant challenge. In this paper we will present a new instrument designed for the deterministic implantation of single ions with high precision.

The SIMPLE (Single Ion Multi-species Positioning at Low Energy) tool, is a new focused ion beam tool in operation designed for the manufacture of quantum technologies. The tool has a 25kV LMIG set up for femtoAmp sample currents, with ultra-fast beam blanking, neutral blocking and a highly efficient secondary electron detection system. Deterministic ion implantation is achieved through extraction of single ions through fast beam blanking with low currents, ion implant detection through collection of secondary electron (SE) signal from the target and high spatial precision in ion placement.

To date we have demonstrated > 85% probability of implanting a single Bi<sup>+</sup> ion into silicon without error, with a 20nm beam determining dopant placement precision. This surface secondary electron detection efficiency has been validated through simultaneous measurements of a transmitted electron signal, achieved by implanting through thin lamellae. The ion placement precision has been determined through imaging of ion induced damage on highly oriented pyrolytic graphite (HOPG) surfaces. Much work has taken place maximizing the detection efficiency for secondary electrons and investigating the factors which affect the SE yield.

Currently the system is running with Bi source, and there are In sources available. Alongside the development of the instrument there is also research into developing a series of liquid-metal ion sources for elements with optical and quantum applications including P, Te, Se and Cd. A second SIMPLE tool has also been installed at the UK National Ion Beam Centre, which operates with a 20kV duoplasmatron arc source, capable of 50nm spot sizes. SIMPLE #2 will initially operate with nitrogen source for the fabrication of NV centres in diamond.

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4:00pm **HI+NS-ThA6 Technology and Applications of a Plasma Ion Source with User-selectable Ion Species**, *Gregory Schwind, S.M. Kellogg, J. Stiller, M. Doud, C. Rue, B. Van Leer*, Thermo Fisher Scientific **INVITED**

The focused ion beam (FIB) has become an indispensable tool for micro- and nano-machining applications. Due to its high brightness and ease of use, the gallium liquid metal ion source (LMIS) has been the source of choice over much of the nearly four decades of FIB history. At the beginning of this decade, a new generation FIB system based on the inductively coupled plasma (ICP) ion source was brought to market, offering beam current and throughput 20 times greater than LMIS-based systems. A next generation plasma source has been developed [1], offering the option to change the ion beam species by switching the feed gas supplied to the plasma source. The ability to dynamically change ion species—for example from a noble gas such as argon to an electronegative species such as oxygen—creates new design challenges for the source, the FIB optical subsystem, and the platform as a whole. Both empirical measurements and numerical simulations were used to better understand the species-specific performance of the source design. Results show that the emission properties depend on both the ion species and the plasma density, which lead to orienting the system design around specific modes of operation optimally suited to each species, FIB current and landing energy [2].

Several new and exciting application areas are enabled by the ability to switch FIB ion species dynamically. Ion-surface interactions such as sputtering, implantation, and the creation of an amorphous damage layer depend on the ion's momentum [3], which in turn depends on ion mass. Furthermore, chemical reactivity between the incoming ion and the target surface seems to play a role in the surface modification process in some instances. Several FIB application examples illustrating these interdependencies will be shown.

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4:40pm **HI+NS-ThA8 Neutral Helium Microscopy**, *Bodil Holst*, University of Bergen, Norway

Neutral helium microscopy is a new imaging technique currently under development. In a neutral helium microscope a beam of neutral helium atoms is created through supersonic expansion from a nozzle and focussed onto the surface to create a scanning instrument. The resolution is determined by the beam spotsize on the surface. The neutral helium microscope has several advantages: the very low energy of the beam (less than 0.02 eV compared to several keV for helium ion or electron microscope), charge neutrality, and inertness of the helium atoms, a potential large depth of field, and the fact that at thermal energies the helium atoms do not penetrate into any solid material. This opens the possibility, among others, for the creation of an instrument that can measure surface topology on the nanoscale, even on surfaces with high aspect ratios. The helium microscope currently exist in two configurations: The pinhole microscope and the zone plate microscope, both are covered in this paper. We begin with a series of images which demonstrate and explores the unique contrast mechanisms of the new instrument. This is followed by a general discussion of helium microscope designs and resolution.

5:00pm **HI+NS-ThA9 GaBiLi Liquid Metal Alloy Ion Sources for Advanced Nanofabrication**, *P. Mazarov*, RAITH GmbH, Germany; *T. Richter*, L. Bruchhaus, *W. Pilz*, R. Jede, Raith GmbH, Germany; *Yang Yu*, R.M. Schmid, J.E. Sanabia, Raith America, Inc.; *L. Bischoff*, Helmholtz Zentrum Dresden-Rossendorf, Germany; *G. Hlawacek*, Helmholtz-Zentrum Dresden Rossendorf, Germany

Nanofabrication requirements for FIB technologies are specifically demanding in terms of patterning resolution, stability and the support of new processing techniques. Additionally, the type of ion defines the nature of the interaction mechanism with the sample and thus has significant consequences on the resulting nanostructures [1]. Therefore, we have extended the technology towards the stable delivery of multiple ion species selectable into a nanometer scale focused ion beam by employing a liquid metal alloy ion source (LMAIS) [2]. This LMAIS provides single and multiple charged mono- as well as polyatomic ion species of different masses, resulting in significantly different interaction mechanisms. Nearly half of the elements of the periodic table are thus made available in the FIB technology as a result of continuous research in this area [3]. This range of ion species with different mass or charge can be beneficial for various nanofabrication applications. Recent developments could make these sources to an alternative technology feasible for nanopatterning challenges. In this contribution, the operation principle, the preparation and testing process as well as prospective domains for modern FIB applications will be presented. As an example we will introduce the GaBiLi LMAIS [4]. It enables high resolution imaging with light Li ions and sample modification with Ga or heavy polyatomic Bi clusters, all coming from one ion source. For sub-10 nm focused ion beam nanofabrication and microscopy, the GaBiLi-FIB or the AuSiGe-FIB could benefit of providing additional ion species in a mass separated FIB without changing the ion source.

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5:20pm **HI+NS-ThA10 Focused Ion Beams in Biology: How the Helium Ion Microscope and FIB/SEMs Help Reveal Nature's Tiniest Structures**, *Annalena Wolff*, Central Analytical Research Facility, Institute for Future Environments, Queensland University of Technology (QUT), Brisbane QLD 4000, Australia; *N. Klingner*, Helmholtz Zentrum Dresden-Rossendorf, Germany; *W. Thompson*, HeelionicsLLC; *Y. Zhou*, Queensland University of Technology (QUT), Australia; *J. Lin*, Affiliated Stomatological Hospital of Xiamen Medical College, China; *Y. Peng*, CSIRO Manufacturing, Australia; *J. Ramshaw*, St. Vincent's Hospital, University of Melbourne, Australia; *Y. Xiao*, The Australia-China Centre for Tissue Engineering and Regenerative Medicine (ACCTERM), Queensland University of Technology, Australia

Focused Ion Beam (FIB) devices such as the Helium Ion Microscope (HIM) as well as FIB/SEMs are increasingly popular within the biological sciences in recent years. High resolution imaging of uncoated non-conductive samples with the HIM helps reveal nature's tiniest structures while the FIB/SEM allows to prepare TEM lamellae, 3D reconstruct the sample or reveal sub surface structures with nanometre precision.

This presentation shows how the HIM as well as FIB/SEMs can be used in biological sciences to reveal nature's tiniest structures. The presented work then focuses on the underlying ion-solid interactions and the effect of ion beam parameters on heating induced by ion beams. The work presented here deals with gallium ion solid interactions, however the broader results are applicable to any type of FIB including the helium ion microscope (HIM) and plasma FIBs. The interactions of gallium ions in skin were simulated using Monte Carlo methods, finite element simulations and numerical modelling for different beam parameters. The program SRIM [4] was used to obtain theoretical results which permit estimation of the ion beam induced temperature increases, using the physical principles of Fourier's law of conductive heat transfer.

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The technique was tested on collagen, a soft biological material which is commonly used in biomedical applications. Collagen was chosen as a suitable test sample as it loses its fibrillary structure when denaturated by heat, permitting damage to easily be recognized. Cross-sections and TEM lamellas were prepared from non-embedded collagen with conventional FIB processing parameters as well as heat reducing FIB parameters.

The results also show that heat damage can be prevented by reducing the local dose rate and area underneath the ion beam. Using lower acceleration voltages allows the operator to select higher local dose rates (ion beam currents) and minimized processing times. A TEM comparison of a microtome prepared lamella and a FIB prepared lamella (using different heat reducing parameters) shows that the fibrillar structures can be maintained, and heat damage avoided. The approach described here can be used to determine suitable parameters for other soft materials.

The authors acknowledge scientific and technical assistance of Peter Hines, Jamie Riches, Rachel Hancock, and Ning Liu and the facilities at the Australian Microscopy & Microanalysis Research Facility (AMMRF) at the Central Analytical Research Facility (CARF), Queensland University of Technology, Brisbane, Australia.

## Frontiers of New Light Sources Applied to Materials, Interfaces, and Processing Focus Topic Room A210 - Session LS+AC+NS-ThA

### Photon Science for Imaging Materials from the Meso- to the Nanoscale

**Moderator:** Maya Kiskinova, Elettra-Sincrotrone Trieste, Italy

2:20pm **LS+AC+NS-ThA1 Triplet Dynamics in Photovoltaic Materials Measured with Time Resolved X-Ray Spectroscopies**, *R. Costantini*, University of Trieste; *R. Faber*, Technical University of Denmark; *A. Cossaro*, *A. Verdini*, *L. Floreano*, CNR - Istituito Officine Materiali; *C. Haettig*, Ruhr-University Bochum, Germany; *A. Morgante*, University of Trieste, Italy; *S. Coriani*, Technical University of Denmark; ***Martina Dell'Angela***, CNR - Istituto Officine Materiali, Italy **INVITED**

Singlet exciton fission (SF) is a multiexciton generation process in organic molecules, where an optically excited singlet exciton is converted into two triplet excitons. The exploitation of this mechanism has been shown capable of boosting the efficiency of solar energy conversion, and it has been proposed as a mean for exceeding the Shockley-Queisser limit of efficiency of solar cells. In the last decade, several studies have investigated different chromophores to identify the ones suitable to produce high yield SF and long living triplets. Such studies spanned from the fundamental to the applicative approach, also dealing with the optimization of the interfaces with the other materials in the device in order to achieve an overall increased efficiency of the charge transport. In particular, the study of the dynamics of the triplet states, when formed and transported across all the interfaces, is crucial for modelling the charge transport properties in a working device. Here we present a new experimental approach to measure the triplet dynamics at the picosecond timescale, that uses the advantage of chemical sensitivity with respect to conventional optical techniques, thus offering the possibility of tracking the dynamics of the triplet states across different materials. We exploit the chemical selectivity of X-ray absorption spectroscopy (XAS) in an optical pump/X-ray probe experiment at a pump-probe setup that we developed at the Elettra synchrotron and with the support of novel implemented calculation methodologies. We studied triplet dynamics in pentacene thin films (the prototypical singlet fission material) with lifetime of about 300ps.

3:00pm **LS+AC+NS-ThA3 Synchrotron X-Ray Tomography to Understand Structure and Physical Transformations in Solid State Batteries**, *Kelsy Hatzell*, *M.B. Dixit*, Vanderbilt University **INVITED**

The increasing demand for portable electronics, stationary storage, and electric vehicles is driving innovation in high-energy density batteries. Solid electrolytes that are strong enough to impede lithium dendrite growth may enable energy dense lithium metal anodes. Currently, the power densities of all-solid state batteries is limited because of ineffective ion transport and chemical and physical decomposition at solid|solid interfaces. The nature of ionic transport at intrinsic and extrinsic interfaces is important for mitigating chemical and structural instabilities. Extrinsic interface instabilities are responsible for high interfacial resistances. In order to displace liquid electrolytes, new materials and engineering strategies need to be developed to negate these degradation pathways. New insight into the governing physics that occurs at these interfaces are critical for

developing engineering strategies for the next generation of energy dense batteries [1,2]. However, buried solid|solid interfaces are notoriously difficult to observe with traditional bench-top and lab-scale experiments. In this talk I discuss opportunities for tracking phenomena and mechanisms in all solid state batteries *in-situ* using advanced synchrotron techniques. Synchrotron techniques that combine reciprocal and real space techniques are best equipped to track relevant phenomena with adequate spatial and temporal resolutions.

## Nanometer-scale Science and Technology Division Room A222 - Session NS-ThA

### SPM for Functional Characterization

**Moderators:** Volker Rose, Argonne National Laboratory, Renu Sharma, National Institute of Standards and Technology (NIST)

2:20pm **NS-ThA1 Interatomic Force Laws That Evade Dynamic Measurement**, *John Sader*, University of Melbourne, Australia **INVITED**  
Atomically-resolved imaging and force measurements using the atomic force microscope (AFM) are performed most commonly in a frequency-modulation (FM) mode. This is achieved by configuring the AFM cantilever as an oscillator, enabling highly sensitive frequency detection with quasi real-time readout. Use of FM-AFM has led to spectacular results, including direct observation of the atomic structure of complex molecules and quantification of chemical and frictional forces at the atomic scale.

In this talk, I will briefly review the theory underpinning FM-AFM force measurements that allows conversion of the measured frequency shift to the interaction force law experienced by the cantilever tip. This will be following by new research [1] showing that this force conversion capability is directly regulated by the shape of the interaction force law – an effect that depends critically on the oscillation amplitude used. Rapidly varying interatomic force laws, which are common in nature, can lead to unphysical results. A mathematical theory is derived that enables reliable force measurements in practice. The validity of this theory is demonstrated by comparison to atomically-resolved measurements.

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3:00pm **NS-ThA3 Intermittent Contact Resonance Atomic Force Microscopy (icr-Afm) for Nanoscale Mechanical Property Characterization**, *Gheorghe Stan*, National Institute of Standards and Technology **INVITED**

In the last two decades, significant progress has been made on developing new dynamic atomic force microscopy-based methods for nanoscale mechanical properties measurements. The changes in the tip-sample contact mechanics during scanning uniquely modify the high-frequency response of the AFM cantilever and much effort is dedicated to correctly retrieve the sample mechanical properties from the measured signal. Recently in a newly proposed dynamic AFM method, namely the intermittent-contact resonance atomic force microscopy (ICR-AFM), the contact stiffness measurement capability of the conventional contact resonance AFM (CR-AFM) was paired with the less-invasive surface probing of a force-controlled intermittent AFM mode. As an AFM tip goes in and out of contact with the sample during scanning, the change in the tip-sample contact stiffness is observed in the change of the eigenmode frequencies of the cantilever and a fast detection is required to measure the frequency changes during each tap. By collecting the depth dependence of the contact resonance frequency at each point in the scan, a three-dimensional (3D) data volume is generated. This data can be used to obtain nanoscale tomographic views of the sub-surface elastic properties of a material. The involved tip-sample contact mechanics also poses some challenges for samples with edge geometries. A very convenient and robust method to address these types of contact geometries was found in the form of the conjugate gradient method applied to contact mechanics. In this talk, ICR-AFM implementation, measurements, and necessary contact mechanics models will be discussed for mechanical property characterization of thin films and nanostructures.

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4:00pm **NS-ThA6 Novel Approaches Towards Cantilevers for Functional Multiparametric AFM Characterization**, *Georg Ernest Fantner, N. Hosseini, M. Neuenschwander, B. Ghadiani*, École Polytechnique Fédéral de Lausanne, Switzerland

The cantilever is arguably the most important part in the measurement chain of an atomic force microscope (AFM), because it transduces the interaction with the sample to a measurable quantity. While a large variety of different cantilevers are available for different AFM modes, most of these cantilevers use the same concepts as the first AFM cantilevers developed 30 years ago. The progress in AFM towards techniques such as high-speed AFM and multiparametric imaging puts new demands on the AFM cantilevers. In this talk I will discuss several ways we are exploring to increase the performance of AFM cantilevers by using non-standard materials, fabrication processes and actuation schemes. Applications of these new cantilevers are high-speed AFM multi-parametric imaging, and correlated microscopy.

4:20pm **NS-ThA7 Fluid Handling using Scanning Probe Lithography for Nanocombinatorics**, *V. Saygin, N. Alsharif, Keith A. Brown*, Boston University

Scanning probes have been widely applied as characterization tools due to their high resolution and versatility. In parallel with the development of these capabilities, scanning probe lithography (SPL) has been advanced such that it is now capable of directly writing nanoscale domains of soft materials such as polymers, a capability that can be massively parallelized across centimeter scales through the use of cantilever-free scanning probe arrays. In this talk, we will discuss recent advances in the development of nanoscale fluid handling using scanning probes and describe how these advances allow for the realization of libraries for nanocombinatorial studies. Despite the utility of these approaches, operating with nanoscale domains of fluid raises interesting challenges in terms of managing capillary phenomena, evaporation, and deterministically directing fluid transfer. In order to address these, we have performed a series of studies using atomic force microscopy to explore nanoscale fluid dynamics. After being written, polymer features can function as reactors for subsequent chemistry or as samples for further characterization. We explore the opportunities and challenges inherent to this class of experiment and highlight recent discoveries made using such libraries. While the majority of functional explorations using scanning probes center around use of these instruments as characterization tools, the concept that scanning probes can also prepare combinatorial libraries is becoming increasingly common and providing new avenues for nanoscale science.

4:40pm **NS-ThA8 Accuracy of Tip-sample Interaction Measurements Using Dynamic Atomic Force Microscopy Techniques**, *O.E. Dagdeviren, Udo D. Schwarz*, Yale University

Atomic force microscopy (AFM) is a versatile surface characterization method that can map a sample's topography with high spatial resolution while simultaneously interrogating its surface chemistry through the site-specific high-resolution quantification of the forces acting between the sample and the probe tip. Thanks to considerable advances in AFM measurement technology, such local measurements of chemical properties have gained much popularity in recent years. To this end, dynamic AFM methodologies are implemented where either the oscillation frequency or the oscillation amplitude and phase of the vibrating cantilever are recorded as a function of tip-sample distance and subsequently converted to reflect tip-sample forces or interaction potentials. Such conversion has, however, been shown to produce non-negligible errors when applying the most commonly used mathematical conversion procedures if oscillation amplitudes are of the order of the decay length of the interaction [1]. The degree of divergence from actual values may also critically depend on both the overall strength of tip-sample interaction and the distance at which the interaction is obtained [2]. These systematic errors can, however, be effectively eliminated by using oscillation amplitudes that are sufficiently larger than the decay length of the interaction potential.

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5:00pm **NS-ThA9 Utilizing AFM to Study the Effect of Malaria-derived EVs on the Mechanical and Morphological Properties of Red Blood Cells**, *Irit Rosenhek-Goldian, E. Dekel, Y. Ohana, S. Maihib, S.R. Cohen, N. Regev-Rudzikib*, Weizmann Institute of Science, Israel

The deformability of Red Blood Cells (RBCs) is critical for the function of the cell and its viability. RBCs deform substantially and repeatedly when

passing through narrow capillaries. There is growing evidence that RBC deformability is impaired in some pathological conditions. This is the case when the human malaria parasite invades these cells, leading to the secretion of Extracellular Vesicles (EVs) whose mechanistic effect on healthy RBCs is unknown.

We have applied atomic force microscopy (AFM) to study the mechanical changes occurring in cells treated with malaria-derived EVs, as well as morphological transformations in the cellular cytoskeleton. Mechanical measurements were made at physiological temperature without covalent linkage of the cells to the substrate to allow closest approximation to their natural state. Indentations were performed using a colloidal tip at applied forces kept sufficiently low to avoid damage to the cells as verified by comparing images taken before and after the mechanical test. Young's modulus values computed by Herzian analysis were achieved with sensitivity of 100 Pa. The results revealed a significant drop in compliance of the infected cells, with the mean value falling by a factor of approximately three for the infected ones. Furthermore, high-resolution images of dried cells with exposed cytoskeleton show distinct morphological differences associated with the breakdown and softening of the cell structure.

These results will be discussed with respect to the currently unknown mechanistic role of parasite-derived EVs on the RBC host membrane.

5:20pm **NS-ThA10 Silicon Oxide for RRAM Application: The SPM Analysis Approach**, *Adnan Mehonic, M. Buckwell, W.H. Ng, A.J. Kenyon*, University College London, UK

**INVITED**

Resistive Random Access Memory (RRAM) has established itself as a promising technology for the next generation of non-volatile memories due to the simple design, high scalability, fast and low-power operation. Additionally, RRAM devices are considered for the implementation of power efficient hardware in applications of artificial intelligence (AI) and machine learning (ML) implemented in non-von Neumann architectures. Redox-based RRAM (ReRAM), based on the formation of conductive filaments in thin metal oxides are particularly popular due to excellent CMOS compatibility. However, significant challenges still exist for the full utilisation of the technology; such as device variability and yield. To better design and optimise the devices it is crucial to understand the physics that underlies the resistance switching processes. Here we present how SPM techniques can be used to characterise silicon oxide-based ReRAM devices. We find these techniques to be invaluable for developing a better sense of the oxide microstructure and the link with resistance switching processes. We also use the method of conductance tomography to directly visualise the shapes and sizes of conductive filaments in three dimensions - this is typically extremely challenging to obtain using conventional microscopy techniques.



# Thursday Evening Poster Sessions, October 24, 2019

## Nanometer-scale Science and Technology Division Room Union Station B - Session NS-ThP

### Nanometer-scale Science and Technology Poster Session

#### NS-ThP1 Probing Intermolecular and Molecule-Substrate Interactions at Angstrom Scale by Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy, *Sayantana Mahapatra, J. Schultz, N. Jiang*, University of Illinois at Chicago

Conventional spectroscopic techniques are limited by the optical diffraction limit to about half wavelength and therefore offers about 200 nm x 200 nm microscopic zone for working in the visible light range. Tip-enhanced Raman spectroscopy (TERS) emerges as an advanced analytical technique, where the plasmonically active probe is not only used to detect the tunneling current but also to interrogate the local chemical environment of surface adsorbed molecules with angstrom scale precision. In this work, we studied two regioisomers (positional isomers), *trans*- and *cis*-tetrakis(pentafluorophenyl)porphodilactone (*trans*- and *cis*-H<sub>2</sub>F<sub>20</sub>TPPDL) using scanning tunneling microscopy (STM), ultrahigh vacuum (UHV) TERS on Ag(100) with the spatial resolution down to 8 Å, which has wide range of applications in various field of surface science & nanotechnology such as regioselective catalysis reaction, chemical reactions, molecular electronics etc. We have shown, it is possible to distinguish these two structurally very similar forms with high accuracy & precision. The two-component molecular junction has been identified using high resolution two-dimensional (2D) Raman mapping. Furthermore, these new class of porphyrinoids i.e. porphodilactones (PDL) have been studied on different single crystals [Ag(100), Cu(100) and Au(100)] to probe the intermolecular and molecule-substrate interactions. This work demonstrates, STM combined with TERS is a complementary technique to characterize a system completely at angstrom scale.

#### NS-ThP4 A Nanoscopic View of Photo-induced Charge Transfer in Organic Nano-crystalline Heterojunctions, *Qian Zhang, S.R. Cohen, B. Rybtchinski*, Weizmann Institute of Science, Israel

Organic photovoltaics are promising as cost-efficient, tunable, and flexible platforms for solar energy conversion, yet their performance and stability are still far from optimal. Here we present a study of photo-induced charge transfer processes between electron donor and acceptor organic nanocrystals, as part of our path-finding effort to develop robust and efficient organic nanocrystalline materials for photovoltaic applications. We produced sub-micron to microns-long nanocrystals of perylene-diimides (PDIs) as electron acceptors, and with Copper Phthalocyanine (CuPc) as the electron donor. Three different configurations of donor-acceptor heterojunctions were prepared. Charge transfer in the heterojunctions was studied with Kelvin-probe force microscopy (KPFM) under laser or white light excitation. We also conducted theoretical calculations and time-resolved photo-luminescence measurements to understand the differences in the photovoltaic processes of these organic nanocrystals. Our work demonstrates that excitonic properties can be tuned by controlling the crystal and interface structures in the nanocrystalline heterojunctions, in order to minimize photo-voltaic losses.

#### NS-ThP5 Ferroic-ionic Interaction in Hybrid Organic Inorganic Perovskites, *Yongtao Liu<sup>1,2</sup>, L. Collins, A.V. Ievlev, A. Belianinov*, Oak Ridge National Laboratory; *M. Ahmadi*, University of Tennessee Knoxville; *S. Jesse, S.V. Kalinin*, Oak Ridge National Laboratory; *B. Hu*, University of Tennessee Knoxville; *O.S. Ovchinnikova*, Oak Ridge National Laboratory

Hybrid organic-inorganic perovskites (HOIPs) such as methylammonium lead iodide (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) have attracted broad research interest due to their outstanding photovoltaic performance. However, fundamental understandings of the origin of the high performance and the anomalous current-voltage (I-V) hysteresis of HOIPs solar cells still lag. Although ferroelectricity is proposed to be a reason of the related behavior, the convincing evidence supporting ferroelectricity in HOIPs is missing because the strong ion motion in HOIPs complicates the ferroic characterization. A clear understanding of the interplay between ferroic behavior and ion motion in HOIPs will be helpful for clarifying this question.

In this work, using multi-modal functional and chemical imaging methods, we unveil a ferroic-ionic interaction in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. In piezoresponse force microscopy (PFM) experiments, we observed ferroelastic twin domain structures in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. Although PFM shows 'piezoelectric-like' contrast

of the twin domains, our studies—including band excitation (BE) PFM, laser Doppler vibrometer (LDV) PFM, and BE contact resonance atomic force microscopy (BE-AFM)—unambiguously reveal the mechanical origin rather than the electromechanical origin of the 'piezoelectric-like' contrast. This ferroelastic domain was accompanied by ion segregation due to the strain-driven ion redistribution, which was observed using helium ion microscopy secondary ion mass spectrometry (HIM-SIMS) and atomic force microscopy infrared spectroscopy (AFM-IR). To further address how ion distribution affects the ferroic behavior of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, we studied the interaction of the ion distribution and the fields (elastic field and electric field) distribution in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. It is shown that the ion redistribution is accompanied by a reversible change in lattice strain, suggesting the dependence of the elastic field on ion distribution. Furthermore, we found that the local ion distribution could manipulate the formation of ferroelastic twin domain. The electric field was studied by Kelvin probe force microscopy (KPFM), which indicates that the ion distribution affects local electric field intensity and the electric field distribution. By combining KPFM and time-of-flight secondary ion mass spectrometry (ToF-SIMS), we observed a screen effect of ion migration on the electric field in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. The remainder of the field is very small due to the compensation of ion migration. These results suggest that the ion motion can alter local field and hence local ferroic behavior of HOIPs. Overall, this work offers an understanding of ferroic-ionic interplay in HOIPs, providing a pathway to develop novel devices.

#### NS-ThP6 Processing of Nanoscale Lamellae in Bulk Al-Cu Eutectic Samples Through Selective Laser Melting, *Jonathan Skelton, J.A. Floro, J.M. Fitzgerald*, University of Virginia

Eutectic alloys with nanoscale lamellar spacing may have a wide range of applications in functional materials such as thermoelectrics and photovoltaics, as well as in enhanced mechanical properties. This is due to an intimate interleaving of two or more phases where the length scales are controlled in part by the solidification rate. Utilization of nanoscale eutectics remains limited as a result of the lack of methods available to readily produce them in bulk materials. Rapid solidification through laser irradiation has been shown to create these structures on the surface of model eutectic materials, such as Al-Cu, with an interphase spacing dependent on the scanning velocity of the laser, but the limited absorption depth of the laser frustrates formation of bulk nanostructured samples. Selective laser melting (SLM) presents an innovative solution to this problem by building 3D samples via a layer-by-layer method, where each pass is rapidly cooled by the bulk material. In this research, the relationship between the SLM processing parameters and the resulting microstructure of bulk Al-Cu eutectic samples is investigated, with a focus on controlling the interphase spacing and directionality of the lamellar microstructure. An SLM Solutions GmbH 125 system was used to process the samples in this study, operating at scan velocities ranging from 50 to 150 mm/s at a CW laser power of 100 W. Cross-sections of samples exhibited lamellar spacing of 40 to 100 nm within narrow eutectic colonies of approximately 3 μm width that extended the height of the individual scan layers (50 μm). The solidification mechanism that produced these colonies is investigated, and the fine lamellar spacing is analyzed in accordance to the Jackson-Hunt theory. Samples in this study were characterized by scanning electron microscopy (SEM), focused ion beam (FIB), and energy dispersive X-ray spectroscopy (EDS). Support for this research from the National Science Foundation grant #CMMI-1663085 is gratefully acknowledged.

#### NS-ThP8 Understanding Tip-induced Nanoscale Wear for Tomographic Atomic Force Microscopy, *Umberto Celano*, IMEC, Belgium; *X. Hu*, University of California-Merced; *L. Wouters, K. Paredis, T. Hatschel, P.A.W. van der Heide*, IMEC, Belgium; *A. Martini*, University of California-Merced

The ability of contact-mode atomic force microscopy (AFM) to remove material while scanning has repeatedly been used for surface modification and small-scale tip-induced nanofabrication.[1] In the simplest form, the physical removal of material can be achieved by scanning the nanosized probe against the surface at high enough pressure.[2] More recently, tomographic capability has been explored for various electrical AFM modes by leveraging the same concept and alternating tip-induced removal and probing, in what is often referred to as Scalpel AFM.[3] Here, high-pressure AFM scans (i.e., high load force) are used for a controlled material removal and alternated with conventional contact-mode scans (i.e., standard load force). The alternation of scanning conditions delivers a slice-and-view methodology that generates three-dimensional (3D) datasets, with nm-precision in depth. This method has found wide application in the analysis of ultra-scaled nanoelectronics, where 3D architectures are currently dominating and the probing of confined volumes is mandatory.[4]

<sup>1</sup> National Student Award Finalist

<sup>2</sup> NSTD Graduate Student Award Finalist

# Thursday Evening Poster Sessions, October 24, 2019

However, for complex nanostructures such as integrated electronic devices, a detailed comprehension of the tip-sample interaction it's required for the precise control of the removal process in heterogenous materials. In this work, we combine experimental AFM data with molecular dynamics (MD) simulations that study the fundamentals of high-pressure tip-induced material removal for heterogenous nanostructures. Metal-oxide nanopillars (80 -120 nm diameter) embedded in SiO<sub>2</sub> are experimentally probed using high pressure sliding contacts (i.e., diamond probes). We select a regime whereby tens of nm<sup>3</sup> are removed targeting a controllable removal rate below 3 nm/scan. The impact of the tip-sample interaction inside the worn regions is investigated in order to generate understanding on the physical wear mechanisms. The experimental results are compared with MD simulations that allow us to study the removal processes as a function of different parameters of the AFM scan, including removal rate and the quality of the machined area. As such, this work paves the way for the development of accurate models to improve the quality of tip-induced material removal in complex nanostructures, with great scientific and technological interest for tomographic probing using AFM.

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## Chemical Analysis and Imaging Interfaces Focus Topic Room A226 - Session CA+AS+NS+SE+SS-FrM

### Novel Applications and Approaches in Interfacial Analysis

**Moderators:** Paul Dietrich, SPECS Surface Nano Analysis GmbH, Germany, Jeong Young Park, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

8:20am **CA+AS+NS+SE+SS-FrM1 Chemical Reactions on Bimetal Surfaces with Operando Surface Techniques, Jeong Young Park**, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea **INVITED**

The origin of the synergistic catalytic effect between metal catalysts and reducible oxide has been debated for decades. Clarification of this effect, namely the strong metal-support interaction (SMSI), requires an understanding of the geometric and electronic structures of metal-metal oxide interfaces under operando conditions.[1] A bimetallic platinum (Pt) alloy catalyst is an excellent platform to uncover the contentious role of the metal-metal oxide interface because the alloyed transition metal can coexist with the Pt surface layer in the form of an oxidized species on the bimetal surface during catalytic reactions.

**In this talk, I present in-situ observation results of structural modulation on Pt-Ni metastable and Ni (111) surfaces at 0.1 Torr pressure of CO, O<sub>2</sub>, and CO oxidation conditions with ambient-pressure scanning tunneling microscopy (AP-STM) and ambient-pressure X-ray photoelectron spectroscopy (AP-XPS).[2] We show that the stable Pt-skin covered Pt<sub>3</sub>Ni(111) surface is broken by segregation of dissociative oxygen-induced Ni oxides under elevated oxygen pressure environment, which evolved clusters could have a crucial relation with enhanced catalytic activity. We show that NiO<sub>1-x</sub>/Pt-Ni nanostructures are on the Pt<sub>3</sub>Ni(111) surface under CO oxidation and these metal-oxide interfaces provide more efficient reaction path for CO oxidation [2]. Furthermore, I will show the research efforts for understand the catalytic behavior of bimetal PtCo and PtNi nanocatalysts using in-situ surface techniques including catalytic nanodiode and transmission electron microscopy. The catalytic nanodiode that consists of metal catalyst film, semiconductor layers, and Ohmic contact pads revealed the strong correlation between the hot electron flux (chemicurrent) and catalytic activity under CO oxidation and hydrogen oxidation. Using this approach, the catalytic activity and hot electron generation on PtCo bimetal nanoparticles were investigated. In-situ transmission electron microscopy reveals the formation of metal oxide layers on bimetal nanoparticle surfaces under oxygen conditions. We show that formation of interface between Pt and CoO enhances both of catalytic activity and chemicurrent yield [3].**

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9:00am **CA+AS+NS+SE+SS-FrM3 Principal Component Analysis to Reveal Camouflaged Information in Spectromicroscopy of (complex) Oxides, David Mueller, M. Giesen, Forschungszentrum Juelich GmbH, Germany; D. Stadler, University of Cologne, Germany; T. Duchon, F. Gunkel, V. Feyer, Forschungszentrum Juelich GmbH, Germany; S. Mathur, University of Cologne, Germany; C.M. Schneider, Forschungszentrum Juelich GmbH, Germany**

Spectroscopic imaging techniques are becoming more and more accurate and available, which results in an increase of data to handle and analyze. Near Edge X-Ray absorption spectroscopy, especially in the soft X-Ray regime, has the ability to identify inhomogeneities in chemistry and electronic structure, which is mostly done by fingerprinting or using internal standards. In a spectromicroscopic image, each pixel contains such a spectrum, and by the lack of rigorous fitting routines that are for example present in XPS, reduction and preevaluation of data is needed. Principal Component Analysis (PCA) of X-PEEM data affords this in an unambiguous and unbiased way by identifying and highlighting spectroscopic features which contribute to a spectrum.<sup>1</sup>

Two cases where PCA revealed information that might have been missed otherwise are presented here: Firstly, iron oxide thin films grown by CVD showed a considerable influence of an external magnetic field on chemistry and crystallinity. Combination of O-K- and Fe-L-Edge X-PEEM unambiguously identified different iron oxide polymorphs (Fe<sub>3</sub>O<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) depending on field strength during deposition. The former XAS Edge showed subtle spatial variations in the EXAFS regime that could be

identified as the breakdown of long-range ordering, pointing to incomplete crystallization when films are deposited without magnetic field assistance.<sup>2</sup>

The second example is the surface decomposition of Pr<sub>0.5</sub>Ba<sub>0.5</sub>CoO<sub>3- $\delta$</sub>  (PBCO), a promising material for the use as water splitting catalyst and solid oxide electrochemical cell electrode. Using spatially resolved O-K-, Co-L-, and Ba- and Pr-M-Edge XAS, changes in surface chemical composition upon annealing and its impact on the electronic structure were observed. Laterally resolved by X-PEEM, PCA could reveal that exposing thin films of the material to technologically relevant conditions (1073 K, 20 mbar of O<sub>2</sub>) leads to a more complex decomposition pathway than simple spinodal unmixing to the end members BaCoO<sub>3</sub> and PrCoO<sub>3</sub> as the spectromicroscopic dataset could only be described satisfactory by a linear combination of three components.

9:20am **CA+AS+NS+SE+SS-FrM4 In situ Electron Microscopy of Catalysts with Atomic Resolution under Atmospheric Pressure, Xiaoqing Pan**, University of California Irvine **INVITED**

Understanding the atomic structures of catalysts under realistic conditions with atomic precision is crucial to design better materials for challenging transformations. For example, under reducing conditions, certain reducible supports migrate onto supported metallic particles and create strong metal-support states that drastically change the reactivity of the systems. The details of this process are still unclear and preclude its thorough exploitation. In the past decade, most of atomic-scale transmission electron microscopy (TEM) studies involving gas-solid interactions were conducted in an environmental TEM, where the gas pressure is typically limited to less than 1/100 of atmosphere. Recently, it has become possible to overcome this limitation through a MEMS-based, electron-transparent closed cell with a heating stage.

In this talk, I will present our recent results using this device (the Protochips Atmosphere™ system) in selected catalyst systems. In a palladium/titania (Pd/TiO<sub>2</sub>) catalyst, we directly observed the formation of the oxide overlayers on the supported Pd particles with atomic resolution under atmospheric pressure and high temperature. It shows that an amorphous reduced titania layer is formed at low temperatures, and that crystallization of the layer into either mono- or bilayer structures is dictated by the reaction environment. This transition occurs in combination with a dramatic reshaping of the metallic surface facets. *In-situ* TEM observations of a modular Pd-ceria core-shell nanostructured catalyst (Pd@CeO<sub>2</sub>) showed that an unexpected structural transformation occurs upon heating at high temperatures. The system reaches to a stable state with the mixture of nanoparticles with two different sizes, which accounts for the exceptional catalytic properties that have been reported. Using the similar techniques, we also studied the core-shell platinum-metal (Pt-M) nanoparticles which show a catalytic performance in the oxygen reduction reaction (ORR) superior to that of pure Pt nanoparticles. To understand the formation mechanism of the Pt shell, we studied thermally activated core-shell formation in Pt<sub>3</sub>Co nanoparticles via *in-situ* electron microscopy with the gas cell. The disordered Pt<sub>3</sub>Co nanoparticle was found to transform into an ordered intermetallic structure after annealing at high temperature (725°C) in 760 Torr O<sub>2</sub>, followed by layer-by-layer Pt shell growth on (100) surfaces at low temperature (300°C). The apparent 'anti-oxidation' phenomenon promoted by the ordered Pt<sub>3</sub>Co phase is favorable to the ORR catalyst, which operates in an oxidizing environment.

10:00am **CA+AS+NS+SE+SS-FrM6 Exposing Buried Interfaces in Thin Film Photovoltaics through Thermo-mechanical Cleaving, Deborah McGott**, Colorado School of Mines; C.L. Perkins, W.K. Metzger, National Renewable Energy Laboratory; C.A. Wolden, Colorado School of Mines; M.O. Reese, National Renewable Energy Laboratory

Thin film solar cells, such as cadmium telluride (CdTe) and Cu(In,Ga)Se<sub>2</sub> (CIGS), contain buried interfaces that are critical to carrier transport, recombination, and device performance, yet are poorly understood due to their inaccessibility within the device stack. In particular, accessing the interface in a way that preserves the chemical structure has historically been extremely difficult. Here, we describe an innovative technique to expose buried interfaces through a two-step thermo-mechanical cleaving process. First, a stressor layer (typically an epoxy or commercially available polymeric backsheets) is applied to the solar cell. Then, the stack is submerged in a cold bath (T  $\leq$  -30°C) to thermally shock the system. This causes the stressor to contract quickly and pull the polycrystalline film cleanly off of its substrate at an interface that is weakened by a monolayer accumulation of 2-D material (CdCl<sub>2</sub> in CdTe and MoS<sub>2</sub> in CIGS).

Focusing on CdTe solar cells, we then use X-ray photoelectron spectroscopy to probe the oxidation states at the newly exposed SnO<sub>2</sub> interface. We

show that the tin oxide front electrode promotes the formation of nanometer-scale oxides of tellurium and sulfur. Most oxidation occurs during  $\text{CdCl}_2/\text{O}_2$  activation. Surprisingly, we show that relatively low-temperature anneals (180–260°C) used to diffuse and activate copper acceptors in a doping/back contact process also cause significant changes in oxidation at the front of the cell, providing a heretofore missing aspect of how back contact processes can modify device transport, recombination, and performance. Device performance is shown to correlate with the extent of tellurium and sulfur oxidation within this nanometer-scale region. Mechanisms responsible for these beneficial effects are proposed.

## 10:20am CA+AS+NS+SE+SS-FrM7 Switchable Dopants on Percolation Networks of 2D Materials for Chemiresistive Sensing Applications in Aqueous Environments, Peter Kruse, McMaster University, Canada

Permanent doping of semiconductors and low-dimensional structures to modulate their electronic properties is a well-established concept. Even in cases where doping of thin films by analytes (e.g. carbon nanotubes by ammonia) is applied in sensors, it is only reversed by physical removal of dopant molecules, e.g. heating. We have introduced the concept of molecular switches as chemical dopants for thin nanocarbon (or other 2D-materials) films. These molecules can be switched between doping and non-doping states in the presence or absence of a particular analyte. They impart selectivity not only due to their change in doping behavior, but also by physically blocking other potential dopants in the analyte solution from interacting with the conductive film. The resulting structures can act as chemiresistive films. Chemiresistive sensors are a well-established technology for gas-phase sensing applications. They are simple and economical to manufacture, and can operate reagent-free and with low or no maintenance. Unlike electrochemical sensors they do not require reference electrodes. While in principle they can be made compatible with aqueous environments, only a few such examples have been demonstrated. Challenges include the need to prevent electrical shorts through the aqueous medium and the need to keep the sensing voltage low enough to avoid electrochemical reactions at the sensor. We have built a chemiresistive sensing platform for aqueous media. The active sensor element consists of a percolation network of low-dimensional materials particles that form a conducting film, e.g. from carbon nanotubes, pencil trace, exfoliated graphene or  $\text{MoS}_2$ . The first member of that platform was a free chlorine sensor. We are currently working to expand the applicability of our platform to other relevant species, in particular anions and cations that are commonly present as pollutants in surface and drinking water. Our sensors can be incorporated into a variety of systems and will also be suitable for online monitoring in remote and resource-poor locations.

## 10:40am CA+AS+NS+SE+SS-FrM8 Analysis Of Radioactive Materials In Liquid Using In Situ Sem And Tof-Sims, Jennifer Yao, X.-Y. Yu, Z.H. Zhu, E.C. Buck, Pacific Northwest National Laboratory

Characterization of nuclear materials in solid particles or particles in liquid slurry, particularly in high level waste, can establish the elemental, organic, and isotopic compositions that effect the properties of the materials during nuclear fuel cycle activities and processes. Techniques to evaluate such detailed information, even at small concentrations, can support nuclear materials and science programs by increasing our ability to manage and control nuclear materials. However, radioactive materials analysis in liquids and slurries can be challenging using bulk approaches. We have developed a vacuum compatible microfluidic interface, system for analysis at the liquid vacuum interface (SALVI), to enable surface analysis of liquids and liquid-solid interactions using scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). In this work, we illustrate the initial results from the analysis of liquid samples of importance in the geologic disposal of UO<sub>2</sub> spent nuclear fuel in a repository environment using in situ liquid SEM and SIMS. Our results demonstrate that multimodal analysis of UO<sub>2</sub> materials is possible using SALVI. Both in situ liquid SEM and SIMS can be used as new approaches to analyze radioactive materials in liquid and slurry forms of high level nuclear waste.

## 11:00am CA+AS+NS+SE+SS-FrM9 Interactions between Synthetic Bilgewater Emulsion and Biofilms, Jiyoung Son, Earth and Biological Sciences Directorate; J. Yao, Earth & Biological Sciences Directorate; X.-Y. Yu, Pacific Northwest National Laboratory

### Presentation Summary:

This presentation will showcase our latest results of the interaction between biofilms and synthetic bilgewater using a surface chemical imaging technique.

### Abstract

Bilgewater, an oil-in-water (O/W) emulsion, is a persistent pollutant released to the ocean from the lowest part of ships. Microbes play an important role in the ocean. It is hypothesized that microbes release organics that can act as surfactants that affect bilgewater formation or weakening. We present the first systematic study of emulsions and biofilms and investigate the effects of biofilms on bilgewater emulsions. Three strains were selected *Pseudomonas*, *Arthrobacter*, and *Cobetia marina*. A Navy O/W emulsion consisting of three oils and a detergent mixture was used as the synthetic bilgewater model [1]. Biofilms were cultured in a microchannel to allow healthy culture [2]. Once a thick layer of biofilms was formed, the medium solution was changed to a mixture consisting of 50 % bilgewater emulsion. Dispersed biofilms were collected at 24 hrs. and 48 hrs. after emulsions were introduced into the channel. Bilgewater emulsions, biofilms, and mixtures of bilgewater emulsions and biofilms were analyzed using multiple *in situ* and *ex situ* techniques including time-of-flight secondary ion mass spectrometry (ToF-SIMS), scanning electron microscopy (SEM), and optical microscopy. Our findings indicate that biofilms change the chemical makeup of the emulsion surface compositions and emulsion droplet size distribution, confirming the hypothesis that extracellular polymeric substance (EPS) related components released from biofilms can function as surfactants and change the oil-in-water interfaces.

**Key words:** bilgewater emulsion, oil-in-water, microfluidics, biofilm, EPS, surfactant

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## 11:40am CA+AS+NS+SE+SS-FrM11 Artificial Intelligence—An Autonomous TEM for In-situ Studies, Huolin Xin, University of California Irvine INVITED

Deep learning schemes have already impacted areas such as cognitive game theory (e.g., computer chess and the game of Go), pattern (e.g., facial or fingerprint) recognition, event forecasting, and bioinformatics. They are beginning to make major inroads within materials science and hold considerable promise for materials research and discovery. In this talk, I will introduce deep convolutional neural networks and how they can be applied to the computer vision problems in transmission electron microscopy. I will also discuss the development and application of liquid TEM to the study of solid/liquid interfaces at the nanoscale.

## Nanometer-scale Science and Technology Division Room A222 - Session NS+AS-FrM

### Electron-Beam Promoted Nanoscience

**Moderators:** Omur E. Dagdeviren, Yale University, Qing Tu, Northwestern University

## 8:20am NS+AS-FrM1 Vibrational Spectroscopy in the Electron Microscope, Ondrej Krivanek, N. Dellby, CE. Meyer, A. Mittelberger, T.C. Lovejoy, NION Co.

Vibrational (phonon) spectroscopy using an electron microscope's primary beam was introduced in 2014, and it has now progressed very significantly. The attainable energy resolution stands at ~5 meV (at 30 keV primary energy), our understanding of the electron-matter interaction has deepened, and several types of new applications have been explored.

Phonons can be excited by fast electrons in two fundamentally different ways: by dipole scattering, which is similar to exciting the sample by infrared light, and by impact scattering, which bears a closer resemblance to neutron scattering. Dipole scattering occurs only in polar materials, and it is characterized by small scattering angles (~0.1 mrad) and interaction distances of tens of nanometers. Impact scattering involves a direct interaction between the fast electron and an atomic nucleus, and it leads to large scattering angles. Selecting the impact scattering (with an aperture in the diffraction plane) allows the vibrational signal in h-BN to be imaged with atomic (0.2 nm) resolution [1,2]. In elemental Si, impact scattering is dominant, and it allows atomic resolution to be reached without angular selection [3].

The angular (momentum) distribution of vibrational scattering has also been explored [4-6]. Attainable spatial resolution is then inversely related

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to the angular resolution. Optical and acoustic branches of vibrational scattering have been mapped in hexagonal and cubic BN, and in graphene and graphite.

Dipole scattering provides another exciting possibility: probing the sample from a small distance, by "aloof spectroscopy". This approach limits the maximum energy that can be transferred to the sample with significant probability as  $1/b$ , where  $b$  is the distance of the confined electron beam from the sample. In this way, vibrational properties of biological and other "fragile" materials can be probed without significant radiation damage [7], and this may well revolutionize analysis in the electron microscope. The technique has recently been used to detect isotopic substitution:  $^{13}\text{C}$  vs.  $^{12}\text{C}$  at a specific site in an amino acid (L-alanine), and to map the distribution of the two species [8].

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9:00am **NS+AS-FrM3 In-situ Electron Microscopy of Localized Surface Plasmon Initiated Reactions**, *Canhui Wang, W.-C. Yang, A. Bruma*, UMD/NIST; *R. Sharma*, National Institute of Standards and Technology **INVITED**

Excitation of localized surface plasmon (LSP) resonance on metal nanoparticles has been shown to overcome the reduced energy barrier for photochemical reactions, even allowing certain reactions to occur at room temperature. (1-2) Understanding the reactions promoted by LSP resonance at the nanoscale is important for designing efficient photocatalytic systems for a wide range of energy and environmental applications. However, many important questions related to this type of reaction process remain unclear due to the complexity of the reaction kinetics, and lack of spatial resolution available with optical methods. Details such as the location of gas adsorption sites, how the energy is being absorbed and released, and how those details are correlated to the structure of the catalyst nanoparticles, remain elusive and are only hinted by theoretical calculations.

Here we use *in-situ* electron microscopy and combine an ensemble of data acquisition and processing techniques to characterize LSP-initiated chemical reactions at high spatial resolution using an aberration-corrected environmental scanning transmission electron microscope. Electron energy loss spectrum (EELS) imaging is used to acquire both elemental and LSP resonance maps from the same area that contains the plasmonic nanoparticles. The elemental maps allow us to locate the gas adsorption sites, the elemental distribution of the reactants and plasmonic nanostructures, as well as the spatial distribution of the solid reaction products, with nanometer resolution. The LSP-EELS maps provide insight into how the energy is channeled from the fast electron to the plasmonic nanostructure. Localized reactant consumption (mass loss) distribution is mapped in terms of thickness changes by subtracting the thickness map acquired after the reaction from the thickness map acquired before the reaction. This allows us to pinpoint the reaction hotspot near the nanoparticle surface. The LSP induced electric field distribution near the nanoparticle surface is simulated using the metallic nanoparticles boundary element method (MNBPEM) (3) and compared with the reactant mass loss map. These techniques allow us to explore and study previously unknown LSP initiated reactions with unprecedented details on the sub-particle level. (4) The results improved the understanding of the dynamics of LSP initiated reactions and give insights into nanoparticle engineering for optimizing reaction efficiency.

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9:40am **NS+AS-FrM5 Nanoscale Manipulation of Redox of Ag by Electron Beam**, *Jianguo Wen, H.P. Sheng*, Argonne National Laboratory; *J.B. Wang*, Wuhan University, China **INVITED**

Employing electrons for direct control of nanoscale reaction is highly desirable since it provides fabrication of nanostructures with different properties at atomic resolution and with flexibility of dimension and location. In 2016, Kalinin et al summarized past experiments of manipulating atoms with scanning transmission electron microscopy (STEM) and proposed to utilize the imaging tool to create structures atom by atom (1). Here, applying *in situ* transmission electron microscopy, we show nanoscale oxidation and reduction of Ag can be manipulated by electron beam. We demonstrated fabrication of an array of 3 nm  $\text{Ag}_2\text{O}$  nanodots in an Ag matrix.

Under high vacuum environment ( $\sim 10^{-7}$  Torr pressure), oxygen in a TEM can be ionized by high-energy electron beam and causes oxidation of Ag. After enough e-beam illumination, a growth of  $\text{Ag}_2\text{O}$  on the surface is observed when electron beam flux is below  $\sim 5 \times 10^5 \text{ e}^-/\text{\AA}^2\text{s}$ .  $\text{Ag}_2\text{O}$  islands epitaxially grow on Ag surface with orientation relationship of  $\langle 110 \rangle_{\text{Ag}_2\text{O}} // \langle 110 \rangle_{\text{Ag}}$  and  $\{111\}_{\text{Ag}_2\text{O}} // \{002\}_{\text{Ag}}$  in most cases. In-situ high-resolution transmission electron microscopy (HRTEM) imaging shows that  $\text{Ag}_2\text{O}$  nucleates at atomic steps on Ag surfaces.

With the increase of electron-beam intensity above  $\sim 5 \times 10^5 \text{ e}^-/\text{\AA}^2\text{s}$ , the formed  $\text{Ag}_2\text{O}$  islands can be fully reduced back to Ag, such that a fully reversible oxidation and reduction of Ag is achieved by varying electron beam intensity. The growth and reduction of  $\text{Ag}_2\text{O}$  island is electron-beam dose rate dependent, a near equilibrium state has been achieved at the dose rate of  $\sim 5 \times 10^5 \text{ e}^-/\text{\AA}^2\text{s}$ . A brief explanation for this electron-beam dose rate dependence is the competition between the electron-beam ionization induced oxidation of Ag and electron stimulated desorption induced reduction of  $\text{Ag}_2\text{O}$ . Aberration-corrected HRTEM observation reveals that O atoms are preferably inserted and extracted along the  $\{111\}$  close-packed planes of Ag, leading to the nucleation and decomposition of nanoscale  $\text{Ag}_2\text{O}$  islands on the Ag substrate.

Taking another step further, patterned oxidation has also been tested to verify the reliability of the electron-beam irradiation as a nanofabrication technique. By controlling probe size, electron flux, and dwell time, we demonstrated fabrication of an array of 3 nm  $\text{Ag}_2\text{O}$  nanodots in an Ag matrix. These findings do not only facilitate the basic understanding of oxidation/reduction kinetics in Ag- $\text{Ag}_2\text{O}$ , but also open up a promising approach for precise fabrication of nanostructures with metal or semiconductor properties in devices.

1) Kalinin, Sergei V., Albina Borisevich, and Stephen Jesse. "Fire up the atom forge." *Nature News* 539.7630 (2016): 485.

10:20am **NS+AS-FrM7 Dynamics of Material Surfaces and Interfaces – The Good, the Bad and the Electron Beam**, *Jakob Birkedal Wagner*, DTU Nanolab, Technical University of Denmark, Denmark **INVITED**

A good understanding of the dynamics and formation mechanisms of surfaces and interfaces at the nanometer scale is of great importance in order to exploit the controllability of nanostructures and their applications in photovoltaics, electronics, sensors, etc. on an industrial scale.

*In situ* electron microscopy serves a unique platform for monitoring and studying structural dynamics at length scales from micrometer down to atomic scale and temporal resolution approaching millisecond range. In addition, elemental and chemical information is gained from spectroscopic techniques with spatial resolution approaching the atomic scale.

Here, I will present a few cases of the surface and interface dynamics studied at the microscopy facility at Technical University of Denmark. This includes surface dynamics of supported nanoparticles (catalyst) [1] under harsh environment (elevated temperature, gas and electron beam), as well as interface dynamics of grain boundaries in metal thin films [2], growth of nanostructures from bottom-up processes [3-6] and volatility of soot oxidation catalysts. [7]

The influence of the high-energetic electron beam will also be discussed in terms of sample damage and controlled reaction enhancement.

## References

- [1] P. Liu, PhD thesis (2018), Technical University of Denmark
- [2] A. Bastos Fanta et al. Materials Characterization **139**, 452 (2018)
- [3] J. Kling et al. Carbon **99**, 261 (2016)
- [4] L. Zhang et al. ACS Nano **11**, 4483 (2017)
- [5] S. Rackauskas et al., Scientific Reports **7**, 12310 (2017)

[6] W. F. van Dorp *et al.*, *Nanotechnology* 24, 345301 (2013)

[7] D. Gardini *et al.*, *Appl. Catal. B*, 183, 28 (2016)

11:00am **NS+AS-FrM9 Atomic-Scale Mechanism of Unidirectional Oxide Growth**, *Xianhu Sun*, *W. Zhu*, *D. Wu*, SUNY Binghamton University; *Z. Liu*, University of Pittsburgh; *X. Chen*, *L. Yuan*, SUNY Binghamton University; *G. Wang*, University of Pittsburgh; *R. Sharma*, National Institute of Standards and Technology (NIST); *G. Zhou*, SUNY Binghamton University

A fundamental knowledge of the unidirectional growth mechanisms is required for precise control on size, shape, and thereby functionalities of nanostructures. Using transmission electron microscopy that spatially and temporally resolves CuO nanowire growth during the oxidation of copper, here we provide direct evidence of the correlation between unidirectional crystal growth and bicrystal boundary diffusion. Based on atomic scale observations of the upward growth at the nanowire tip and oscillatory downward growth of atomic layers on the nanowire sidewall, we clearly show that bicrystal boundary diffusion is the mechanism by which Cu atoms are delivered from the nanowire root to the tip. Together with density-functional theory calculations, we further show that the asymmetry in the corner-crossing barriers promotes the unidirectional oxide growth by hindering the transport of Cu atoms from the nanowire tip to the sidewall facets. We expect broader applicability of our results in manipulating the growth of nanostructured oxides by controlling the bicrystal boundary structure that favors anisotropic diffusion for unidirectional, one-dimensional crystal growth for nanowires or isotropic diffusion for two-dimensional platelet growth.

11:20am **NS+AS-FrM10 Application of Electron-beam-excited Localized Surface Plasmon Resonance to Provide Guidelines for Plasmonic Catalysts**, *Wei-Chang Yang*<sup>1</sup>, *C. Wang*, *L.A. Fredin*, *H.J. Lezec*, *R. Sharma*, National Institute of Standards and Technology (NIST)

Optically-excited localized surface plasmon (LSP) resonances have been used to induce chemical reactions, such as hydrogen dissociation and ethylene epoxidation. Energy harnessed by plasmonic nanostructures and transferred to adsorbed reactants is theorized to initiate these chemical processes by compensating for the heat required otherwise. As we know, there are three important steps for designing a plasmonic catalyst system: (1) adsorption of reactants; (2) adequate resonance energy to overcome the reaction barrier; and (3) desorption of products. However, they have not been resolved at a sub-nanoparticle scale using optical methods. Herein, we demonstrate that the sub-particle information, gained from electron energy-loss spectroscopy (EELS) and cathodoluminescence (CL), can be used to measure these steps for selected reactions.

LSP resonances, excited by electrons, on shape-controlled Au nanoparticles, were exploited to drive CO disproportionation:  $2\text{CO}_{(g)} \rightarrow \text{CO}_{2(g)} + \text{C}_{(s)}$ , at room temperature (commonly initiated by heat above 400 °C) in an environmental scanning transmission electron microscope equipped with a monochromated electron gun. Triangular Au nanoprisms were synthesized and loaded on  $\text{TiO}_2$  support in a cantilevered configuration. *In situ* core-loss EELS was used to detect CO adsorption on the Au surfaces, for the first time, revealing the preferential adsorption sites at selective edges but not on the entire surfaces. Low-loss EELS maps of the Au nanoprisms showed that the electron beam was most efficiently coupled with the LSP dipole mode, indicated by the maximum EELS intensity, when placed at the cantilevered corner, suggesting a strong electric field caused by this specific mode at the same corner. *In situ* EELS showed that energy shifts occurred to the LSP resonance in CO environment and disappeared after CO evacuation, indicating a change in electron density of the Au particle as CO was adsorbed and desorbed, respectively. Energy transferred to the adsorbed CO was identified based on the spectral difference between EELS and CL. Carbon deposits, resulting from room-temperature CO disproportionation mediated by the LSP resonance, were detected by core-loss EELS at the cantilevered corner edge after evacuating CO. This shows that the active sites on the nanoprisms are where the preferable CO adsorption sites and the locations of maximum field amplitude superimpose.

Our findings provide unprecedented information on an LSP-induced chemical reaction with nanometer precision, shedding light on the design principles for new plasmonic catalysts that enable low-temperature reactions.

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<sup>1</sup> NSTD Early Career Award Finalist

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