

## 2D Materials Focus Topic

Room 201B - Session 2D+EM+MI+NS+TF-MoM

## 2D Materials Growth and Fabrication

Moderator: Jing Xia, University of California Irvine

8:20am **2D+EM+MI+NS+TF-MoM-1 Wafer Scale Epitaxial Growth of Monolayer and Few-Layer WS<sub>2</sub> by Gas Source Chemical Vapor Deposition, Mikhail Chubarov, T Choudhury, J Redwing, The Pennsylvania State University**

Tungsten disulfide (WS<sub>2</sub>) has been widely investigated due to its outstanding properties compared to other 2D TMD including a bandgap of 2 eV, relatively high theoretical electron mobility, valley spin polarization, among others. Commonly, the films are grown on amorphous substrates like SiO<sub>2</sub> and, consequently, consist of high angle grain boundaries after coalescence due to the random orientation of domains. These can act as scattering and recombination centers for charge carriers limiting device performance. To avoid this, a crystalline substrate and epitaxial growth is typically employed for general thin film deposition although this approach has not been extensively investigated for 2D TMD monolayers. Large area growth is also crucial to show technological feasibility of the material for wafer-scale device fabrication.

In this work, we employ cold wall gas source chemical vapor deposition for the growth of WS<sub>2</sub> films on 2" (0001)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. To achieve coalesced monolayer growth over the entire substrate, we implemented a multi-step growth process modulating the metal precursor concentration during each of the steps. W(CO)<sub>6</sub> and H<sub>2</sub>S were used as precursors in H<sub>2</sub> carrier gas. The deposition experiments were conducted over the temperature range from 750 °C to 1000 °C at a pressure of 50 Torr. Characterization of resulting samples was conducted using atomic force microscopy (AFM), in-plane X-ray diffraction (XRD) and room temperature Raman and photoluminescence (PL) measurements.

Initial studies showed that the WS<sub>2</sub> films exhibit multiple crystal orientations which evolve with growth temperature. At lower deposition temperature (750 °C), two orientations rotated 30° one from another were observed. At the high deposition temperature (1000 °C), five different crystal orientations were present. Among others, orientation with epitaxial relation of (10-10)WS<sub>2</sub>//(10-10) $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was present at all temperatures. It was established that the unwanted orientations can be suppressed by increasing the H<sub>2</sub>S concentration. Further adjustment of the growth and use of the multi-step growth process led to the formation of a coalesced epitaxial monolayer WS<sub>2</sub> on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with XRD FWHM of 10-10 peak in  $\omega$  being 0.09°. This value suggests well in-plane oriented domains with low edge dislocation density. A high intensity, narrow (FWHM=40 meV) PL peak positioned at 2.01 eV was observed for WS<sub>2</sub> films. Monolayer formation was confirmed from the AFM height profile (D =0.9 nm) and Raman measurements by observing spectral region where layer breathing and shear modes would appear. A fully coalesced, monolayer film was achieved using the multi-step growth process in a total time of 80 minutes.

8:40am **2D+EM+MI+NS+TF-MoM-2 Wafer Scale Deposition of Monolayer Transition Metal Dichalcogenides, Kortney Almeida, M Wurch, G Stecklein, L Bartels, University of California, Riverside**

Monolayer transition metal dichalcogenide (TMD) films are promising materials in the continuing development of nanoscale devices. Methods to produce wafer-scale monolayer TMD films have included tube-furnace chemical vapor deposition (CVD), liquid-phase exfoliation, and metal-organic CVD. These methods suffer from issues with particulate contamination, pyrophoric precursors, and high cost. Here we demonstrate the growth of homogeneous wafer-scale monolayer molybdenum disulfide (MoS<sub>2</sub>) using solid inorganic and liquid organic precursors in a high-vacuum environment. These results are achieved using an amorphous SiO<sub>2</sub> substrate and without any powder or metal-organic precursors. Growth proceeds by the decomposition of carbon disulfide at a hot molybdenum filament, which yields volatile MoS<sub>x</sub> precursors that precipitate onto a heated wafer. The continuous and homogeneous single-layer film of MoS<sub>2</sub> is deposited at wafer scale with a total growth time of fifty minutes. Various thicknesses of the thin films are also demonstrated by the manipulation of the filament power. Optical and electrical characterization indicates performance comparable to or better than MoS<sub>2</sub> film grown by other wafer-scale growth techniques. Our method provides a scalable process to deposit thin TMD films in a high vacuum environment.

9:00am **2D+EM+MI+NS+TF-MoM-3 Crystal Growth of 2D Materials: From Model Systems to Integrated Manufacturing, Stephan Hofmann, University of Cambridge, UK**

INVITED

In order to serve the industrial demand for "electronic-grade" 2D materials, we focus on chemical vapour deposition (CVD), and in this talk I will review our recent progress in scalable CVD [1] and device integration approaches of highly crystalline graphene, hexagonal boron nitride (h-BN) and transition metal dichalcogenide films. The systematic use of in-situ metrology, ranging from high-pressure XPS to environmental electron microscopy, allows us to reveal some of the key growth mechanisms for these 2D materials that dictate crystal phase, micro-structure, defects, and heterogeneous integration control at industrially relevant conditions [2,3]. I will focus on tailored CVD processes to achieve large monolayer h-BN domains with lateral sizes exceeding 0.5 mm. Importantly we show that depending on the process catalyst as-grown h-BN mono-layers can be easily and cleanly transferred using an entirely exfoliation-based approach.[4] We demonstrate sequential h-BN pick-up, opening a pathway to integrate CVD films in high quality 2D material heterostructures. Progress in growth reached a level where adequate characterisation of such 2D crystal layers over large areas has become a key challenge. Hence we also explore new non-contact characterisation methods [5,6]. We work on applications ranging from magnetic tunnel junctions [7] to sensing and single molecule analysis [8,9], and the talk will focus on some of the diverse yet connected integration challenges for CVD 2D films that present a key bottleneck towards reliable scale-up manufacturing and commercialisation.

### References

1. Hofmann et al., J. Phys. Chem. Lett. 6, 2714 (2015).
2. Weatherup et al., Nano Lett. 16, 6196 (2016).
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5. Lin et al., Sci. Rep. 7, 10625 (2017).
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9. Walker et al., ACS Nano 11, 1340 (2017).

9:40am **2D+EM+MI+NS+TF-MoM-5 Understanding the Edge-Controlled Growth and Etching in Two-Dimensional Materials, Kai Xiao, X Li, X Sang, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; W Zhao, J Dong, Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan,44919, South Korea; A Puretzky, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; C Rouleau, Center for Functional Nanomaterials Brookhaven National Laboratory; F Ding, Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan,44919, South Korea; R Unocic, D Geohegan, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory**

Understanding the atomistic mechanisms governing the growth and etching of two-dimensional (2D) materials is of great importance in guiding the synthesis of large area, single-crystalline, high quality 2D crystals and heterostructures. In this talk, the growth-etching-regrowth process of monolayer 2D crystals by a CVD method will be discussed. We found that switching from growth to etching formed pores with various shapes in the single crystal domains which can be explained by edge-structure dependent growth process. In addition, combined with first principles theory, and ab initio simulations, in situ STEM imaging was used to understand the evolution of edge structure around pores in monolayers as a function of temperature and Mo chemical potential. Our results demonstrate that by varying the local chemical environment, we can trigger formation of 2D monolayer nanostructures terminated by different edge reconstructions during in situ heating and electron beam irradiation and form edge structures with metallic and/or magnetic properties. The ability to synthesize 2D nanostructures with metastable NW edges having predictable atomic structures opens the door to a wide range of novel 2D materials and heterostructures with electrical and magnetic properties as revealed by DFT, which could potentially act as functional building blocks for next-generation nano-devices.

### References:

- [1] X. Li, J. Dong, J. C. Idrobo, A. A. Puretzky, C. M. Rouleau, D. B. Geohegan, F. Ding, K. Xiao, J. Am. Chem. Soc. 139, 482 (2017).

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[2] X. Sang, X. Li, W. Zhao, J. Dong, C. M. Rouleau, D. B. Geohegan, F. Ding, K. Xiao, R. R. Unocic, Nature Comm. Accepted (2018).

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10:00am **2D+EM+MI+NS+TF-MoM-6 Synthesis and Characterization of 1T, 1T', and 2H MoTe<sub>2</sub> Thin Films, Thomas Empante**, University of California, Riverside; *Y Zhou*, Stanford University; *S Naghibi Alvililar*, El Camino College; *E Reed*, Stanford University; *L Bartels*, University of California, Riverside

Transition metal dichalcogenides (TMDs) have been of interest over the past few decades for their intriguing structural, electronic, and optoelectronic properties, particularly when scaled down to thin films. One of the most interesting TMD materials is molybdenum ditelluride (MoTe<sub>2</sub>) because of its relative ease to attain multiple phases at room temperature, namely the metallic 1T' phase and the semiconducting 2H phase. Here we show a facile chemical vapor deposition process to synthesis not only the aforementioned phases but the elusive unreconstructed 1T phase by regulating the cooling rate and the addition of carbon dioxide during the reaction. Our experimental Raman spectroscopy results were compared to theoretical density functional theory calculations which verify the synthesis of all three phases. Electronic transport measurements were also used to characterize the films and show that the newly synthesized 1T phase is in good agreement with theoretical models depicting semi-metallicity as the material shows increased conductivity with elevated temperatures. In addition to the pure phase materials, mixed phase materials, such as 2H/1T, can be synthesized with slight alterations to the parameters leading to enhancements of the 2H phases' conductivity.

10:40am **2D+EM+MI+NS+TF-MoM-8 2D Anisotropic Semiconductors: Competing Phases by Alloys Engineering, Sefaattin Tongay**, Arizona State University **INVITED**

Akin to the enormous number of discoveries made through traditional semiconductor alloys, alloying selected 2D semiconductors enables engineering of their electronic structure for a wide range of new applications. 2D alloys have been demonstrated when two components crystallized in the same phase, and their bandgaps displayed predictable monotonic variation. By stabilizing previously unobserved compositions and phases of GaSe<sub>1-x</sub>Te<sub>x</sub> at nanoscales on GaAs(111), we demonstrate abnormal band bowing effects and phase instability region when components crystallize in different phases. Advanced microscopy and spectroscopy measurements show as tellurium is alloyed into GaSe, nanostructures undergo hexagonal to monoclinic and isotropic to anisotropic transition. There exists an instability region ( $0.56 < x < 0.67$ ) where both phases compete and coexist, and two different bandgap values can be found at the same composition leading to anomalous band bowing effects. Findings also identify other potential systems including NbTiS<sub>3</sub> and shows the efficacy of the approach. Results highlight unique alloying effects, not existing in single-phase alloys, and phase engineering routes for potential applications in photonic and electronics.

11:20am **2D+EM+MI+NS+TF-MoM-10 Low-Defect, High-Uniformity Transfer-Free Graphene on SiO<sub>2</sub> by Thermal Chemical Vapor Deposition, Leslie Chan**, *D Tsai*, *Z Wang*, *C Carraro*, *R Maboudian*, University of California, Berkeley

Chemical vapor deposition (CVD) has emerged as the customary approach for scalable, controllable production of graphene for integrated devices. Standard CVD graphene must be transferred from a generic metal growth substrate onto the desired substrate (e.g., SiO<sub>2</sub>), but this extra transfer often leads to wrinkles, contamination, and breakage that ultimately result in poor device performance. Several groups have demonstrated metal-catalyzed direct CVD-graphene growth on insulating substrates, but the final graphene products are deficient in quality and uniformity. This work details an expansion of the parameter space that enables lower-defect, higher-uniformity graphene than previously reported using nickel and copper catalysts, respectively. We introduce a mechanism based on carbon permeability that provides deeper insight into the growth process. Ultimately, these studies seek to inform the judicious choice of process parameters that will lead to large-area, high-quality, layer-controlled graphene directly on target substrates.

11:40am **2D+EM+MI+NS+TF-MoM-11 Barrier Based Approach to Modify Vapor Phase Concentrations for High Quality MoS<sub>2</sub> Growth, Dongzhi Chi**, *S Wong*, Institute of Materials Research and Engineering, Agency for Science Technology and Research, Singapore

Transition metal dichalcogenides, in particular, MoS<sub>2</sub>, has attracted significant attention due to its unique electronic and physical properties. Much research efforts are directed towards achieving large area, high quality monolayer MoS<sub>2</sub> films. Using NiO foam as a reactive barrier, we achieved growth of highly homogeneous single layer MoS<sub>2</sub> on sapphire through chemical vapor deposition. As the NiO barrier reacts with MoO<sub>3</sub>, the concentration of precursors reaching the substrate and thus nucleation density is effectively reduced. By doing so, single crystal MoS<sub>2</sub> grain sizes of up to 170 μm, together with continuous monolayers on the centimeter length scale are obtained. Angle-resolved photoemission spectroscopy measurements performed describe very well-resolved electronic band structure and spin orbit splitting of the bands at room temperature. Furthermore, the measurement reveals only two major domain orientations, indicating the successful growth of a highly crystalline and well-oriented MoS<sub>2</sub> monolayer.

## Industrial Physics Forum

### Room 101B - Session IPF+AS+BI+NS-MoM

#### Biofabrication: From Tissue to Organ

**Moderators:** Jason Bardi, American Institute of Physics, Jim Hollenhorst, Agilent Technologies

8:20am **IPF+AS+BI+NS-MoM-1 Strategic Thinking on the Architecture and Design of Scaffolds for Regenerative Medicine, Buddy D. Ratner**, University of Washington, Seattle **INVITED**

Scaffolds for use in medicine and biology might be traced back to the 1940's when parachute cloth was first used for vascular prostheses. However, in the mid-1980's scaffolds took off as an essential tool in tissue engineering. This talk will explore some of the basic biology of porosities, roughness and textures on cell responses in vitro and tissue responses in vivo. University of Washington studies will be presented demonstrating enhanced healing and regeneration with precision control of pore structures for in vivo applications. The use of surface techniques and tools will be addressed for decorating the surfaces of scaffolds with biological molecules. Finally, the potential of secondary ion mass spectrometry (SIMS) for analyzing and imaging pore structure will be addressed.

9:00am **IPF+AS+BI+NS-MoM-3 Sequential Bottom-up Assembly of Synthetic Cells, Joachim Spatz**, Max Planck Institute for Medical Research, Germany **INVITED**

The evolution of cellular compartments for spatially and temporally controlled assembly of biological processes became an essential step in developing life. Synthetic approaches towards cellular-like compartments are still lacking well-controlled functionalities as would be needed for more complex synthetic cells. In part, this is due to the mechanical and chemical instabilities of the lipid-based protocells and a lack of technical means for their well-controlled manipulation. We developed droplet supported lipid bilayer vesicles by microfluidics to generate mechanically and chemically stable and, therefore, manipulable cell-like compartments with a well-defined chemical and biophysical microenvironment. The enhanced stability enabled the sequential loading of such compartments with biomolecules by pico-injection microfluidics without compromising their functionality as synthetic cells. We demonstrate a successful sequential bottom-up assembly of a compartment with lipids, transmembrane proteins (integrin, F<sub>0</sub>F<sub>1</sub>-ATP synthase) and cytoskeleton proteins which would not assemble in a fully functional way by mixing and including them in one pot at once

9:40am **IPF+AS+BI+NS-MoM-5 Activation of Inkjet Printed Cells Enhances Microvasculature Formation in Host Tissues, Thomas Boland**, *B Oropeza*, *L Solis*, University of Texas at El Paso; *M Yanez*, University of South Carolina **INVITED**

Bioprinting refers to the co-deposition of cells alongside scaffolding materials to build two- and three-dimensional constructs for tissue engineering applications. The technology faces several limitations that present interesting engineering opportunities. The nature and scope of the problems will be discussed in the context of the fabrication of microvasculature. The current tissue-engineering paradigm is that successfully engineered thick tissues must include vasculature. Studies of membrane properties of thermal inkjet printed cells by evaluating showed

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normal electrophysiology, but short-term membrane disruptions, which allow small molecular weight molecules to enter. Cell viability was high and apoptotic behavior was not upregulated. Alginate (1%) and gelatin type B (2.5%) constructs or scaffolds were prepared by bioprinting of a crosslinker with endothelial and endothelial /  $\beta$  cells. Control scaffolds were manually pipetted with the same cells and without any cells. Upon implantation the bioprinted endothelial cell constructs showed a nearly ten-fold increase in blood vessels was observed ( $p=0.009$ ), a dose response was observed but the  $\beta$  cells seemed to inhibit vessel formation. The explanted implants show large complete vascular features on the H&E and CD31 stains; Immunohistochemistry showed the tissue were regenerated with the human cells that made up a large part of the vasculature. Further insights into how the inkjet printing process activated endothelial cells will be presented. Understanding these processes will improve bioprinting and may eventually lead to creating fully vascularized large soft tissues, which have not been successfully grown thus far.

10:40am **IPF+AS+BI+NS-MoM-8 Challenges in Organ-specific Vascular Engineering and Tissue Assembly**, *Ying Zheng*, University of Washington  
**INVITED**

Engineered tissues have emerged as promising new approaches to repair damaged tissues as well as to provide useful platforms for drug testing and disease modeling. Outstanding challenges remain in 1) the lack of well-defined and mature cell sources to facilitate translational outcomes and 2) the lack of control over vascular structure and perfusion efficiency in engineered 3D tissue constructs, preventing large-scale tissue fabrication, and leading to insufficient perfusion after implantation *in vivo*. In this talk, I will present recent progress in my lab in engineering microvasculature from human pluripotent stem cell derived endothelial cells, and their anastomosis *in vitro* and infarcted heart *in vivo*. The eventual goal of this drive is to use the single cell source to derive organ-specific vascular cells and tissue for regeneration. Next I will discuss our work in understanding the human microvascular endothelial cell heterogeneity from four major organs, heart, lung, liver and kidney and describe their distinct structure and function. I will show an example of using human kidney-specific microvascular cells to model kidney specific injury. Finally I will discuss challenges and future perspectives towards engineering human organ-specific tissue models.

11:20am **IPF+AS+BI+NS-MoM-10 Bioprinting for Translational Applications: The Quest for Whole Organ Fabrication**, *James J. Yoo*, Wake Forest School of Medicine  
**INVITED**

Tissue engineering and regenerative medicine has emerged as an innovative scientific field that focuses on developing new approaches to repairing cells, tissues and organs. Over the years, various engineering strategies have been developed to build functional tissues and organs for clinical applications. However, challenges still exist in developing complex tissue systems. In recent years, 3D bioprinting has emerged as an innovative tool that enables rapid construction of complex 3D tissue structures with precision and reproducibility. This developing field promises to revolutionize the field of medicine addressing the dire need for tissues and organs suitable for surgical reconstruction. In this session novel and versatile approaches to building tissue structures using 3D printing technology will be discussed. Clinical perspectives unique to 3D printed structures will also be discussed.

**In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic**

**Room 202B - Session MM+AS+NS+PC-MoM**

**Mechanical, Electrical, Thermal and Optical Systems for In situ TEM (9:00-10:100 am)/Beam Induced Effects and Processing in Liquid/Gas Cells for TEM/SEM (10:40-11:40 am)**

**Moderators:** Suneel Kodambaka, University of California Los Angeles, Olga Ovchinnikova, Oak Ridge National Laboratory

9:00am **MM+AS+NS+PC-MoM-3 Cantilever Substrates for Quantitative Growth Experiments in the Environmental Transmission Electron Microscope**, *Frances Ross*, IBM T. J. Watson Research Center, MIT **INVITED**  
Environmental TEM is an excellent tool for obtaining quantitative information on growth processes and materials transformations. However, it is essential to measure the local temperature, pressure, and other key conditions at the sample location. Well controlled and accurately calibrated

*in situ* experiments often make use of specially designed samples and involve various methods for direct measurement of the reaction parameters. Here we describe some of these strategies, but focus on one particular sample design which we suggest is well suited for experiments addressing chemical vapor deposition. In this sample design, growth takes place at the tip of a hairpin cantilever microfabricated from single crystal silicon and heated by direct current. Epitaxial growth is possible on the cantilever surfaces, and deposition on materials such as amorphous silicon nitride is achieved by first coating the cantilever. We discuss how the local temperature and pressure can be measured by monitoring a calibrated growth process. We also discuss how growth can be examined under more complex environments, such as electric fields, using designs involving multiple cantilevers and actuators. We finally discuss approaches to higher pressure than is possible in conventional ETEM by integrating cantilevers in a closed gas cell. Custom substrates based on microfabricated designs appear poised to expand the possibilities of quantitative *in situ* growth experiments to exciting new regimes and materials systems.

9:40am **MM+AS+NS+PC-MoM-5 In Situ Laser Heating and Excitation in the Transmission Electron Microscope: Recrystallization, Grain Growth, Phase Separation and Dewetting in  $Ag_{0.5}Ni_{0.5}$  Thin Films**, *Philip D. Rack*, University of Tennessee Knoxville; *Y Wu*, University of Notre Dame; *C Liu*, University of Tennessee Knoxville; *T Moore*, *G Magel*, Waviks Inc.; *D Garfinkel*, University of Tennessee Knoxville; *J Camden*, University of Notre Dame; *M Stanford*, *G Duscher*, University of Tennessee Knoxville

Motivated by the desire to image excited state and high temperature materials phenomena at the nano and atomic scale, Waviks Inc. has recently developed an *in situ* optical delivery tool for the (scanning) transmission electron microscope (S)TEM. The tool used in these experiments contains two optical delivery channels and is mounted on a Zeiss Libra 200 (S)TEM system. A 785 nm wavelength laser diode system coupled through a 5  $\mu$ m mode field diameter single-mode fiber is used to deliver >200 mW to the sample surface. The laser can be gated from a few ns to continuous wave (cw) at repetition rates up to 16 MHz. A second optical channel with a 100  $\mu$ m core diameter broad spectrum multimode fiber is also available for coupling to any excitation source in the wavelength range from 200 to 2100 nm using a standard SMA fiber connector. The system is mounted to a 3 axis (+/- x,y,z) nanomanipulator for focusing to the electron/sample coincident point (with sample tilted at ~45 degrees). The system contains a lens system to re-image the fiber optics (1x) at a working distance of ~10 mm, which is long enough eliminate charging and minimizes re-deposition of material. To demonstrate the functionality of the tool, we will show photothermal annealing results of a supersaturated  $Ag_{0.5}Ni_{0.5}$  film. We will demonstrate recrystallization, grain growth, phase separation and solid state dewetting of the films via various laser powers, pulse widths, pulse numbers, laser radius. Finally, we will demonstrate interesting *in situ* excited state phenomena via electron energy gain spectroscopy of plasmonic silver nanoparticles.

10:00am **MM+AS+NS+PC-MoM-6 In situ Transmission Electron Microscopy Study of the Mechanical and Electrical Properties of Single III-V Semiconductor Nanowires**, *Lunje Zeng*, Chalmers University of Technology, Gothenburg, Sweden; *C Gammer*, Austrian Academy of Sciences, Austria; *B Ozdol*, Lawrence Berkeley National Laboratory; *T Nordqvist*, *P Krogstrup*, University of Copenhagen, Denmark; *A Minor*, Lawrence Berkeley National Laboratory; *W Jäger*, *E Olsson*, Chalmers University of Technology, Gothenburg, Sweden

III-V semiconductor nanowires possess outstanding electronic and mechanical properties that can be utilized in future high-speed electronic devices, solar cells and sensors. To better understand these properties and their relations to the microscopic structure of the nanowires, it is critical to directly correlate the structure and properties of single nanowires. However, the direct characterization of the mechanical and electrical properties of single nanowires, in particular, the correlation between them is still a challenge. In this study, we directly investigate the intrinsic mechanical and electromechanical properties of individual InAs nanowires using *in situ* transmission electron microscopy (TEM).

Quantitative stress, strain and electrical transport measurements were carried out on single InAs nanowires simultaneously. A Hysitron PI95 nanoindentation TEM holder was used for the *in situ* TEM study. By using an electrical push-to-pull (EPTP) device in the *in situ* TEM holder, tensile stress was applied via the nanoindenter in the holder while the force applied on the nanowire was measured by a transducer in the holder. The EPTP device also enables current-voltage (I-V) measurements on single

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nanowires. Nanoscale lattice strain mapping within the nanowire was performed using scanning transmission electron microscopy (STEM) combined with nanobeam electron diffraction (NBED). NBED diffraction patterns were acquired using a Gatan K2 direct detection camera. Based on the detailed strain and stress measurements, Young's modulus and Poisson's ratio of single InAs nanowires were directly determined. The Young's modulus of single InAs nanowire is smaller than that of the bulk, while the Poisson's ratio of the InAs nanowire is similar as the bulk InAs. The electrical measurements showed that the resistivity of the InAs nanowires decreased continuously with increasing tensile stress. The piezoresistance coefficient of the nanowire was found to be significantly larger than that of bulk InAs. Moreover, significant inhomogeneous strain distribution within the nanowire under stress was unveiled by STEM-NBED strain mapping. The inhomogeneous strain distribution at nanometer scale can increase the resistivity of the nanowire by enhancing electron scattering. The findings demonstrate unique mechanical and electromechanical properties of the nanoscale InAs wires and provide new insights of the correlation between mechanical strain and electrical transport properties in free-standing nanostructures.

Financial support from Swedish Research Council and Nanoscience and Nanotechnology Area of Advance at Chalmers University of Technology are acknowledged.

10:40am **MM+AS+NS+PC-MoM-8 Radiolytic Synthesis of Nanostructured Materials using *In situ* Liquid Cell Microscopy**, *Raymond Unocic, X Sang, A Belianinov, O Ovchinnikova, K More, S Jesse*, Oak Ridge National Laboratory  
**INVITED**

There are a wide range of solution-based strategies available for the size- and shape-controlled synthesis of functional nanomaterials for applications in catalysis, energy storage, biomedical, optical, and electronics. To elucidate growth mechanisms, *in situ* liquid scanning transmission electron microscopy (STEM) plays a role for directly imaging and quantifying growth dynamics of nanoparticles from liquid-phase precursors. In this work, we report several strategies for the *active* controlled synthesis of metallic and bimetallic nanoscale architectures using the concept of radiolytic synthesis. In one approach, we developed a direct-write, template-free method to fabricate self-supporting, hollow, metallic nanostructures, and we interpret the formation mechanisms based on direct observations of nucleation and growth. The electron beam used for imaging stimulates radiolysis, promoting the dissociation of water (H<sub>2</sub>O) molecules and the formation of complex radical species such as aqueous electrons (e<sub>aq</sub><sup>-</sup>) and other reducing and oxidizing species. The highly reducing radiolytic species assist in the chemical reduction of metal ions from the precursor solution, resulting in the formation of a metallic nanocrystal seed, which then acts as a catalyst for H<sub>2</sub> gas generation forming a metal encapsulated hollow nanobubble. In another approach, a custom-built electron beam nanopositioning and scan-generator system is used to precisely control the position and electron dose of the focused electron or ion beam to fabricate metallic and bimetallic nanostructured materials. These strategies enable fundamental electron beam interaction studies and open a new pathway for direct-write nanolithography from liquid-phase solutions.

This research was supported by the Center for Nanophase Materials Sciences, which is a United States Department of Energy Office of Science User Facility.

11:20am **MM+AS+NS+PC-MoM-10 Electron Beam Induced Cross-Linking in Liquid Hydrogels**, *Tanya Gupta, A Kolmakov*, National Institute of Standards and Technology (NIST)

Advances in additive manufacturing of bio-friendly polymeric materials over the last decade has revolutionized the diverse fields like rapid prototyping, tissue engineering, drug delivery etc. The technology currently relies on laser, thermal or UV induced 3D printing. Other triggers with similar effects can in principle be used as ionizing radiation to carry out the crosslinking. In this work we explore the use of electron beam to perform 3-D patterning at mesoscale and explore its potential towards rapid prototyping. In particular, knowledge of electron interaction with the printing ink allows us to predict effect of various control parameters like beam energy, current and dwell time on the topology of the features formed. A Monte-Carlo simulation coupled with a rigorous kinetic model is built to study the interplay of dose distribution, total interaction volume and diffusional effects of the active radiolytic species.

11:40am **MM+AS+NS+PC-MoM-11 Nanoscale Chemical Reactor Based on Localized Surface Plasmon Energy in Environmental Transmission Electron Microscope**, *Canhui Wang<sup>1</sup>, W Yang, UMD/NIST; R Sharma*, National Institute of Standards and Technology

Miniaturizing chemical processes in a research context has many advantages, including the ability to examine the reaction at atomic resolution, the reduced usage of costly and/or hazardous chemical reagents, and the ability to be integrated into analytical devices. [1-2] However, the current efforts of miniaturizing chemical processes have been limited by achievable minimum reaction volume and the lack of precision control over the reaction locations. Herein, we demonstrate a nanoscale chemical reactor utilizing localized surface plasmon (LSP) resonance as the energy source in an environmental transmission electron microscope (ETEM). This approach allows us to confine the reaction within proximity of the nanoparticle while taking advantage of the high spatial resolution capability of the electron microscope to monitor the reaction.

Plasmonic nanoparticles, such as Au or Al, are placed in a reactive environment inside the ETM. The composition and partial pressure of the gases are controlled by a gas handling system. Electron energy-loss spectra (EELS) imaging is used to acquire both elemental and LSP maps from the same nanoparticle. This allows the mapping and quantification of different gas adsorption on the nanoparticle surface. The energy required for the reaction of interest is provided by the LSP resonance excited by the high energy electron beam. The reaction location is confined within proximity of the nanoparticle due to the local field enhancement of the LSP resonance. Using a non-negative matrix factorization machine learning algorithm [3], we map the energy transfer pathways from the electron beam to the nanoparticle at nanometer spatial resolution and 0.08 eV energy resolution. The temperature distribution of the nanoparticle is monitored with few-nanometer spatial resolution using time-resolved EELS. Reaction processes, including morphological changes and transition of crystalline phases, are monitored using aberration-corrected atomic-resolution movies. By utilizing LSP resonance to initiate the reaction, we show that chemical processes can be confined in a nanometer scale volume, and modulated by electron flux. Important factors of the reaction, including composition of the reactants, adsorption of gases, transfer of energy, change of temperature, as well as reaction dynamics, can be monitored with nanometer or atomic resolution. Our approach paves the way to understanding a wide range of chemical reactions at the atomic scale.

References:

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## Materials and Processes for Quantum Computing Focus Topic

### Room 203A - Session MP+EM+MN+NS-MoM

#### Systems and Devices for Quantum Computing I

**Moderator:** Vivekananda Adiga, IBM, T.J. Watson Research Center

9:00am **MP+EM+MN+NS-MoM-3 Quantum Supremacy: Checking a Quantum Computer with a Classical Supercomputer**, *John Martinis*, Google Inc  
**INVITED**

As microelectronics technology nears the end of exponential growth over time, known as Moore's law, there is a renewed interest in new computing paradigms such as quantum computing. A key step in the roadmap to build a scientifically or commercially useful quantum computer will be to demonstrate its exponentially growing computing power. I will explain how a 7 by 7 array of superconducting qubits with nearest-neighbor coupling, and with programmable single- and two-qubit gate with errors of about 0.2%, can execute a modest depth quantum computation that fully entangles the 49 qubits. Sampling of the resulting output can be checked against a classical simulation to demonstrate proper operation of the quantum computer and compare its system error rate with predictions. With a computation space of  $2^{49} = 5 \times 10^{14}$  states, the quantum computation can only be checked using the biggest supercomputers. I will show experimental data towards this demonstration from a 9 qubit adjustable-coupler "gmon" device, which implements the basic sampling algorithm of quantum supremacy for a computational (Hilbert) space of about 500. We have begun testing of the quantum supremacy chip.

<sup>1</sup> NSTD Postdoc Finalist

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9:40am **MP+EM+MN+NS-MoM-5 Active Protection of a Superconducting Qubit against Josephson Amplifier Backaction**, *Baleegh Abdo, N Bronn, O Jinka, S Olivadese, A Corcoles, M Brink*, IBM T. J. Watson Research Center; *R Lake, D Pappas*, National Institute of Standards and Technology; *J Chow*, IBM T. J. Watson Research Center

Nonreciprocal microwave devices, e.g., isolators and circulators, are key components in high-fidelity, quantum-nondemolition (QND), measurement schemes. They separate input from output and protect the quantum systems from unwanted backaction originated by the output chain. However, state-of-the-art, cryogenic circulators and isolators are disadvantageous in scalable architectures because they are lossy, bulky and use magnetic materials and strong magnetic fields, which are not compatible with superconducting circuits. In this work, we realize and characterize nonreciprocal, superconducting devices suitable for qubit readout, which are formed by coupling two nondegenerate Josephson mixers in interferometric schemes. Nonreciprocity is generated by applying a phase gradient between the same-frequency pumps feeding the devices, which play the role of the magnetic field in a Faraday medium. We incorporate these Josephson-based, nonreciprocal devices into a qubit setup and demonstrate fast, high-fidelity, QND measurements of the qubit while actively protecting it against Josephson amplifier backaction.

10:00am **MP+EM+MN+NS-MoM-6 Nonlinear Light-matter Interaction: From Superconducting Qubits to Spins in Diamond**, *Eyal Buks*, Israel Institute of Technology, Israel

Cavity quantum electrodynamics (CQED) is the study of the interaction between matter and photons confined in a cavity. In the Jaynes-Cummings model the matter is described using the two-level approximation, and only a single cavity mode is taken into account. The interaction has a relatively large effect when the ratio  $E/\hbar\omega$  between the energy gap  $E$  separating the two levels and the cavity mode photon energy  $\hbar\omega$  is tuned close to unity.

The talk is devoted to the study of the light-matter interaction in the nonlinear regime using three different CQED systems. In the first experiment a Josephson flux qubit serves as a two-level system and a superconducting resonator as the cavity [1]. We experimentally find that the cavity response exhibits higher order resonances (called superharmonic resonances) in the nonlinear regime when the ratio  $E/\hbar\omega$  is tuned close to an integer value larger than unity. In the second experiment the interaction between a spin ensemble of diphenylpicrylhydrazyl (DPPH) molecules and a superconducting resonator is explored in the region where  $E/\hbar\omega \gg 1$  [2]. We find that the cavity response is significantly modified when the spins are intensively driven close to their Larmor frequency. Retardation in the response of the spin ensemble gives rise to effects such as cavity mode cooling and heating. In the third experiment the interaction between localized spins in diamond (nitrogen-vacancy and nitrogen substitutional) and a superconducting resonator is studied [3]. We find that nonlinearity imposes a fundamental limit upon sensitivity of CQED-based spin detection.

## References

1. Eyal Buks, Chunqing Deng, Jean-Luc F.X. Orgazzi, Martin Otto and Adrian Lupascu, Phys. Rev. A 94, 033807 (2016).
2. Hui Wang, Sergei Masis, Roei Levi, Oleg Shtempler and Eyal Buks, Phys. Rev. A 95, 053853 (2017).
3. Nir Alfasi, Sergei Masis, Roni Winik, Demitry Farfurnik, Oleg Shtempler, Nir Bar-Gill and Eyal Buks, arXiv:1711.07760.

10:40am **MP+EM+MN+NS-MoM-8 Variations in Surface Dipole-Moment Density with Coverage for C/Au(110) – (2 × 1) and Electroplated Au Ion-trap Electrodes**, *Dustin Hite, K McKay*, National Institute of Standards and Technology (NIST); *H Jooya*, ITAMP, Harvard-Smithsonian Center for Astrophysics; *E Kim*, University of Nevada, Las Vegas; *P Weck*, Sandia National Laboratories; *H Sadeghpour*, ITAMP, Harvard-Smithsonian Center for Astrophysics; *D Pappas*, National Institute of Standards and Technology (NIST)

Ion traps, designed to test the feasibility of scalable quantum information processing, suffer from excessive electric-field noise that increases strongly as the ion-electrode spacing decreases in progressively smaller traps. This noise couples to the charge of the ions in the trap causing motional heating, which can result in the decoherence of quantum logic gates. This heating can be reduced by orders of magnitude with the use of cryogenic trap electrodes or by in-situ surface cleaning with ion bombardment in traps with room-temperature electrodes. Many experiments over the past two decades have supported theories that model this noise source as being caused by fluctuations in the dipole moments of contaminant adsorbates

on the metallic trap electrode surfaces. Gold electrodes are often used to avoid oxidation and other contaminants, nevertheless a thin carbonaceous layer of approximately 3 monolayers (ML) develops on Au, even due to air exposure alone. In this work, we have studied the model system of C/Au(110) – (2 × 1) to understand the mechanisms for the variations in the surface dipole-moment density as a function of the degree of carbon coverage. We have implemented Kelvin probe force microscopy, along with x-ray photoelectron spectroscopy, to determine an average dipole-moment density with increasing carbon coverage, and have compared the results to density functional theory aided by ab-initio molecular dynamics techniques. We find a nearly linear decrease in the work function with a rate of approximately -0.7 eV/ML for sub-monolayer coverages, a regime in which trapped ions have been observed to have a maximum rate of heating. Finally, we compare the results for the model system to those for a microfabricated ion-trap chip with electroplated Au electrodes contaminated with a native hydrocarbon layer incrementally removed by ion bombardment.

11:00am **MP+EM+MN+NS-MoM-9 A Compact Cryogenic Setup for Quantum Computing with Trapped Atomic Ions**, *Ismail Inlek, R Spivey, G Vrijsen, Z Jia, J Kim*, Duke University

Trapped atomic ions are standard qubits for quantum computing with their long coherence times and high-fidelity qubit operations for universal quantum logic gates. However, conventional trapped ion systems often utilize bulky vacuum and optics setups, hindering scalability and ease of use. We aim to address these infrastructure issues by packaging micro-fabricated ion traps in an ultra-high vacuum (UHV) environment and designing optics to be an integral part of the overall system. Additionally, small footprint of the sealed UHV package allows users to easily install it on a cryostat to benefit from lower heating rates and further reduced vacuum levels. Moreover, these ion trap packages can be conveniently swapped to benefit from micro-fabricated ion trap manufacturing improvements without external UHV maintenance requirements. Towards achieving this goal, we report successful ion trapping in a compact cryogenic setup and characterize the performance of our apparatus for quantum computing applications.

11:20am **MP+EM+MN+NS-MoM-10 Advances in Trapped Ion Quantum Computing**, *Jungsang Kim*, Duke University **INVITED**

Trapped ions provide a highly desirable physical substrate on which to construct a scalable quantum computer. All qubits are exactly identical by nature, can be well isolated from the environment to establish long coherence times, and high fidelity quantum logic gates have been readily available. Furthermore, the long-range Coulomb interactions used for multi-qubit gates in a chain allows for highly connected network of qubits that are fully programmable, opening up opportunities for advanced and flexible quantum computer architectures. Some of the most advanced and complex quantum algorithms have been implemented in trapped ion systems leveraging these features. On the other hand, the ion trap systems so far have mainly relied upon conventional methodology used in atomic physics labs to set up the lasers, vacuum chambers and their optical alignments to realize the system. Novel integration technologies, including micro-fabrication, micro-electromechanical system (MEMS), and advanced packaging approaches have been adopted in the past decade to push the integration level for trapped ion systems. In this presentation, I will summarize the state-of-the-art systems used to implement quantum computing applications in the laboratories today, and also outline system design approach currently undertaken to improve the stability, reliability, and programmability of trapped ion quantum computers. Then, I will discuss the opportunities and challenges ahead for reaching a scalable quantum computer capable of executing useful tasks.

## Nanometer-scale Science and Technology Division

### Room 102B - Session NS+2D+AN+EM+MN+MP+PC+RM-MoM

#### IoT Session: Nanostructured Devices and Sensors

**Moderators:** David Czaplewski, Argonne National Laboratory, Liya Yu, NIST Center for Nanoscale Science and Technology

8:20am **NS+2D+AN+EM+MN+MP+PC+RM-MoM-1 Integrating Nanodiamonds with Augmented Artificial Intelligence and Digital Health to Optimize Combination Therapy**, *Dean Ho*, UCLA **INVITED**  
Dean Ho, Ph.D.

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Nanodiamonds have emerged as promising candidates for clinical drug delivery due to their ability to carry a wide range of candidate therapies, unique surface properties, and biological tolerability. This lecture will highlight our recent clinical trial to validate a nanodiamond-embedded biomaterial for root canal therapy indications [1]. We will discuss the broad spectrum of efficacy, safety, characterization, and other studies that bridged in vitro with preclinical and downstream in-human studies. This lecture will also discuss upcoming clinical nanodiamond-based drug carrier studies, as well as our work in augmented artificial intelligence (AI) to develop globally optimized nanodiamond-modified therapy. Pairing nanodiamond platforms with augmented AI will lead to major advances in drug development and markedly improve response rates and treatment outcomes for a broad spectrum of disorders. Our recent clinical trials using these powerful combination therapy optimization technologies and digital health platforms to scale their implementation to usher in a new era of nanomedicine-based treatment will also be discussed [2].

1. Lee et al., Proceedings of the National Academy of Sciences, 2017

2. Zarrinpar et al., Science Translational Medicine, 2016

## 9:00am NS+2D+AN+EM+MN+MP+PC+RM-MoM-3 Morphology-Controlled Large-Scale Tin Oxide Nanostructures for Highly Sensitive Room Temperature Gas Sensor, *Amrit Sharma*, Norfolk State University

Highly sensitive large-scale tin oxide (SnO<sub>2</sub>) nanostructures were grown on a glass substrate by vapor-liquid-solid (VLS) process using a mixture of anhydrous tin (II) chloride (SnCl<sub>2</sub>) and zinc chloride (ZnCl<sub>2</sub>) powders. We demonstrate a new kind of single cell vapor deposition system to precisely control nanostructural morphology by changing the weight ratio of SnCl<sub>2</sub> and ZnCl<sub>2</sub> and growth temperature. The morphology and structural property of as-grown nanostructures were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The SEM images revealed that the SnO<sub>2</sub> nanostructures with different densities, sizes, and shapes can be achieved by adjusting the weight ratio of SnCl<sub>2</sub> and ZnCl<sub>2</sub>. SnO<sub>2</sub> nanostructures with diameter ~20 nm and length ~100 nm showed ~85% sensitivity and 53 seconds of response time, whereas the nanorods with diameter ~100 nm and length ~1 μm showed ~50% sensitivity with 198 seconds response time. The nanostructured material with small size and shape showed better sensitivity on sensing at room temperature compared to previously reported SnO<sub>2</sub> based sensors.

## 9:20am NS+2D+AN+EM+MN+MP+PC+RM-MoM-4 Improving the Localized Surface Plasmonic Resonance Sensing Properties by Composite Metal/Dielectric Mixtures, *Steven Larson*<sup>1</sup>, *Y Zhao*, University of Georgia

Localized surface plasmon resonance (LSPR)-based sensors, whose resonance absorbance wavelength responds to the change in the local dielectric environment have attracted great attention and have been widely studied over the past decade. These sensors are traditionally improved by modifying the shape, size, and gap in the plasmonic nanostructure of the sensor. The sensitivity can also be tuned by the dielectric constant of the plasmonic material, such as noble metal alloys, but the improvements are not significant. Here we show that using a metal-dielectric composite, one can significantly improve the sensitivity of a LSPR sensor. Regular nanotriangle pattern samples composed of a mixture of Ag and MgF<sub>2</sub> with different composition ratios are prepared by combining nanosphere lithography and electron beam co-deposition. The plasmon resonance of these composite nanostructures at high Ag composition (C<sub>Ag</sub>) are shown to redshift with C<sub>Ag</sub> until a composition threshold (C<sub>Ag</sub> ≤ 90%) is met, where the resonance wavelength is nearly constant, slightly blue shifting. Multiple morphological and compositional characterization techniques are used to confirm that the shifts in the plasmonic properties are due to the change in composition and not a change in the morphology. The resulting LSPR sensor at C<sub>Ag</sub> = 90 at.% can achieve a sensitivity of 696 RIU/nm, as compared to 312 RIU/nm for the same nanotriangle with pure Ag. This significantly improved sensitivity is due to the modified dispersion relationship of the dielectric constant by the composite and will play an important role in future plasmonic material design and applications.

## 9:40am NS+2D+AN+EM+MN+MP+PC+RM-MoM-5 Improving the Selectivity of Tin (IV) Oxide Paper Based Gas Sensors with Plasma Surface Modification, *Kimberly Hiyoto*, *E Fisher*, Colorado State University

Metal oxide nanomaterials are desirable for solid-state gas sensors because of their ability to detect a wide variety of gases through changes in resistance resulting from gas-surface interactions. When optimizing these

sensors, the supporting substrate is rarely considered, resulting in devices that are often brittle and have a fixed amount of nanomaterial that can be exposed to target analytes. Recent work using paper as the supporting substrate yields more affordable sensors that are flexible, allowing for a more robust device. Furthermore, the porous morphology of the paper also provides a larger surface area to attach metal oxides when compared to a traditional flat substrate of the same dimensions. Another limitation of these metal oxide sensors is inherent in the detection method. The lack of selectivity and required operating temperature of ≥300 °C limits the widespread use of metal oxide sensors. Dopants or the addition of a filter in the device design are typical approaches to address these problems; however, this increases fabrication complexity and cost. Plasma processing is a promising strategy to address these issues because it maintains desirable bulk properties but modifies the surface of the material to enhance gas sensor performance.

Here, we describe the Ar/O<sub>2</sub> plasma modification of paper based, tin (IV) oxide (SnO<sub>2</sub>) nanoparticle devices as a function of applied rf power and precursor pressure. After plasma modification, the paper-based sensors exhibited improved response to carbon dioxide, ethanol, and benzene when compared to the untreated material on a more traditional substrate, zirconium dioxide. Additionally, sensor response to a target gas changed depending on the plasma modification parameters used, indicating the selectivity of these SnO<sub>2</sub> sensors can be easily tailored via plasma processing. Response and recovery studies of both the treated and untreated sensors will be discussed to demonstrate the dynamic behavior of these devices to the target gases as another measure of gas sensor performance and durability. Along with sensing behavior, optical emission spectroscopy and X-ray photoelectron spectroscopy provide insight into how the plasma modified the material, ultimately elucidating the relationship between material surface chemistry and sensor selectivity. Finally, preliminary work using this same fabrication process with another type of metal oxide gas sensor will be discussed to demonstrate the applicability of this method for other types of materials. Ultimately, these data work toward improved understanding of the gas sensing mechanism to design better performing gas sensors.

## 10:00am NS+2D+AN+EM+MN+MP+PC+RM-MoM-6 TiN@Si<sub>3</sub>N<sub>4</sub> Core-shell Heterostructures as Nanoantennas for Photocatalytic Reforming of Methanol, *Alejandro Alvarez Barragan*, *L Mangolini*, University of California, Riverside

The light-harvesting capacity of plasmonic nanoparticles has recently garnered attention in the synthesis of nanoantennas for photocatalysis. Aluminum, gold, and silver have been used to successfully drive hydrogen dissociation and CO oxidation reactions by injecting hot electrons into chemically active catalysts—such as platinum and palladium—adsorbed to their surface. However, the low response of aluminum at visible-near infrared (vis-NIR) wavelengths, the high cost of silver and gold, and the low thermal stability of these three metals, inspire the quest for alternative plasmonic materials that could potentially expand the field towards more ambitious and cost-effective applications. Titanium nitride (TiN) is a conductive ceramic with high hardness and bulk melting point (2930 °C). Its plasmon resonance located in the vis-NIR region, low cost relative to gold and silver, and well-understood properties as a thin film in the semiconductor industry, make it a strong alternative to mainstream plasmonic metals. The present work encompasses a comprehensive study of the oxidation kinetics of TiN particles at the nanoscale and an exploration of its role as nanoantennas for light-induced methanol reformation. TiN particles are synthesized via a scalable, modular, non-thermal plasma method. Titanium and nitrogen precursors are transported into a RF frequency plasma where TiN particles nucleate and grow. The high surface area and nitrogen deficiency of the particles facilitate the oxidation of the material and weaken its plasmonic response. The introduction of a secondary reactor with an input of SiH<sub>4</sub> as precursor gas leads to the formation of a Si<sub>3</sub>N<sub>4</sub> coating. STEM and XPS analyses show that Si<sub>3</sub>N<sub>4</sub> acts as a diffusion barrier, dramatically reducing the oxidation of the ~8 nm TiN particles. UV-vis-NIR spectrophotometry data show that the core-shell heterostructures experience a substantial blue-shift of the plasmon peak and an increase in intensity compared to the bare TiN. Platinum nanoparticles were subsequently deposited on the TiN@Si<sub>3</sub>N<sub>4</sub> by photo-induced reduction of an aqueous solution of chloroplatinic acid. After rinsing and centrifuging, the Pt/TiN@Si<sub>3</sub>N<sub>4</sub> heterostructures were diluted in a 50:50 water/methanol solution. Upon photoexcitation via white light illumination, hydrogen generation was readily detected by gas chromatography. This work also highlights the wide range of applications available for light-induced processes, ranging from materials processing

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

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(deposition of Pt particles) to photocatalysis (methanol reforming). It also strengthens the case for alternative plasmonic materials in a field dominated by precious metals.

10:40am **NS+2D+AN+EM+MN+MP+PC+RM-MoM-8 Nanostructured Sensor and Device Applications of Infiltrated Zinc Oxide, Leonidas Ocola**, Argonne National Laboratory; *Y Wang, J Chen*, University of Wisconsin-Milwaukee; *P Blaisdell-Pijuan*, California State University-Fullerton; *R Divan*, Argonne National Laboratory

**INVITED**

With the increased portfolio of materials deposited using atomic layer deposition (ALD) there has been an increased interest in infiltrated metal oxides such as zinc oxide for novel applications. We find that ZnO metal oxide ALD infiltration can be useful for nanoscale resolution imaging of biological samples and to fabricate novel UV and gas nanosensors with high sensitivity. The ALD infiltration utilizes similar concepts of the ALD coating process with the significant difference in process exposure times, pressure, and purpose. The purpose is to allow the precursor gases infiltrate a porous media (such as a dry biological sample or a photoresist polymer) and allow the reaction to occur inside the material matrix.

In terms of device fabrication we use SU8 as a negative resist that allows for localization of the infiltration process. We have used this property to make a device that is UV sensitive, and that is sensitive to ppm concentrations of gases by using infiltrated zinc oxide. The large bandgap and semiconductor properties of ZnO allow for a visible-blind ultra violet light sensor. We used a standard UV flashlight that emits at 408 nm as the UV source. We also tested the same device for sensing gases like nitrous oxide and formaldehyde. We show that the device can detect these gases with concentrations of 5 ppm. The change in current for such low concentrations was measured to be between 25% and 35 %.

With the purpose of investigating quantum applications of infiltrated ZnO, we also have characterized the growth of ZnO in PS-b-PMMA block copolymers (BCP) of spherical and cylindrical sub-20 nm morphologies and studied how the photoluminescence of these nanostructures varies per its seed layer. We report blue-shifted photoemission at 335nm (3.70eV), suggesting quantum confinement effects. Samples of ZnO prepared with an alumina seed layer showed additional defect state photoemission at 470nm and 520nm for spherical and cylindrical BCP morphologies, respectively. Defect photoemission was not observed in samples prepared without a seed layer. No Raman peaks were observed for any samples with less than four cycles of ZnO, implying the absence of phonons and the functionality of these ZnO nanostructures as isolated emitters. To that effect we have demonstrated a fabrication path to isolate single infiltrated cylinders, paving the way for further studies of optical properties of individual 20 nm ZnO nanostructures.

- Use of the Center for Nanoscale Materials an Office of Science user facility, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

11:20am **NS+2D+AN+EM+MN+MP+PC+RM-MoM-10 Templates for the Investigation of Size-Selected Nanocluster Networks, Patrick Edwards, V Kresin**, University of Southern California

The study of metal nanoclusters has revealed quantum nanoscale effects unique to the fully size-resolved regime. A highly notable example is electronic shell structure, akin to that in atoms and nuclei, which arises when confined conduction electrons organize into discrete energy levels. One consequence is the possibility of dramatic enhancement in electron Cooper pairing. Recent research from our group has provided evidence of this enhancement in certain free Al nanoclusters, with the electronic transition taking place at a temperature two orders of magnitude above that of bulk aluminum. We now aim to take advantage of this phenomenon by exploring the pairing transition in size-selected nanoclusters soft-landed on an appropriate substrate. Of particular interest are graphene and nanotube device architectures which provide unique templates for organizing nanocluster arrays. For example, a network of such superconducting nanoislands may induce superconductivity in graphene even at low coverages. Theory also predicts that an array of nanoclusters will not only support, but even enhance the Josephson current by 2-3 orders of magnitude. Carbon allotropes offer two distinct advantages for our system. First, the weak out-of-plane bonding provides a surface with less potential to disturb the structure of the soft-landed nanoclusters. Second, the tunability of graphene and carbon nanotube-based field effect transistors offers a versatile probe of nanocluster properties. We are also investigating the use of biological nanowires (bacterial flagella) as potential scaffolds upon which to deposit such nanocluster networks. These abundant and naturally occurring nanowires could serve as low cost and

highly reproducible alternatives to the more common metallic or semiconductor templates.

Research supported by the Army Research Office (W911NF-17-1-0154).

11:40am **NS+2D+AN+EM+MN+MP+PC+RM-MoM-11 High Performance Detection for X-ray and  $\gamma$ -ray with MAPbX<sub>3</sub> Perovskite Single Crystals, X Wang, Z Zhu, Q Li, J Wu, X Zhang, B Wang, Wei Lei**, Southeast University

Recently, organometallic lead trihalide perovskites have emerged as a new generation of opto-electronic materials. However, the high performance detection for x-ray and gamma-ray with MAPbX<sub>3</sub> is still a big challenge. For x-ray and gamma-ray detections, the detectors should have high sensitivity. If the photon counting method is adopted, the high energy resolution and high time resolution are also required. In this work, the large area MAPbBr<sub>3</sub> single crystal has been fabricated with a facile methodology. Due to the quite thick active material and large carrier mobility, the x-ray photons and gamma-ray photons can be absorbed with high efficiency. The photo generated electrons and holes can also be collected effectively with the large electric field. To decrease the dark current in the detection, a novel photo-diode structure is proposed here. In crystallization process of MAPbI<sub>3</sub> single crystal, the p-n junction can be formed with doping of selenium atoms into MAPbI<sub>3</sub> single crystal.

With various temperature method, the 30mm×30mm×7mm MAPbBr<sub>3</sub> single perovskite crystal is fabricated. As the experimental results shown, almost all of the 100 keV x-ray photons are absorbed when the MAPbBr<sub>3</sub> SPC is 7mm thick. The detection sensitivity is as high as 305  $\mu\text{C Gy}_{\text{air}}^{-1}\text{cm}^{-2}$  when the anode voltage of x-ray tube is 30 kV .

To reduce the dark current in the detection, two type of photo diode structures have been proposed here. Firstly, a photo diode with structure of Au/TPD/MAPbBr<sub>3</sub> PSC/C<sub>60</sub>/PCBM/Ag has been fabricated with spin coating and sputtering methods. Although the dark current density can be reduced to 20 nA/cm<sup>2</sup> with -30V bias voltage, the temporal response time is nearly 50  $\mu\text{s}$  due to the defects on the interfaces between PSC and carriers transport layers. Then, by doping selenium (Se) in MAPbI<sub>3</sub> perovskite single crystals (DPC) crystallization process, low dark current p-n junctions were fabricated without any organic layers. This photodiodes gives the high detection sensitivity as 21000 mC Gy<sub>air</sub><sup>-1</sup>cm<sup>-2</sup> and 41 mC Gy<sub>air</sub><sup>-1</sup>cm<sup>-2</sup> for 60 keV x-ray and 1.33 MeV gamma-ray respectively. In this photodiode, the transition time becomes shorter under higher electric field, and the carrier lifetime also becomes shorter due to the dopant of Se atoms. Finally, the temporal response time is measured as 3  $\mu\text{s}$  by experiments. The FWHM width of energy spectrum is decreased to 3.2%@1330 keV.

## Advanced Surface Engineering Division Room 202C - Session SE+NS+TF-MoM

### Nanostructured Thin Films and Coatings

**Moderators:** Jianliang Lin, Southwest Research Institute, Matjaz Panjan, Jozef Stefan Institute, Slovenia

8:20am **SE+NS+TF-MoM-1 The Role of Mechanical and Chemical Bonding Mechanisms in Adhesion of Nanoporous Anodic Aluminium Oxides (AAO), Shoshan Abrahami**, Vrije Universiteit Brussel (VUB), Belgium; *V Gudla*, Technical University of Denmark; *K Marcoen*, Vrije Universiteit Brussel, Belgium; *J de Kok*, Fokker Aerostructures; *T Hauffman*, Vrije Universiteit Brussel, Belgium; *R Ambat*, Technical University of Denmark; *A Mol*, Technical University Delft, Netherlands; *H Terry*, Vrije Universiteit Brussel, Belgium

Anodic aluminum oxides (AAOs) are important nanostructures in many engineering applications. But despite their popular use, the important parameters that control their (dis-)bonding to an organic coating are not fully understood. This study uses an original approach that employs porous- and barrier AAO specimens for both chemical characterization and mechanical tests, thereby enabling the distinction between chemical and morphological contributions to the surface affinity for interfacial bonding. A validation for the cooperative effect of mechanical and chemical bonding mechanisms is given in this study. This was achieved by post-anodizing immersion of AAO's in sodium fluoride solution after anodizing in sulfuric acid (SAA) or a mixture of phosphoric- and sulfuric acid (PSA). Transmission electron microscopy (TEM) cross-section images show that fluoride-assisted dissolution smoothed the oxide surface, removing the fibril-like top nanostructure of the porous oxides, which are important for dry adhesion. However, chemical surface modifications were dependent on the initial oxide composition, as measured by X-ray photoelectron



spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Chemical analysis reveals that the surface hydroxyls of AAO are partially replaced by fluorides that do not form interfacial bonding with the epoxy resin. As a result, the peel strength of SAA under wet conditions is severely reduced due to these chemical changes. Conversely, fluoride-assisted dissolution of surface phosphates in PSA compensates for the adsorbed fluorides and the wet peel strength of PSA panels is not further deteriorated.

[1] S.T. Abrahami et al., *J. Phys. Chem. C*, 119, 19967-19975 (2015).

[2] S.T. Abrahami et al., *npj Materials Degradation*, 1, 8 (2017).

[3] S.T. Abrahami et al., *J. Phys. Chem. C*, 120, 19670-19677 (2016).

**8:40am SE+NS+TF-MoM-2 Tuning Surface States of Nanocrystalline ZnO Films by Atomic Layer Deposited TiO<sub>x</sub>**, *C Yi, Ich Tran, M Law*, University of California, Irvine

We developed a facile route to tune the surface states of sol-gel prepared nanocrystalline zinc oxide (ZnO) thin films using ultrathin coatings of titanium oxide (TiO<sub>x</sub>) grown by atomic layer deposition (ALD). The electronic structure, surface states, and optical properties of the resulting ZnO/TiO<sub>x</sub> films are characterized by X-ray and ultraviolet photoelectron spectroscopy (XPS, UPS), reflection electron energy loss spectroscopy (REELS), UV-vis absorption spectroscopy, and photoluminescence (PL) spectroscopy. The surface bandgap of TiO<sub>x</sub>/ZnO is slightly increased comparing with that of ZnO. More importantly, we found that the surface gap states and interband transitions of ZnO were significantly suppressed by the TiO<sub>x</sub> layer, which may be useful for enhancing the performance of optoelectronic devices that utilize ZnO interlayers

**9:00am SE+NS+TF-MoM-3 Two-dimensional Hexagonal Boron Nitride (hBN) Layer Promoted Growth of Highly-oriented, Trigonal-structured Ta<sub>2</sub>C(0001) Thin Films via Ultra-high Vacuum Sputter-deposition on Al<sub>2</sub>O<sub>3</sub>(0001)**, *Koichi Tanaka, P Arias, M Liao, Y Wang, H Zaid, A Aleman, M Goorsky, S Kodambaka*, University of California, Los Angeles

It is generally believed that single-crystalline substrates with either the bulk or surface structure and lattice constant identical or similar to that of the film being deposited are required for the growth of high-quality crystalline thin films. Recent studies have shown that deposition on van der Waals (vdW) layers can lead to highly-oriented thin films of a variety of crystal structures and lattice parameters. Here, we show that two-dimensional (2D) hexagonal boron nitride (hBN) layers ( $a = 0.250$  nm and  $c = 0.667$  nm) improve the crystallinity of trigonal-structured Ta<sub>2</sub>C ( $a = 0.310$  nm and  $c = 0.494$  nm) thin films sputter-deposited on Al<sub>2</sub>O<sub>3</sub>(0001) substrates. Ta<sub>2</sub>C layers of desired thickness ( $t = 17 \sim 75$  nm) are grown on bare and hBN-covered Al<sub>2</sub>O<sub>3</sub>(0001) substrates via ultra-high vacuum direct current magnetron sputtering of TaC compound target in 20 mTorr pure Ar gas atmospheres at 1327 K. hBN layers are deposited via pyrolytic cracking of borazine (~600 L) onto Al<sub>2</sub>O<sub>3</sub>(0001) substrates at 1327 K. The as-deposited Ta<sub>2</sub>C films are characterized *in situ* using Auger electron spectroscopy and low-energy electron diffraction and *ex situ* using X-ray diffraction (XRD) and transmission electron microscopy (TEM) based techniques.  $\omega$ -2 $\theta$  XRD scans acquired from both Ta<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub>(0001) and Ta<sub>2</sub>C/hBN/Al<sub>2</sub>O<sub>3</sub>(0001) films with  $t = 17$  nm exhibit only Ta<sub>2</sub>C 0002n reflections (corresponding to  $c = 0.494$  nm) while thicker layers ( $t = 75$  nm) reveal the presence of additional 10 1 reflections. However, the 0002 reflection peak intensities are 5.4-fold stronger for the Ta<sub>2</sub>C layers on hBN/Al<sub>2</sub>O<sub>3</sub>(0001) than bare Al<sub>2</sub>O<sub>3</sub>(0001). High-resolution TEM images and associated Fourier transforms indicate that the layers are single-crystalline. XRD  $\phi$  scans show six 60°-rotated 1 0 - 1 2 peaks of Ta<sub>2</sub>C at the same  $\phi$  angles for 1 1 - 2 6 of Al<sub>2</sub>O<sub>3</sub> based on which we determine the epitaxial crystallographic relationships between the film and the substrate as Ta<sub>2</sub>C(0002) || Al<sub>2</sub>O<sub>3</sub>(0006) with in-plane orientation of Ta<sub>2</sub>C[1 0 - 1 0] || Al<sub>2</sub>O<sub>3</sub>[1 1 - 2 0]. We further show that 0002-oriented Ta<sub>2</sub>C thicker films can be obtained by inserting hBN layers at regular intervals during the deposition of thicker Ta<sub>2</sub>C films.

**9:20am SE+NS+TF-MoM-4 Nitride High Entropy Alloy Thin Films Deposited by Magnetron Sputtering and Cathodic Arc on Polymer Substrates: Structure and Electro-Mechanical Properties**, *Ao Xia*, Montanuniversität Leoben, Austria; *R Dedoncker*, Ghent University, Belgium; *M Cordill*, Erich Schmid Institute of Materials Science, Austria; *D Depla*, Ghent University, Belgium; *R Franz*, Montanuniversität Leoben, Austria

In recent years a new class of materials has emerged in the field of metallurgy: high entropy alloys (HEAs). These metallic alloys consist of 5 to 13 metallic elements in an approximately equimolar ratio. Studies conducted on HEA bulk materials revealed promising combinations of properties, such as strength, ductility, corrosion resistance, wear

resistance, hardness, diffusion and thermal conductivity. While research on bulk high entropy alloys has seen quite a boost over the past years, investigations on thin films are still a relatively unexplored area.

The focus of this report lies on the synthesis of MoNbTaVW HEA thin films by two different physical vapor deposition techniques, magnetron sputtering and cathodic arc deposition. The films were synthesized in Ar/N<sub>2</sub> atmosphere with varying gas flows in order to study the influence of N addition on structure and properties of the HEA thin films. Analysis by X-ray diffraction revealed a phase change from body-centered cubic (bcc) in case of the metallic HEA films to face-centered cubic (fcc) for the nitrides. A slightly lower N<sub>2</sub> gas flow is necessary in the case of magnetron sputter deposition to trigger the phase change than in the case of cathodic arc deposition. However, in both cases an increase in hardness was observed. For example, in the case of the films deposited by cathodic arc, the hardness increased from 18 to 30 GPa with the change from bcc to fcc phase. To further characterize the mechanical and electrical properties, the films were deposited on polymer substrates. The adhesion energy as determined from the geometry of buckles formed on the surface due to compressive stresses was a few J/m<sup>2</sup>. In-situ uniaxial tensile tests revealed a brittle behavior of all films with crack onset strains of up to 3 %. The formation of elongated through thickness cracks caused a rather abrupt increase of the resistivity upon the crack appearance.

**9:40am SE+NS+TF-MoM-5 Isomeric Phase Composition and Mechanical Properties of NbN Nanocomposite Coatings Deposited by Modulated Pulsed Power Magnetron Sputtering**, *Y.G. Li, H Yuan, Z Jiang, N Pan, M Lei*, Dalian University of Technology, China

Isomeric NbN nanocomposite coatings on stainless steel substrate with face-centered cubic phase  $\delta$ -NbN and hexagonal phase  $\delta'$ -NbN were deposited by modulated pulsed power magnetron sputtering under nitrogen flow rate  $f_{N_2}$  from 15% to 30%. It was found that the nitrogen flow rate  $f_{N_2}$  had a significant influence on the energy delivered in each macropulse, which led to a marked change in the phase composition and mechanical properties. The peak power decreases from 54 kW to 16 kW as  $f_{N_2}$  increases from 15% to 30% with the energy delivered in each macropulse from 23.2 J to 9.8 J. When  $f_{N_2}$  is at 15%, NbN coatings are mainly composed of  $\delta'$ -NbN phase which usually exists at high  $f_{N_2}$  or under high compressive residual stress showing (100) and (102) preferred orientation, while  $\delta$ -NbN gradually appears with the preferred orientation from (111) to (200) as  $f_{N_2}$  increases accompanied with the decrease of  $\delta'$ -NbN phase composition. The hardness and modulus of isomeric NbN nanocomposite coatings go up to 36 GPa from 30 GPa and 460 GPa from 366 GPa as  $f_{N_2}$  increases to 20% with residual compressive stress from 0.47 GPa to 1.93 GPa, then decrease to 29 GPa and 389 GPa with residual compressive stress of 1.01 GPa showing a nonlinear response with peak power. The NbN nanocomposite coatings with more  $\delta'$ -NbN phase show higher hardness and better toughness due to the composition variation of  $\delta'$ -NbN and  $\delta$ -NbN phases. The phase composition from  $\delta'$ -NbN to  $\delta$ -NbN phase should attribute to the delivered energy difference by peak power, and the anomalous increase in hardness should be originated from strengthening of the nanocomposite structure.

**10:00am SE+NS+TF-MoM-6 Ab initio Guided Development of Ternary Borides: A Case Study of Ti-B-N, Ti-Zr-B, Ti-W-B, Ta-W-B, and V-W-B Systems**, *V Moraes, R Hahn, M Bartosik, H Riedl*, TU Wien, Austria; *H Euchner*, Ulm University, Austria; *D Holec*, Montanuniversität Leoben, Austria; *Paul Heinz Mayrhofer*, TU Wien, Austria

Transition-metal borides are a special class of ultra-high temperature ceramics. Among these, refractory borides such as TiB<sub>2</sub>, ZrB<sub>2</sub>, VB<sub>2</sub>, TaB<sub>2</sub>, and WB<sub>2</sub> are attractive candidates for many applications – ranging from high temperature electrodes, cutting tools, and molten metal containment to microelectronic buffer layers – because of their thermomechanical and chemical properties, their high melting temperatures up to ~3500 °C, and excellent high temperature strengths. However, these diborides have a comparably low fracture toughness of  $K_{Ic} \sim 1$  MPa $\sqrt{m}$  (here, basically obtained by in-situ micromechanical cantilever bending tests).

How diboride materials can be designed – implementing quantum chemistry guided materials design concepts – to allow for a combination of high strength, ductility, and thermal stability, is the focus of this talk. We will use recent developments of diborides – where we applied alloying and architecture concepts (e.g., composition and/or phase modulated layers) – to explore such materials-science-based guidelines for improved properties. Especially the phase stability (with respect to chemistry and temperature) of diborides is an extremely interesting task. For example, only WB<sub>2</sub> (among all binary diborides, except for TcB<sub>2</sub>) provides a G/B ratio



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below 0.5 (~0.34) and a positive Cauchy pressure  $C_{13}-C_{44}$  (~73 GPa), which are typical indications for dominating non-directional bonds and thus a more ductile behavior. But  $WB_2$  provides these properties only in its metastable  $\alpha$ -structure (AlB<sub>2</sub>-prototype) and not for its thermodynamically stable  $\omega$ -structure (WB<sub>2</sub>-prototype). With the help of ternary diborides, such as (Ti,W)B<sub>2</sub> or even (Ta,W)B<sub>2</sub>, the  $\alpha$ -structure can be stabilized (even up to ~1200 °C). Even more important is a selective sensitivity of the  $\alpha$ - and the  $\omega$ -structure for the formation of vacancies. Especially, when using physical vapor deposition (PVD) techniques at moderate temperatures (here ~400 °C) the content of vacancies (and point defects in general) is rather high. Such defects are less penalized in the  $\alpha$ - than in the  $\omega$ -structure, allowing for growing even single-phased  $\alpha$ -WB<sub>2</sub> by PVD, exhibiting hardnesses H of ~40 GPa combined with high fracture toughness of  $K_{IC}$  ~3 MPa $\sqrt{m}$ .

With the help of superlattices, nanocolumnar and nanocomposite structures, we show that also with architectural concepts, strength (H ~45 GPa) and ductility ( $K_{IC}$  ~3.5 MPa $\sqrt{m}$ ) can be improved simultaneously.

The individual concepts will allow designing materials to meet the ever-growing demand for further improved coatings, tailor made for specific applications.

10:40am **SE+NS+TF-MoM-8 Toughness Enhancement in Hard Ceramic Films by Alloy Design**, **Hanna Kindlund**, Department of Mechanical and Aerospace Engineering, University of California Los Angeles (UCLA) **INVITED** Transition-metal nitrides are refractory ceramics with high hardness, excellent wear resistance, high temperature stability, and good chemical inertness. Therefore, they are attractive in many applications, especially, as protective coatings against scratches, erosion, corrosion, and wear.

Tremendous efforts have been dedicated in enhancing hardness of ceramic films. However, in addition to high hardness, most applications also require high ductility, to avoid brittle failure due to cracking when coatings are subjected to high thermo-mechanical stresses. However, transition-metal nitrides, as most ceramics, are usually brittle, exhibiting low ductility and hence poor toughness.

Enhancing toughness in ceramic films is a challenging task that requires a fundamental understanding of the mechanical behavior of materials, which depends on their microstructure, electronic structure, and bonding nature. Theoretical studies using *ab initio* calculations predicted that alloys of VN with WN or MoN exhibit enhanced toughness as a result of their high valence electron concentrations, leading to an orbital overlap which favors ductility during shearing.

Here, I present experimental results on the growth of  $V_{1-x}W_xN_y$  and  $V_{1-x}Mo_xN_y$  alloy thin films, their microstructure, mechanical properties and electronic structure, and relate these properties with their enhanced ductility, demonstrating that it is possible to develop hard-yet-ductile ceramic coatings.

11:20am **SE+NS+TF-MoM-10 From Ab-Initio Design to Synthesis of Multifunctional Coatings with Enhanced Hardness and Toughness**, **D Edström**, **D Sangiovanni**, **L Hultman**, Linköping University, Sweden; **I Petrov**, **J Greene**, University of Illinois at Urbana Champaign; **Valeriu Chirita**, Linköping University, Sweden

Enhanced toughness in hard and superhard thin films is a primary requirement for present day ceramic hard coatings, known to be prone to brittle failure. Density Functional Theory (DFT) investigations predicted significant improvements in the toughness of several B1 structured transition-metal nitride (TMN) alloys, obtained by alloying TiN or VN with MoN and WN. The calculations reveal that the electronic mechanism responsible for toughness enhancement stems from the high valence electron concentration (VEC) of these alloys, which leads to the formation of alternating layers of high/low charge density orthogonal to the applied stress, and allows a selective response to deformations. This effect is observed for ordered and disordered ternary TMN alloys. Recently, these results have been validated experimentally. Single-crystal VMoN alloys, grown by dual-target reactive magnetron sputtering together with VN and TiN reference samples, exhibit hardness > 50% higher than that of VN, and while nanoindented VN and TiN reference samples suffer from severe cracking, the VMoN films do not crack. New DFT calculations, suggest similar toughness improvements may be obtained in pseudobinary NaCl structured transition-metal carbide (TMC) compounds by alloying TiC or VC with WC and MoC, as inferred from the electronic structure analysis and stress/strain curves obtained for the newly formed ternary TMC alloys.

KEYWORDS: nitrides, carbides, toughness, hardness, ductility.

11:40am **SE+NS+TF-MoM-11 Mechanical Properties of  $V_{0.5}Mo_{0.5}N_{1-x}O_x$  Thin Films**, **Daniel Edström**, **D Sangiovanni**, Linköping University, Sweden; **L Landälv**, Linköping University, Sandvik Coromant AB, Sweden; **L Hultman**, Linköping University, Sweden; **I Petrov**, **J Greene**, University of Illinois at Urbana Champaign, Linköping University, Sweden; **P Eklund**, **V Chirita**, Linköping University, Sweden

Improved toughness is one of the central goals in the development of wear-resistant coatings. Extensive theoretical and experimental work has revealed that single-crystal NaCl-structure VMoN ceramics possess inherently enhanced ductility, as well as high hardness (~20 GPa) [Kindlund et al. APL Mat 2013]. These surprising findings demonstrate that VMoN-based materials are very promising candidates for replacing other ceramics in hard, refractory protective-coating applications. However, during applications, hard coatings inevitably oxidize which can compromise material properties. Herein, we use density functional theory to evaluate the mechanical properties, as well as the thermodynamical stability, of  $V_{0.5}Mo_{0.5}N_{1-x}O_x$ , with x approximately equal to 0.05, 0.1, and 0.5. We study cubic  $V_{0.5}Mo_{0.5}N_{1-x}O_x$  solid solutions characterized by both high and low short-range cation/anion ordering.  $V_{0.5}Mo_{0.5}N_{1-x}O_x$  is predicted to be thermodynamically stable for  $x < 0.1$ , although higher oxygen ratios can possibly be achieved with non-equilibrium growth techniques such as physical vapor deposition. Our results show that oxygen concentrations  $x = 5\%$  and  $10\%$  have little effect on the mechanical properties of random  $V_{0.5}Mo_{0.5}N_{1-x}O_x$  alloys, which retain both hardness and ductility. At  $x = 50\%$ , bulk, elastic, and shear moduli, as well as Cauchy pressure, are reduced by ~25%, but the material is still predicted to remain ductile. For ordered  $V_{0.5}Mo_{0.5}N_{1-x}O_x$ ,  $x = 6\%$  already results in a drastic change in mechanical properties, likely due to disruption of the cubic symmetry. A further increase in the oxygen content yields significant reductions in Cauchy pressures, indicating reduced ductility. However, the Cauchy pressure remains positive for all oxygen concentrations, suggesting that none of the investigated alloys are brittle according to the Pugh and Pettifor criteria.

KEYWORDS: oxides, nitrides, toughness, hardness, ductility.

## Tribology Focus Topic

### Room 201A - Session TR+AS+NS+SS-MoM

#### Tribology Focus Session

Moderator: Filippo Mangolini, University of Leeds, UK

8:20am **TR+AS+NS+SS-MoM-1 Structural Superlubricity: History, Breakthroughs, and Challenges**, **Mehmet Z. Baykara**, University of California, Merced **INVITED**

The idea of *structural superlubricity* holds immense potential for the realization of nearly frictionless sliding in mechanical systems, with implications for fields as diverse as environmental conservation and space travel. The basic principle of structural superlubricity involves the proposition that friction should diminish at an interface formed by atomically-flat and molecularly-clean crystalline surfaces with different lattice parameters and/or incommensurate orientation. Despite the rather straightforward character of its basic principle, the realization of structural superlubricity under ambient conditions has been challenging due to the requirement of molecular cleanliness at the interface.

In this talk, we will first briefly review three decades of structural superlubricity research by emphasizing important milestones and breakthroughs. Subsequently, we will present results of nano-manipulation experiments from our lab, which demonstrate the remarkable occurrence of structural superlubricity for gold and platinum nano-islands sliding on graphite under ambient conditions. Complementary to the experiments, results of *ab initio* calculations will be discussed, which (i) reveal that the noble metal-graphite interface is expected to remain largely free from contaminant molecules, leading to structurally superlubric sliding under ambient conditions, and (ii) confirm the experimental observation of larger friction forces for platinum, attributable to higher energy barriers encountered during sliding. The experiments additionally demonstrate that the scaling power between friction force and contact size is independent of the chemical identity of the sliding atoms, but is determined by the geometric qualities of the interface. The talk will conclude with a review of remaining challenges for structural superlubricity, in particular those involving size- and deformation-related limits.

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9:00am **TR+AS+NS+SS-MoM-3 An Examination of the Nature of Bonding Indentation and Sliding using MD and in-situ Nanoindentation**, *Judith Harrison*, United States Naval Academy **INVITED**

Adhesion between DLC tips and diamond counterfaces was examined using a nanoindenter coupled to TEM and molecular dynamics (MD). Additional MD simulations of sliding contact between the same tip-substrate materials were also carried out. Strong interactions between the surfaces in vacuum led to gradual nanoscale wear of the DLC. Force-separation curves show an approximate correlation between pull-off force and applied load for various contact points, while pull-in force was fairly constant for all contact points and independent of applied load. MD simulations were designed to replicate experiment as closely as possible and used the AIREBO and the REBO+S potentials. DLC tips with the same general shape (which often deviated from the assumed paraboloidal tip geometry due to wear) were brought into contact with diamond surfaces. MD results demonstrate that pull-off force is correlated with bonds formed during contact, providing an explanation of the trends observed in the TEM data. The effects of contact point and hydrogen-termination on pull-off forces and the nature of bond formation during sliding as a function of speed and hydrogen termination will be presented. The results of similar experiments and MD simulations using Si tips in contact with diamond counterfaces of adhesion and sliding using the ReaxFF potential will also be discussed.

9:40am **TR+AS+NS+SS-MoM-5 The Chemistry of Friction, Wear, and Tribofilm Growth on 2D Materials**, *Jonathan Felts*, Texas A&M University **INVITED**

The evolution of a sliding interface between two objects is difficult to theorize, predict, and measure due to the complexity of the interface, which is often described phenomenologically. Here we utilized a nanometer sized single asperity of an atomic force microscope tip sliding against atomically flat graphene and graphene oxide to study the origins of friction, wear, and tribofilm growth phenomena at the atomic scale. We hypothesize that all of the observed contact phenomena at the macroscale can be described using fundamental thermochemistry. At low applied tip loads, the friction of graphene oxide is non-monotonic with tip velocity, initially increasing for speeds from 100 – 10,000 nm/s, followed by a decrease and a subsequent increase above 50,000 nm/s. At sufficiently high applied loads, we observe wear of oxygen groups from graphene oxide at temperatures between 50-400 °C and loads between 10-700 nN, and find an exponential increase in wear rate with applied load. For the case of an electrically biased tip oxidizing pristine graphene, the oxidation rate somewhat paradoxically increases with applied load, despite previously observed enhancement in wear rate with load. All of the above observations can be understood in the context of mechanically driven thermochemical reactions. The friction behavior depends on two competing factors—aging of the sliding contact due to chemical bonding between tip and substrate, and hopping of unbonded tip atoms between graphene lattice sites. Atomic wear of graphene oxide is well described by the tilted potential energy surface theory of mechanically driven chemistry, which predicts a non-linear reduction in the energy barrier with applied load. We further show that the tilted potential energy surface model also well describes the enhancement of oxidation rate. The work presented here creates a foundation for describing the mechanics of sliding contacts as chemical processes, and further paves the way towards quantitatively understanding how mechanical force drives chemical reactions in general.

10:40am **TR+AS+NS+SS-MoM-8 Nanomechanics of Soft, Hierarchical Polymer- and Biological-Networks**, *Prathima Nalam*, University at Buffalo - SUNY **INVITED**

Soft networks based on synthetic polymer chains or biological filaments, with architecture that are anisotropic or hierarchical in nature, offer a path towards the development of tough and reliable flexible structures. These structures find applications in numerous areas including healthcare delivery, environmental purification systems, energy storage systems, flexible electronics, and tribology. Further, the ability of these networks to present a wide range of tunable functional properties, through alterations in the chemical structure of the monomers, synthesis or operational conditions, etc., which otherwise is rarely possible with other hard materials, promise the development of smart materials. In this study, we present the nanomechanical and nanotribological behavior of two stimuli-responsive networks consisting of (a) polyelectrolyte films with a thin layer of chitosan (CH) grafted on top of poly (acrylic acid) (PAA) brushes (CH/PAA) and (b) naturally grown mycelium-based networks. The CH/PAA network is a synthetic hierarchical structure, in which each layer exhibits a strong structural change with variation in solution pH. On the other hand, Mycelium is a soft biological network (derived from mushrooms) composed

of multicellular or unicellular filaments, known as hyphae, with anisotropic micro-architecture.

A detailed investigation of the depth-dependent elastic moduli on these networks is conducted using atomic force microscope (AFM, Oxford Instruments) to study the impact of local structural heterogeneity of the network on its mechanical properties. A colloid-attached AFM cantilever was employed to study the surface interactions and to indent the material in the linear elastic deformation regime. The study of the impact of the network structure on the material rigidity, measured at both nano- and macro- scales, has enabled to probe the validity of affine network deformation theories for hierarchical networks. With this understanding, the design and development of antibacterial platforms (with CH/PAA platforms) and water-filtration membranes (with mycelium networks) using hierarchical soft structures is discussed.

11:20am **TR+AS+NS+SS-MoM-10 Mechanisms for Controlling Friction and New Approaches for Achieving Superlubricity Regime in 2D Materials**, *Diana Berman*, University of North Texas; *A Erdemir*, *A Sumant*, Argonne National Laboratory **INVITED**

Friction is an important aspect of many areas of everyday life. Varieties in mechanical systems from nano to macroscale and efforts to minimize energy losses intersect with challenges of controlling the friction. The popularity of recently discovered 2D materials and their usefulness for multiple applications enabled understanding the friction at a more fundamental level and opened new routes for manipulating friction to superlubricity or near zero friction values.

Here, we review the basic mechanisms that complies the frictional energy dissipation, such as wear, molecular deformation, thermal effect, electronic effect, bonding, environment and chemistry, phonons, and structural effect. We present the case studies highlighting how these mechanisms are controlled in 2D materials. Finally, we highlight recent advances in implementing 2D materials for friction reduction to superlubricity across scales from nano- up to macroscale contacts. We show that nanoscale superlubricity mechanisms originating from the formation of frictionless nanoscale systems, as in case of graphene-nanodiamond scrolls and carbon nanonion structures, can be successfully transferred to macroscale effects. Development of 2D materials opened a new pathway for manipulating friction, which makes superlubric friction today's reality.

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- [2] D. Berman, et al., special issue in Diamond and Related Materials, 54, 91 (2015).
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## 2D Materials Focus Topic

### Room 201B - Session 2D+MI+NS-MoA

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

**Moderators:** Stephan Hofmann, University of Cambridge, UK, Richard Vanfleeter, Brigham Young University

#### 1:20pm 2D+MI+NS-MoA-1 Observing the Mechanisms of Graphene Growth during Chemical Vapor Deposition: Routes to Controlling Layer Number and Domain Size, *Robert Weatherup*, University of Manchester, UK

INVITED

Chemical vapor deposition (CVD) on polycrystalline metal foils has emerged as the most economic and versatile means for producing 2D materials over large areas,<sup>1</sup> and directly integrating them with other device materials to achieve new functionality.<sup>2</sup> To tailor these materials to specific applications, a detailed understanding of the underlying growth mechanisms is required such that parameters such as domain size, defect density, and layer number can be precisely controlled. However, the elevated temperatures and reactive gas environments involved in growth make direct observation challenging, whilst ex situ measurements are often ambiguous.

Here we apply environmental scanning electron microscopy (ESEM) and ambient pressure X-ray photoelectron spectroscopy (APXPS) to directly observe graphene growth under realistic CVD conditions on polycrystalline Pt foils.<sup>3</sup> This reveals a variety of processes involved in graphene formation including isothermal growth by direct hydrocarbon dissociation, isothermal dissolution into the catalyst bulk, and precipitation on cooling. The balance of these processes, and thus growth outcome, is shown to depend critically on the distribution of carbon close to the catalyst surface, which is in turn intimately linked to the processing profile. We thereby develop a growth model for graphene CVD that considers precursor dissociation, mass-transport, attachment to the edge of growing graphene domains.<sup>4</sup> This is shown to be generally applicable to several transition metal catalysts,<sup>5</sup> and serves as a general framework for understanding and optimizing the growth of 2D materials on polycrystalline catalysts.

We thus demonstrate that the CVD process can be rationally designed to yield different desired growth outcomes from the same polycrystalline starting catalyst, including uniform SLG with large domain sizes (>100  $\mu\text{m}$ ), large isolated BLG domains (>50  $\mu\text{m}$ ), and uniform BLG. Our results show that through targeted operando experiments the influence of key process parameters can be established, enabling precise control over 2D material growth including domain sizes and layer number.

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#### 2:00pm 2D+MI+NS-MoA-3 Band Alignment of 2-D Materials by Internal Photoemission, *Q Zhang, S Zhang*, Theiss Research & National Institute of Standards and Technology; *B Sperling, Nhan Nguyen*, National Institute of Standards and Technology

Two-dimensional (2-D) materials have brought new possibilities for the future electronic and optoelectronic applications [1], [2]. Electronic band alignment at the interface is one of the important parameters in many device designs. For instance, staggered band alignment is preferred to separate photon generated electron-hole pairs in optoelectronic and photovoltaic devices [3]. For the 2-D materials in the monolayer (ML) limit, it has been a challenge to accurately measure the electron affinity which determines how the bands align at the interface. In fact, most 2-D heterojunctions are designed using calculated or theoretically predicted band alignments [4]. In this work, we present an experimental measurement using internal photoemission spectroscopy (IPE) to determine the band offset of MX<sub>2</sub> semiconductors (M = Mo, W; X = S, Se) in relative to an oxide barrier and suggest possible combination of the MX<sub>2</sub> materials to be used for optoelectronic and photovoltaic applications. This IPE approach is seen as a unique method that can be applied to characterize other 2-D materials.

The IPE test structure is fabricated by exfoliating MX<sub>2</sub> flakes on to the Al<sub>2</sub>O<sub>3</sub>/p<sup>+</sup>Si substrate and depositing Ti/Pt contacts on the flakes with large open areas for light absorption. By using gold film mediated exfoliation method [5], large area (> 75 x 75  $\mu\text{m}^2$ ) ML MX<sub>2</sub> flakes are obtained, confirmed by Raman spectrum and photoluminescence mapping.

Photocurrents of the MX<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-p<sup>+</sup>Si structure are measured with the incident photon energy swept from 2.0 eV to 5.5 eV and gate voltage  $V_{GS}$  (applied to the Si back gate) stepped from -1.0 V to 1.6 V. The oxide flat band voltage ( $V_{FB}$ ) is extracted by the voltage where the photocurrent switches sign near and above photoemission thresholds. The band offsets at the MX<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>/Si interfaces are extracted as the thresholds of the cube root of photoemission quantum yield (Y) being the ratio of the photocurrent over the incident light flux [6]. At gate bias below  $V_{FB}$ , the band offset between Al<sub>2</sub>O<sub>3</sub> and Si is measured and found to be 3.4 eV for all the 4 devices, which is also a well-established value. More importantly, the band offset at the MX<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> interfaces combined with the known optical band gaps of ML MX<sub>2</sub> suggest that MoS<sub>2</sub>/WS<sub>2</sub> and MoSe<sub>2</sub>/WSe<sub>2</sub> can possibly form the staggered heterojunction.

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#### 2:20pm 2D+MI+NS-MoA-4 Visible to mid-IR Nanoscale Characterization of 2D Materials via Photo-induced Force Microscopy, *Pdraic O'Reilly, D Nowak, S Park*, Molecular Vista

While several 2D materials have been studied with scattering scanning near-field optical microscopes (s-SNOM) with nanoscale spatial resolution, most have focused on the study of surface phonon polariton (SPP) [1]. In this paper, we introduce a relatively new technique called photo-induced force microscopy (PiFM), which combines atomic force microscope (AFM) and broadband optical spectroscopy to analyze both topography and polarizability of samples with sub-10 nm spatial resolution [2]. With PiFM, the near-field optical information is acquired by measuring the photo-induced force between the AFM tip and the sample rather than by collecting photons with a far-field photo-detector; this near-field excitation and near-field detection configuration provides excellent signal-to-noise without the far-field background signal from the much larger focal spot, making the technique robust and easy-to-use. With mid-IR sources, PiFM can image nanoscale SPP as with s-SNOM. With supercontinuum visible-infrared light source, it can directly probe the exciton resonances with equally impressive spatial resolution. With its capability to image number of layers, quality of samples, and plasmonic fields, PiFM is an ideal nanoscale characterization tool for wide range of 2D materials. Results from graphene, MoS<sub>2</sub>, WS<sub>2</sub>, and hBN will be presented.

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#### 2:40pm 2D+MI+NS-MoA-5 Polymorphic Structures and Diversified Properties of Low-dimensional Materials Investigated by In situ Electron Microscopy, *Kazu Suenaga*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

INVITED

Two-dimensional transition metal dichalcogenides (TMDs), consisting of an atomic plane of a transition metal (M: Ti, Nb, Mo, Re, etc.) sandwiched between two chalcogen atomic planes (X: S, Se, Te). This crystalline structure combined with a wide variety of constituent elements give rise to diverse electronic properties, strongly governed by the number of its *d*-orbital electrons. MoS<sub>2</sub> and WS<sub>2</sub> are the most representative “group 6” TMDs featuring trigonal prismatic (H) phase semiconductor with a direct band gap. The TMDs can exhibit various polymorphs and present different electronic properties as the atomic arrangement changes originating from charge transfer. A metallic octahedral (T) phase has been reportedly stabilized by alkali metal intercalation [1], and another distorted octahedral phase zigzag-shape phase (Z) with clusterization of metal atoms into zigzag chains by using solvent-based exfoliation. Some simulations indicate that the Z phase may undergo the Peierls distortion and be transformed into a diamond-shape (DS) phase where atoms reconstruct in a way that four metal atoms appear as a diamond (rhombus) in the plane [2]. We show in this talk the experimental evidences for these polymorphic structures and diversified properties found in a family of 2D TMDs.

These monolayer forms in TMDs are typically the same as a single layer of the bulk material. However, PdSe<sub>2</sub> presents a puzzle. Its monolayer form has been theoretically shown to be stable, but there have been no reports that monolayer PdSe<sub>2</sub> was fabricated. Here, we demonstrate that the preferred monolayer form of this material amounts to a melding of two

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bulk monolayers accompanied by the emission of Se atoms so that the resulting stoichiometry is Pd<sub>2</sub>Se<sub>3</sub>[3].

[1] Y.-C. Lin, D. O. Dumcenco, Y.-S. Huang and K. Suenaga, *Nature Nanotechnology*, 9 (2014) pp.391-396

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**3:40pm 2D+MI+NS-MoA-8 Probing Interlayer Interaction in van der Waals Materials by Low-energy Electron Microscopy (LEEM), Johannes Jobst, D Geelen, Leiden University, Netherlands; R Tromp, IBM, T.J. Watson Research Center; S van der Molen, Huygens-Kamerlingh Onnes Laboratory, Netherlands**

**INVITED**

Knowledge on the interaction between layers is crucial to tailor the properties of van der Waals (vdW) materials. We investigate these using newly developed techniques based on low-energy electron microscopy (LEEM). With LEEM, we probe the reflection of electrons as a function of incoming energy (0-100 eV). We have recently extended our UHV instrument to also measure low-energy electron transmission (eV-TEM).

We apply LEEM and eV-TEM to few-layer graphene. With each layer, an unoccupied interlayer state is added, which hybridizes with the other states. In LEEM, the resulting eigenstates appear as minima in the reflection spectrum. In transmission, they show up as maxima. From both functions, we determine the hybridization energies of the interlayer states, which extend in 2D.

Next, we study the 2D-dispersion relations of these states. For that, we have developed *angle-resolved reflected-electron spectroscopy* (ARRES) [1]. With ARRES, we investigate few-layer graphene, hBN, as well as their combination. For the latter case we find negligible interaction. [2]

[1] Jobst *et al.*, *Nat. Comm.* 6, 8926 (2015)

[2] Jobst *et al.*, *Nat. Comm.* 7, 13621 (2016)

**4:20pm 2D+MI+NS-MoA-10 Fast Full Wafer Analysis for Graphene and 2D-materials by Imaging Ellipsometry, Sebastian Funke, Accurion GmbH, Germany; P Braueniger-Weimer, S Hofmann, University of Cambridge, UK; P Thiesen, Accurion GmbH, Germany**

By combining the resolution of optical microscopy and the sensitivity of thin films, imaging ellipsometry (IE) is a powerful tool to characterize thin materials. It allows to measure monolayers of 2D-materials but also to visualize these monolayers on arbitrary substrates. It overcomes the need of specially tuned SiO<sub>2</sub> thicknesses to visualize e.g. Graphene in an optical microscope.

In the talk we present [1], the characterization of Graphene throughout all stages of the manufacturing process from the growth on Cu-foil up to the transferred sample on Si wafers. Unlike other methods IE directly visualizes graphene on the rough Cu. We apply IE to resolve a large area map of Graphene on Cu. The Graphene is directly characterized on the Cu-foil, no oxidation of the Cu is needed. To overcome the waviness of the foil, an autofocus algorithm is developed and applied.

IE is also able to distinguish a Graphene monolayer and hBN monolayer after the transfer process to a Si/SiO<sub>2</sub> substrate. We show large area map of the transferred sample. The contrast mode of IE is able to distinguish the different regions: (a) substrate only, (b) hBN only, (c) Graphene only and (d) an overlapping region of hBN and Graphene. The complete sample approx. 1cm x 0.8 cm is recorded in less than 6 minutes and shows defects and wrapping of hBN of a size as small as 4 μm.

Lastly, we apply IE to characterise full 4" wafers of graphene on Si.

[1] Braueniger, Funke *et al.* submitted

## Electronic Materials and Photonics Division

### Room 101A - Session EM+AM+NS+PS-MoA

#### Atomic Layer Processing: Selective-Area Patterning (Assembly/Deposition/Etching)

**Moderators:** Michael Filler, Georgia Institute of Technology, Jessica Hilton, RHK Technology

**1:20pm EM+AM+NS+PS-MoA-1 Area-Selective Deposition of Crystalline Perovskites, E Lin, Brennan Coffey, Z Zhang, P Chen, B Edmondson, J Ekerdt, University of Texas at Austin**

Epitaxial growth of crystalline perovskites enables opportunities in integrating perovskite properties into electronic and photonic devices. Pattern definition is a necessary step in many device applications and definition through etching can be problematic with titanium-based perovskites. We report a process to grow the perovskite film into the final patterned-dimensions through area-selective atomic layer deposition (ALD) followed by epitaxial regrowth from a crystalline substrate to form a single crystal perovskite film. Epitaxial barium titanate (BTO) films can be grown by ALD on strontium titanate (STO(001)) and STO(001)/Si(001) substrates. The substrates are coated with 40 nm of polystyrene (PS) and 185- and 264-nm UV light projected through a shadow mask is used to crosslink the PS under a N<sub>2</sub> atmosphere. The unexposed PS is stripped using toluene to expose the STO surface. Amorphous BTO films are deposited by ALD at 225 °C on the PS-patterned STO(001) surfaces. The low temperature process prevents the degradation of the PS layer. The PS mask is subsequently removed with an oxygen plasma exposure step. Atomic force microscopy and scanning electron microscopy after BTO growth and crosslinked-PS removal demonstrate high fidelity pattern transfer in the BTO films. Reflective high-energy electron diffraction and x-ray diffraction show that the film crystallizes after annealing the sample in vacuum at ≥ 750 °C, with oxygen partial pressure of 1 x 10<sup>-6</sup> Torr. Film orientation as a function of annealing temperature is established with transmission electron and piezoresponse force microscopy.

**1:40pm EM+AM+NS+PS-MoA-2 A Dry NF<sub>3</sub>/NH<sub>3</sub> Plasma Clean for Removing Si Native Oxide and Leaving a Smooth Si Surface, Christopher Ahles, J Choi, University of California, San Diego; A Kummel, University of California at San Diego**

As devices are scaled to sub 5nm, it is critical to prepare clean and atomically flat surfaces. The traditional aqueous HF clean for removal of native Si oxide suffers from an inevitable air exposure resulting in re-oxidation of the Si surface as well as carbon contamination. The Siconi™ process is a dry clean which utilizes a low temperature (<30C) NF<sub>3</sub>/NH<sub>3</sub> based plasma to selectively etch the native oxide layer on Si without etching the underlying Si layer. However the Siconi™ process leaves behind a (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> salt which must be removed in a subsequent anneal. In this work we present a dry clean which eliminates (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> salt formation and provides a surface which is just as flat as with the traditional aqueous HF clean.

The silicon surface following removal of the native oxide with an NF<sub>3</sub>/NH<sub>3</sub> plasma was studied using X-Ray Photoelectron Spectroscopy (XPS) for elemental analysis as well as Atomic Force Microscopy (AFM) for surface roughness measurements. It was found that when the silicon substrate is held at 65-70C during the etching no (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> salt formation is observed. The NF<sub>3</sub>:NH<sub>3</sub> ratio was found to be a critical parameter for controlling the surface roughness, with the surface roughness decreasing with decreasing NF<sub>3</sub>:NH<sub>3</sub> ratios. A NF<sub>3</sub>:NH<sub>3</sub> ratio of 1:5 gave a Si surface with an RMS roughness of 3.4nm while a NF<sub>3</sub>:NH<sub>3</sub> ratio of 1:10 gave a Si surface with an RMS roughness of 1.9nm. Further decreasing the NF<sub>3</sub>:NH<sub>3</sub> ratio is expected to provide an even smoother surface, and experiments towards this end are ongoing. The plasma time was also optimized, and it was found that exposure to the NF<sub>3</sub>/NH<sub>3</sub> plasma for 10 seconds and 1 minute resulted in essentially no removal of the native oxide, while exposure for 2 minutes resulted in complete removal of the native oxide. For comparison, Si surfaces cleaned with aqueous HF in our laboratory typically have ~10% oxygen and ~10% carbon contamination, while after cleaning with a NF<sub>3</sub>/NH<sub>3</sub> plasma with NF<sub>3</sub>:NH<sub>3</sub> = 1:10 for 2 minutes at 70C there was 3% O, 0% C, 4% F and 4% N impurities. Additionally, all of the silicon was in an oxidation state of 0 which means that there was no (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> salt formation since this salt has silicon in an oxidation state of +4. To validate the applicability of this process, a molybdenum silicide film was deposited via atomic layer deposition (ALD) on dry-cleaned Si as well as on HF cleaned Si. The RMS roughness of the ALD MoSi<sub>x</sub> film on the dry-cleaned Si was 2.26nm while on the HF cleaned Si the RMS roughness was 2.78nm. This

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shows that the dry clean developed in this study is capable of producing cleaner and smoother Si surfaces than the traditional aqueous HF clean.

2:00pm **EM+AM+NS+PS-MoA-3 Probing Strategies for Selective Deposition that Exploit Competitive Interactions, James Engstrom**, Cornell University

INVITED

Selective thin film processes, including atomic layer deposition, have the potential to enable next-generation manufacturing and patterning at the 5 nm node and beyond, with direct applications in the nanofabrication of functional layers such as gate dielectrics, metal contacts, and capping/barrier layers. Well-known for its ability to deposit atomically thin films with Å-scale precision along the growth direction and conformally over complex 3D substrates, atomic layer deposition (ALD) has emerged as a key nanomanufacturing process. In this regard, the range and scope of ALD-based applications and capabilities can be substantially extended by also controlling the in-plane growth—a timely and significant development that can be realized *via* area-selective deposition processes that depend on the chemical composition of the underlying surface. In this presentation we will review the approaches that have been taken to achieve area-selective ALD, and we shall highlight both the strengths and shortcomings of these approaches. We will also discuss our efforts to achieve selective deposition that exploit competitive interactions—these interactions can occur both on the surface(s) where the film is, or is not, being deposited, and in the gas phase. In our approach we couple well controlled experiments that involve *in situ* surface analysis using techniques such as X-ray photoelectron spectroscopy and high level quantum chemistry calculations of specific and non-specific binding of molecules to target surfaces. We find that this combination of techniques is capable of shedding considerable light on deposition processes that are both potentially fast and leave no trace of their use in guiding thin film deposition to those areas where growth is desired.

2:40pm **EM+AM+NS+PS-MoA-5 The Interconnect Resistivity Bottleneck, Daniel Gall, T Zhou, E Milosevic**, Rensselaer Polytechnic Institute; P Zheng, Micron Technology

The effective resistivity of conventional Cu interconnect lines increases by more than two orders of magnitude as their width is decreased from 30 to 6 nm. The resulting increase in signal delay and energy consumption limits downscaling of integrated circuits. This presentation will discuss the search for the most conductive metal solutions for narrow interconnect lines, focusing on three key aspects. (i) Electron surface scattering: *In situ* transport measurements on epitaxial Cu(001) layers with various monolayer cap-layers demonstrate specular electron surface scattering when the local surface density of states at the Fermi level is negligible, resulting in a considerable copper resistivity reduction. (ii) Alternative metals: The resistivity scaling at reduced dimensions is measured using epitaxial metal layers (Cu, Ag, W, Ta, Ru, Mo, Ni) and directly compared to results from classical transport models using first-principles electronic structure calculations. Multiple elemental metals are expected to be more conductive than Cu for polycrystalline lines <10 nm. (iii) Confined transport model: First-principles non-equilibrium transport simulations in combination with measurements of the resistivity vs roughness and dimensionality are used to develop a new model that accurately accounts for electron surface scattering in quantum-confined 1-D and 2-D conductors. This model will replace semiclassical models that fail to predict the resistivity <10 nm.

3:00pm **EM+AM+NS+PS-MoA-6 Sub 0.3 micrometer Copper Patterns Etched with a Plasma-Based Process and Pattern Dependent Electromigration Failure Mechanism, Yue Kuo**, Texas A&M University

Copper (Cu) is a popular interconnect material for high density ICs, large area TFT LCDs, and many advanced electronic and optical devices. Since Cu does not form volatile products under the conventional plasma etching condition, the only available method in preparing fine lines is the chemical mechanical polishing (CMP), i.e., the single or dual damascene, method. The author's group has invented a new plasma-based Cu etching method that has a high rate at room temperature (1). This method has been successfully demonstrated in defining submicron lines for IC chips as well as being used in the large area TFT LCDs (2). However, there are few papers on defining the sub 0.5 micrometer Cu line using this new etch method. The lifetime of the plasma-etch Cu line on the flat and stepped surfaces has been studied with the electromigration method (3,4). However, the pattern size effect is rarely discussed.

In this talk, the author will discuss the process that can be used to prepare sub 0.3 micron dimension Cu patterns. The success of this process is due to the simultaneous Cu conversion reaction and sidewall passivation. In

addition, the failure mechanism of the plasma-etched Cu line over a large range of line widths, i.e., from 1.5 to 30 micrometers, will be examined based on the electromigration test result. In summary, Cu lines prepared from the plasma-based process can be reliably applied in the many nano electronic and photonic products.

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3. G. Liu and Y. Kuo, *J. Electrochem. Soc.*, 156(6) H579-H584 (2009).

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3:40pm **EM+AM+NS+PS-MoA-8 The Effect of Metal Diffusion on Contacts to Semiconducting Chalcogenides: Examples for 2D and 3D Materials, Suzanne E. Mohney, K Cooley, M Abraham, A Domask, H Simchi, L Kerstetter, C Lawrence, T Walter**, The Pennsylvania State University

INVITED

We review our recent studies of contacts to a variety of chalcogenide semiconductors, including few-layered molybdenum disulfide and tungsten diselenide, as well as the phase-change material germanium telluride. In some cases, diffusion of a transition metal into the semiconductor has been correlated with an especially low contact resistance. For example, annealing silver contacts on field effect transistors fabricated from few-layered molybdenum disulfide resulted in a reduction in contact resistance by a factor of 4–5 to 0.2–0.7 kOhm- $\mu$ m, while the ON/OFF current of the device remained high. Diffusion of silver into molybdenum disulfide was confirmed by secondary ion mass spectrometry. On the other hand, nickel appears to be even more soluble in molybdenum disulfide (as observed by Auger electron spectroscopy), but annealing nickel contacts resulted in an increase in resistance. For the phase-change material germanium telluride, incorporation of iron seems to play a role in achieving a low contact resistance of 0.004 Ohm-mm in annealed Au/Fe/Sn/p-GeTe contacts. Diffusion of iron into germanium telluride at a low but detectable level was found beneath a narrow-gap tin telluride interfacial reaction product using energy dispersive spectroscopy in the scanning transmission electron microscope. Using only iron or tin without the other did not result in such a low contact resistance. The influence of iron on the electronic properties of germanium telluride is now under study. Besides diffusion of metals into the semiconductor, we also present cases of reactive contacts to germanium telluride, whereby the contact resistance is greatly increased by interfacial reactions that led to the formation of a new phase (especially nickel tellurides and platinum tellurides). Finally, we consider the influence of surface diffusion on quasi van der Waals epitaxy of metals on layered transition metal dichalcogenides.

4:20pm **EM+AM+NS+PS-MoA-10 TiN<sub>x</sub> and TaN<sub>x</sub> Films via Low-T Thermal ALD using Anhydrous N<sub>2</sub>H<sub>4</sub>, Steven Wolf, M Breeden, M Kavrik**, University of California at San Diego; D Alvarez, J Spiegelman, RASIRC; M Naik, Applied Materials; A Kummel, University of California at San Diego

For device back end of line processing, there is a need to deposit conformal barrier layers on high aspect ratio 3D architectures via low-T ALD. Titanium nitride (TiN) and tantalum nitride (TaN) have been studied as diffusion barriers to WF<sub>6</sub> during W metal fill and to Cu, as Cu can readily diffuse, causing device reliability issues. Organometallic-grown films are required when Cu is present to prevent etching, however, metal halide precursors are preferred for gate stack applications as films typically contain lower levels of carbon and oxygen contamination; this has been correlated with improved film conductivity. This work aims to deposit thermal ALD titanium nitride and tantalum nitride utilizing anhydrous N<sub>2</sub>H<sub>4</sub> at lower temperatures than previously reported with NH<sub>3</sub> while still maintaining good film properties.

In this study, low temperature thermal ALD TiN<sub>x</sub> from anhydrous N<sub>2</sub>H<sub>4</sub> vs. NH<sub>3</sub> and TiCl<sub>4</sub> was performed on degreased and UHV annealed SiO<sub>2</sub>/Si substrates at temperatures of 300°C and 400°C. The deposited films were studied using x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). TaN<sub>x</sub> films were grown at 150°C utilizing N<sub>2</sub>H<sub>4</sub> and tris(diethylamido) (tertbutylimido)tantalum (TBTDET) and characterized similarly. In addition, the resistance of air-exposed ultra-thin films was measured using a 4-point probe technique. Resistivities were estimated from thicknesses obtained from cross-sectional scanning electron microscopy (SEM) images. First, saturation dosing was performed to determine optimal half-cycle pulses of TiCl<sub>4</sub> and N<sub>2</sub>H<sub>4</sub>. After TiN<sub>x</sub> ALD cycles, AFM imaging showed uniform deposition with sub-nanometer RMS surface roughness. The corrected and normalized XPS showed near stoichiometric Ti<sub>3</sub>N<sub>4</sub> with low O and C and ~10% Cl. There was approximately 2x more O and C and 50% more Cl in NH<sub>3</sub> grown films at 400°C. N<sub>2</sub>H<sub>4</sub> films exhibited

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lower resistivities (359 vs. 555  $\mu\text{ohm-cm}$ ), attributed to this lower contamination and likely better nucleation density. For  $\text{Ta}_x\text{N}_x$  films, XPS of 15 cycles ALD  $\text{Ta}_x\text{N}_x$  films resulted in 9% O and 4% C and had a Ta/N ratio of 4/5. Analysis on the Ta 4d peaks confirmed nucleation after the initial exposure of TBTDET (Si-O-Ta formation) based on the Ta 4d  $5/2$  peak BE of  $\sim 231.5$  eV. A chemical shift to 229 eV was observed upon forming Ta-N bonds. Resistance measurements indicated insulating films consistent with the formation of  $\text{Ta}_3\text{N}_5$ . In summary,  $\text{N}_2\text{H}_4$  grown  $\text{TiN}_x$  films showed lower resistivities with fewer impurities. The anhydrous  $\text{N}_2\text{H}_4$  chemistry was extended to an organometallic Ta precursor, in which nearly stoichiometric films were deposited with low contamination at a modest substrate temperature of  $150^\circ\text{C}$ .

## Magnetic Interfaces and Nanostructures Division

### Room 201A - Session MI+2D+EM+NS-MoA

#### IoT Session: Symposium on new Magnetic Materials, Devices and Concepts for the Information Society

Moderator: Hendrik Ohldag, SLAC National Accelerator Laboratory

1:20pm **MI+2D+EM+NS-MoA-1 "ZOOMING in on Data Storage and the Superb HDD", Roger Wood, Western Digital** **INVITED**

Get ready for a wild ride starting with the vast distances of outer space and ending with the tiny

distances that separate atoms. For a very different perspective on data storage, each slide in the

presentation looks at things on a scale that is a factor of ten smaller than the previous slide. The

common thread is the technology of information storage. Information storage is what defines human

history and it is the machine-readable data storage developed in the last half-century that provides the

foundation of the modern information age. More than anything, data storage implies magnetic

recording and the hard disk drive. The humble Hard Disk Drive contains such exquisite technologies

and operates at such astounding precision that it almost defies belief. Yet, our industry churns out

these devices by the hundreds of millions and sells them for a few tens of dollars each. Please enjoy

this light-hearted logarithmic romp through storage technology from interstellar space to interatomic

spacings.

(The presentation is based on a talk given at the annual ASME ISPS banquet in Santa Clara, California, in June 2016, while the author was with Western Digital Corporation.)

2:00pm **MI+2D+EM+NS-MoA-3 Physics and Applications of Spin-transfer Torques, Andrew Kent, New York University** **INVITED**

The magnetization of a magnetic material can be reversed by using electric currents that transport spin angular momentum [1]. This was predicted in magnetic tunnel junctions—two metallic ferromagnetic layers separated by a thin insulating barrier—by John Slonczewski in 1989 and demonstrated experimentally about a decade later. This discovery has had an enormous impact on magnetism research and technology [2], as prior to this the primary means to reorient the magnetization of a magnet was by applying magnetic fields (dating to 1819 and Oersted!). In this talk I will highlight some of the physics and applications enabled by the discovery of spin-transfer torques. This includes recent experiments that create localized spin-wave excitations (magnons droplets) in thin films with uniaxial magnetic anisotropy [3]. Spin-transfer torques also permit study of magnetic analogues of superconductivity, superfluidity and the Josephson effect that promise to increase our understanding of collective quantum effects. They may even enable braiding Majorana fermions [4]. Finally, I will discuss spin-torque switching of perpendicularly magnetized magnetic tunnel junctions [5], the basic device used in spin-transfer torque magnetic random access memories.

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\*Work done in collaboration with Dirk Backes, Gabriel Chaves, Daniel Gopman, Christian Hahn, Jinting Hang, Yuming Hung, Ferran Macia, Daniele Pinna, Laura Rehm, Debansu Roy, Javad Shabani and Volker Sluka at NYU; Georg Wolf, Bartek Kardasz, Steve Watts and Mustafa Pinarbasi at Spin Transfer Technologies Inc.; and Hendrik Ohldag at SSRL

2:40pm **MI+2D+EM+NS-MoA-5 Hybrid Magnetic Heterostructures, Ivan K. Schuller, A Basaran, University of California, San Diego; J de la Venta, Colorado State University; J Ramirez, Universidad de los Andes, Colombia; T Saerbeck, Institute Laue-Langevin, France; I Valmianski, University of California, San Diego; X Batlle, University of Barcelona, Spain** **INVITED**

Hybrid materials allow the engineering of new material properties by creative uses of proximity effects. When two dissimilar materials are in close physical proximity the properties of each one may be radically modified or occasionally a completely new material emerges. In the area of magnetism, controlling the magnetic properties of ferromagnetic thin films without magnetic fields is an on-going challenge with multiple technological implications for low-energy consumption memory and logic devices. Interesting possibilities include ferromagnets in proximity to dissimilar materials such as antiferromagnets or oxides that undergo metal-insulator transitions. The proximity of ferromagnets to antiferromagnets has given rise to the extensively studied Exchange Bias[1].

In a series of recent studies, we have investigated the magnetic properties of different hybrids of ferromagnets (Ni, Co and Fe) and oxides, which undergo metal-insulator and structural phase transitions. Both the static as well as dynamical properties of the ferromagnets are drastically affected. Static properties such as the coercivity, anisotropy and magnetization [2-3] and dynamical properties such as the microwave response are clearly modified by the proximity effect and give rise to interesting perhaps useful properties.

Work supported by US-AFOSR and US-DOE

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3:40pm **MI+2D+EM+NS-MoA-8 Organismic Materials and Intelligence, Shriram Ramanathan, Purdue University** **INVITED**

Intelligence in the natural world is panspermic to life, ranging from basic survival skills in non-neural organisms to co-operative foraging and complex mating strategies in higher level animals. We ask the question whether such remarkable features can be implemented in the physical world utilizing adaptive matter. We have identified strongly correlated semiconductors, one class of quantum materials as particularly suited for this effort, owing to their remarkable electronic plasticity. One may refer to these systems as organismic materials that display certain well-defined characteristics of living beings. In this presentation, we will present examples from the animal kingdom focusing on intelligence and episodic memory. Then we will discuss recent collaborative studies on correlated oxides demonstrating ancestral intelligence. We will conclude with examples of neural networks that can be designed with quantum materials

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that can replicate fundamental animal learning traits. The role of defects, strain and orbital occupancy control in design of electronic plasticity will be highlighted.

## In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic

Room 202B - Session MM+AS+NS+PC+SS-MoA

### X-ray and Electron Spectromicroscopy in Liquids and Gases & Flash Networking Session

Moderator: Piran Kidambi, Vanderbilt University

1:20pm **MM+AS+NS+PC+SS-MoA-1 Bridging the Material and Pressure Gap in Synchrotron based Photoelectron in Situ/Operando Studies**, *Luca Gregoratti, M Amati, P Zeller*, Elettra-Sincrotrone Trieste, Italy **INVITED**

Modelling the real behavior of technologically relevant materials at typical laboratory environmental conditions is a longstanding challenge. Not only classical pressure conditions are generally far from usual industrial environments (pressure gap) but also heterogeneous materials are very different from those often used to simplify the modelling strategies (material gap). For instance to monitor in-situ/operando the lateral distribution of the chemical state of surfaces and interfaces during a catalytic or electrochemical reaction at sub-micron level at environmental conditions as close as possible to the operational ones is of crucial importance to shed light on the running processes. But the possibility to investigate chemical reactions with X-ray photoelectron spectroscopies by overcoming material and pressure gaps is still a challenge also for modern experimental setups.

The Escamicroscopy team of Elettra which operates a Scanning Photoemission Microscope (SPEM) has recently developed novel concepts for a new generation of SPEM working under more realistic pressure conditions. The graphene sealed cells, combined for the first time with XPS by A. Kolmakov [1], allow the possibility to investigate systems which require an ambient pressure regime (e.g. liquid/solid interfaces). Despite the huge ongoing progress in the development and performance of these cells several crucial issues are unsolved and will be addressed by this presentation.

Another recent development is an effusive cell for near-ambient pressure SPEM setups where the highest static pressure achievable is around 1 mbar. Samples are encapsulated in a vacuum sealed cell and located behind a 200  $\mu\text{m}$  diameter size pinhole through which the focused X-ray beam illuminates surfaces and photoelectrons reach the high vacuum path towards the electron analyzer [1].

2:00pm **MM+AS+NS+PC+SS-MoA-3 Transition Metal Complexes in Aqueous Solutions Characterized by Liquid Jet Ambient Pressure X – ray Photoelectron Spectroscopy**, *Jared Bruce, J Hemminger*, University of California, Irvine

Transition metals in aqueous solution have been investigated by a multitude of techniques and are a cornerstone of many aspects of chemistry. Recently, the atmospheric chemistry community has begun to shift their attention to iron, manganese and copper containing aqueous solutions due to their propensity to generate hydroxyl radicals at the air/water interface through a Fenton mechanism. Understanding the chemical state of the transition metal present at the air/water interface, in addition to the distribution as a function of depth, would provide critical insight to the active species of hydroxyl generation. Solvation effects have been shown to significantly affect the distribution of small ions as a function of depth from the vacuum/water interface; first through molecular dynamics (MD) simulations then corroborated by liquid – jet X – ray photoelectron spectroscopy (LJ-XPS). Solvation of transition metals in aqueous solution have added complexity compared to small ions because of complexation of ligands and equilibria with the surrounding solvent.

In our work, using both a lab – based LJ - XPS and synchrotron measurements at the Advanced Light Source, we have shown the distribution of chemical states on a model Fenton reagent,  $\text{Fe}^{2+}_{(\text{aq})}$ , change with depth relative to the air/liquid interface. The chemical state is also sensitive to “spectator” ions in the solution. The presence of  $\text{Cl}^-$  leads to a binding energy shift in the Fe 2p spectra and a change in the distribution as a function of depth. This is also observed in the Cl 2p spectrum where a binding energy shift of 0.3 eV indicates the presence of an inner sphere Cl that follows the distribution change in the Fe 2p spectrum

2:20pm **MM+AS+NS+PC+SS-MoA-4 Interfacial Electrochemistry in Liquids Probed with Photoemission Electron Microscopy**, *S Nemsak*, Forschungszentrum Juelich GmbH, Germany; *E Strelcov*, NIST Center for Nanoscale Science and Technology; *Tomas Duchon*, Forschungszentrum Juelich GmbH, Germany; *H Guo*, National Institute of Standards and Technology; *J Hackl*, Forschungszentrum Juelich GmbH, Germany; *A Yualev*, NIST Center for Nanoscale Science and Technology; *I Vlasiouk*, Oak Ridge National Laboratory; *D Mueller*, *C Schneider*, Forschungszentrum Juelich GmbH, Germany; *A Kolmakov*, NIST Center for Nanoscale Science and Technology

The use of photoemission spectromicroscopy as a probe of liquid electrolytes has been an elusive goal, motivated by the breadth of information the technique can provide, but hindered by many technical difficulties. Here, we present a universal multichannel array platform employing graphene capping that allows for investigation of interfacial liquid electrochemistry via soft x-ray absorption and photoemission spectromicroscopy. The methodology is demonstrated in the case of copper electroplating from a sulphuric acid solution, that, along with cycles of copper deposition on gold electrodes, reveals hindered nucleation at the electrified graphene membrane evidenced by the presence of stable  $\text{Cu}^+$  ions.

3:40pm **MM+AS+NS+PC+SS-MoA-8 Practical Liquid Cell Microscopy - Opportunities and Challenges**, *Daan Hein Alsem, K Karki*, Hummingbird Scientific; *T Mefford, W Chueh*, Stanford University; *N Salmon*, Hummingbird Scientific **INVITED**

Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and synchrotron X-ray microscopy (XRM) are powerful characterization tools and are routinely used to study a wide range of material-systems at the nanoscale. This has generated strong interests in acquiring more reliable quantitative *in-situ* and *operando* measurements in realistic reaction environments, as is possible with liquid environmental cells. This approach has already started to produce new insights on the dynamics and structural changes during electrochemical processes as lithium ion insertion/extraction, dendrite formation, metal nucleation and corrosion. However, practical aspects of replicating representative electrochemical data reminiscent of bulk behavior are still a challenge in these systems.

Here, we will discuss practical aspects of conducting *operando* liquid cell microscopy experiments relating to the typical geometry of these liquid-cell microscopy systems as well as artifacts coming from the microscope during *operando* experiments. We will also present a TEM/SEM/XRM microscopy platform that enables true electroanalytical measurements mimicking bulk behavior of the material system.

The example study shown here is performed using electrochemical cells, which consist of two microfabricated chips sandwiched with transparent  $\text{SiNx}$  membranes for encapsulating liquid and viewing in the microscope. A newly developed hardware system and specially optimized electrochemistry chips with a custom configuration for working electrode (WE), counter electrode (CE) and reference electrode (RE) allows quantitative measurements of electrochemical processes with details resembling the complete cycle of the bulk. As illustrations, we present cyclic voltammetry (CV) studies of some model compounds such as 0.1M  $\text{CuSO}_4$  and 20 mM  $\text{K}_3\text{Fe}(\text{CN})_6$ /20 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1M KCl solutions. In the former case, the copper deposition and stripping occurs at the working electrode at distinct redox peaks in liquid cell and the result mimics the bulk electrochemical cells with large electrode areas and larger volume of electrolyte solution. This work highlights the fact that with suitable hardware systems and with knowledge and correction of microscope-induced artifacts, bulk behavior of the electrochemical processes can be both observed and measured quantitatively.

4:20pm **MM+AS+NS+PC+SS-MoA-10 Observation of Electric Double Layer under Graphene by Scanning Electron Microscopy**, *Hongxuan Guo, A Yulaev, E Strelcov*, National Institute of Standards and Technology (NIST)/University of Maryland, College Park; *A Tselev*, CICECO and Department of Physics, University of Aveiro, Portugal; *A Kolmakov*, National Institute of Standards and Technology

The formation of the electric double layer is a fundamental phenomenon occurring at electrified solid-liquid electrolyte interfaces and which has a key importance for energy devices, chemical engineering and biomedical applications. The structure and composition of electric double layer can be accessed using optical methods<sup>1</sup>, and more recently with X-ray spectroscopy<sup>2,3</sup>, as well as scanning probe microscopy<sup>4</sup>.



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In this presentation, we demonstrate the feasibility of *in-situ* scanning electron microscopy to observe the changes in electric double layer in different electrolytes upon polarization. We designed an electrochemical liquid cell with electron transparent electrode made of bilayer graphene.<sup>5,6</sup> We monitored the changes in secondary electron yield from the graphene-liquid interface upon electrolyte polarization. We found that the normalized SEM image contrast is linear with the applied bias voltage and is related to the concentration and distribution of the ions at the interface. The analysis of SEM videos provide insight on long term kinetics of ionic moieties in electrolyte during polarization. This experimental methodology will be helpful for understanding the structure, property, and dynamics of the electric double layer at solid -electrolyte interfaces.

## Reference

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- [4]. J. M. Black, M. Zhu, P. Zhang, R. R. Unocic, D. Guo, M. B. Okatan, S. Dai, P. T. Cummings, S. V. Kalinin, G. Feng, and N. Balke, Scientific Reports 6 (2016), 32389
- [5]. A. Yulaev, H. Guo, E. Strelcov, L. Chen, I. Vlassiuk, A. Kolmakov, ACS applied materials & interfaces 9 (2017), 26492-26502
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## Materials and Processes for Quantum Computing Focus Topic

### Room 203A - Session MP+AM+EM+NS-MoA

#### Systems and Devices for Quantum Computing II

Moderator: Josh Mutus, Google Inc

1:20pm **MP+AM+EM+NS-MoA-1 Quantum Engineering of Superconducting Qubits, William Oliver**, MIT Lincoln Laboratory **INVITED**  
Superconducting qubits are coherent artificial atoms assembled from electrical circuit elements and microwave optical components. Their lithographic scalability, compatibility with microwave control, and operability at nanosecond time scales all converge to make the superconducting qubit a highly attractive candidate for the constituent logical elements of a quantum information processor. Over the past decade, spectacular improvement in the manufacturing and control of these devices has moved superconducting qubits from the realm of scientific curiosity to the threshold of technical reality. In this talk, we review this progress and our own work at MIT that are creating a future of engineered quantum systems.

2:00pm **MP+AM+EM+NS-MoA-3 The Quantum Socket: A Wiring Method for Superconducting Quantum Computing, Matteo Mariani**, University of Waterloo, Canada **INVITED**

I will provide a brief introduction to the main technological and scientific challenges to be faced in order to build a practical quantum computer, with emphasis on the case of superconducting quantum computing. I will then delve into a detailed explanation of a method to address the wiring of a two-dimensional array of superconducting quantum bit (qubits): The quantum socket [1]. Next, I will show how the quantum socket can be extended to a medium-scale quantum computer and how it can help mitigate coherent leakage errors due to qubits interacting with spurious cavity modes [2]. I will then show thermocompression bonding technology [3], a method that allows us to further protect qubits from the environment. In particular, I will propose a new qubit design based on our experimental implementation of thermocompression bonded chips, where vacuum gap capacitors are used to reduce dissipation due to so-called two-level state defects in amorphous dielectrics, which are the insulators presently use in our qubits.

[1] J.H. Béjanin, T.G. McConkey, J.R. Rinehart, J.D. Bateman, C.T. Earnest, C.H. McRae, Y. Rohanizadegan, D. Shiri, B. Penava, P. Breul, S. Royak, M. Zapatka, A.G. Fowler, and M. Mariani, Three-Dimensional Wiring for Extensible Quantum Computing: The Quantum Socket, Phys. Rev. Applied 6, 044010 (2016)

[2] T.G. McConkey, J.H. Béjanin, C.T. Earnest, C.R.H. McRae, Z. Pagel, J.R. Rinehart, M. Mariani, Mitigating Coherent Leakage of Superconducting Qubits in a Large-Scale Quantum Socket, Quantum Sci. Technol. 10.1088/2058-9565/aabd41 (2018)

[3] C.R.H. McRae, J. H. Béjanin, Z. Pagel, A.O. Abdallah, T.G. McConkey, C.T. Earnest, J.R. Rinehart, and M. Mariani, Thermocompression Bonding Technology for Multilayer Superconducting Quantum Circuits, Appl. Phys. Lett. 111, 123501 (2017)

2:40pm **MP+AM+EM+NS-MoA-5 Pogo Pin Packaging for High Coherence Qubits, Nicholas Bronn, V Adiga, S Olivadese, O Jinka**, IBM, T.J. Watson Research Center; X Wu, National Institute of Standards and Technology; J Chow, IBM, T.J. Watson Research Center; D Pappas, National Institute of Standards and Technology

The connectivity between qubits in large superconducting quantum processors prevents the qubits from being addressed by control lines routed to the edge of the chip. In these nontrivial circuit topologies, internal qubits must instead be coupled to control and measurement electronics by a nonplanar technique. Here we present a pogo package consisting of commercially available parts and requiring modest machining tolerances. Through careful engineering of the package for cryogenic and microwave considerations, we measure high coherence times and gate fidelities for qubits in a quantum processor connected by pogo pins. This work was supported by IARPA under contract W911NF-16-1-0114-FE.

3:00pm **MP+AM+EM+NS-MoA-6 50 Ohm Superconducting Kinetic Inductance Traveling-Wave Amplifier with flexible pump frequency for Four Wave Mixing and Three Wave Mixing, Xian Wu, M Bal, J Long, H Ku, R Lake, D Pappas**, National Institute of Standards and Technology

We developed a 50 Ohm transmission-line based superconducting kinetic inductance traveling-wave (KIT) amplifier using high inductance material NbTiN. The nonlinearity originates from the kinetic inductance of the superconductor and enables amplification. Often, the impedance of the transmission line is significantly higher than the 50 Ohm microwave environment due to the dominance of kinetic inductance over geometric inductance at micron size scales. To address this impedance mismatch, we engineered “fingers” on each side of the original coplanar waveguide KIT [1] to introduce extra capacitance that decreases the impedance to approximately 50 Ohm [2,3]. Those extra “fingers” also function to create a band stop at higher frequency to bend the dispersion relation between wave vector (k) and frequency (f), which allows us to apply the pump frequency within a wide span of a few GHz and achieve several GHz gain bandwidth for chosen pump frequency. Another advantage of this structure is that it significantly reduces the phase velocity, hence shortening the physical length of this device. Gain measurements based on both four wave mixing and three wave mixing will be presented.

[1] Appl. Phys. Lett. **108**, 012601 (2016); <https://doi.org/10.1063/1.4937922>

[2] Journal of Applied Physics **119**, 083901 (2016); <https://doi.org/10.1063/1.4942362>

[3] Appl. Phys. Lett. **110**, 152601 (2017); <https://doi.org/10.1063/1.4980102>

3:40pm **MP+AM+EM+NS-MoA-8 Near Term Development of Short Depth Quantum Processors, Jerry Chow**, IBM Research Division, T.J. Watson Research Center **INVITED**

Quantum processors are currently in their infancy though the community is poised to explore bringing them to a state where they can outperform classical computations in relevant application. The challenges that lie ahead are plentiful and touch all aspects of the quantum computer, ranging from finding algorithms to building control software and control hardware as well as engineering and fabricating and testing the quantum hardware. In an effort to accelerate the development of quantum computing IBM launched the IBM Q experience. The Q Experience is a cloud-based platform which allows anyone to get familiar with quantum computing. It allows users to run experiments on actual quantum hardware.

In this talk I will focus on the development and characterization of short depth superconducting quantum hardware. Crosstalk and decoherence are some of the most pressing issues that we face today. Decoherence limits the number of operations that can be performed on the hardware (the depth of the circuit) whereas crosstalk can limit what operations can be performed in parallel on the circuit. The processors featured on the IBM Q experience are based on fixed frequency transmon qubits with a cross-resonance based two qubit gate. For this platform only a very narrow frequency range for the qubits is possible. This leads to problems related to

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frequency crowding and spurious interactions. Methods for characterizing and addressing both the frequency allocation and characterizing crosstalk will be discussed.

4:20pm **MP+AM+EM+NS-MoA-10 Frequency Crowding in Lattices of Transmon Qubits**, *Sami Rosenblatt, J Hertzberg, J Chavez-Garcia, N Bronn, H Paik, M Sandberg, E Magesan, J Smolin, J Yau, V Adiga, M Brink, J Chow, IBM, T.J. Watson Research Center*

A key goal in quantum computing is to develop scalable fault-tolerant quantum logic circuits. One promising architecture involves lattices of fixed-frequency transmon qubits coupled via cross-resonance gates. Fixed-frequency qubits offer high coherence and the all-microwave gate reduces circuit complexity. To optimize gate performance, excitation energies of neighboring qubits must be similar but non-degenerate. This architecture is thus sensitive to any variation in device parameters affecting transmon frequency. In this talk we will discuss a statistical model for the resulting 'frequency crowding' behavior, and suggest improvements in both architecture design and qubit fabrication in order to achieve scalable circuits with good gate fidelity.

\*We acknowledge support from IARPA under Contract No. W911NF-16-0114.

## Nanometer-scale Science and Technology Division Room 102B - Session NS+2D+AS+PC-MoA

### SPM - New Imaging and Spectroscopy Methodologies

**Moderators:** Aubrey Hanbicki, U.S. Naval Research Laboratory, Sidney Cohen, Weizmann Institute of Science, Israel

1:20pm **NS+2D+AS+PC-MoA-1 A Connection Between Stability of STM Control System and Local Barrier Height: Implications on Imaging and Lithography**, *S.O. Reza Moheimani*, University of Texas at Dallas **INVITED**  
Poor performance of the Scanning Tunneling Microscope (STM) control system may result in tip-sample crash, a prevalent failure in STMs. Since its invention, about thirty-five years ago, few attempts have been made to improve the STM control system. Consequently, nearly all STMs are today operated with experimentally selected fixed-gain PI controllers. Selection of controller gains is often done without much attention to the electromechanical dynamics of the scanning tunneling microscope. Performance of such poorly-tuned controllers is limited and a key contributor to the tip-sample crash.

We perform closed loop system identification on a scanning tunneling microscope and show that the system DC gain is proportional to the square root of Local Barrier Height (LBH), a quantum mechanical property of the sample and/or tip that affects the tunneling current. We demonstrate that during a scan the LBH may undergo significant variations and thus it may adversely affect the closed-loop stability if the controller parameters are fixed. Feedback instabilities increase the risk of tip-sample crash in STMs.

In order to improve the closed loop performance, we estimate the LBH, on the fly, and use this information to adaptively tune the PI controller parameters. Experimental results obtained with the self-tuning PI controller confirm the improved STM performance compared to the conventional fixed gain PI controller. Further experiments confirm effectiveness of the proposed method in extending the tip lifetime by lowering the chance of the tip/sample crash.

2:00pm **NS+2D+AS+PC-MoA-3 Distinctive Microstructures in a Complex Polymer Evolve with Time and Composition**, *X Yu*, Worcester Polytechnic Institute; *S Granados-Focil*, Clark University; *M Tao*, *Nancy Burnham*, Worcester Polytechnic Institute

The diverse microstructures observed by atomic force microscopy (AFM) in asphalt binder – a complex polymer – suggest complicated intermolecular associations. These microstructures contribute to binders' bulk mechanical properties; therefore, it is essential to understand chemical-microstructural-mechanical relationships for optimal design of binder-related applications, which range from roads to roofs. The US market for asphalt binders in 2019 is predicted to reach 148 million barrels. [1]

Binders annealed at room temperature for over two months showed time-dependent microstructures, which correlate well with room-temperature steric hardening behavior as verified by other researchers using modulated differential scanning calorimetry. Microstructures of the binder films stabilized after different annealing durations, depending on the dimensions of the molecular structures and the complexity of the molecular interactions among the multiple phases in each bitumen. Distinctive

microstructures were observed for remixed binders with increasing asphaltene concentrations. Consistency between our observations [2] and other literature suggests that microstructures observed by AFM are probably not just a surface phenomenon.

Furthermore, the complex nature of binder and the various influencing factors often lead to practical challenges in investigation of its microstructures and their chemical origins. Some of the main concerns related to AFM characterization of binders' microstructures, namely the dependence of the microstructures on such factors as sample preparation methods, annealing conditions and durations, and chemical composition, were also addressed in this study.

The above findings provide practical knowledge and deeper insights into the establishment of the complicated chemical-mechanical relationships for asphalt binders that pave the way toward tuned binder performance.

[1] <https://www.reportlinker.com/p0158665/US-Asphalt-Industry.html>

[2] "Time- and composition-dependent evolution of distinctive microstructures in bitumen." X. Yu, S. Granados-Focil, M. Tao, and N.A. Burnham, *Energy Fuels* 32, 67-80 (2018).

2:20pm **NS+2D+AS+PC-MoA-4 Offering new Characterization Capabilities at the XTIP beamline by Combining Scanning Tunneling Microscopy with Synchrotron Radiation**, *Volker Rose, H Chang, M Fisher, S Hla, N Shirato*, Argonne National Laboratory

The race is on for chemical x-ray imaging with nanoscale resolution. Specifically, there are currently substantial efforts underway at synchrotron facilities worldwide that aim to combine x-rays with scanning probe microscopy. Recently, substantial progress was made on Argonne's Synchrotron X-ray Scanning Tunneling Microscopy (SX-STM) project. SX-STM enables an entirely new view into the nanoworld by combining the best of two worlds: the exceptional chemical, magnetic, and structural sensitivity of synchrotron x-rays combined with the high spatial resolution of scanning probe microscopy accompanied by its ability to engineer and manipulate surfaces down to the level of single atoms.

To fully exploit the special capabilities of a unique new cryogenic x-ray microscope, XTIP, a dedicated beamline for SX-STM will become available at the Advanced Photon Source in early 2019. To meet the scientific objective of the nanoscience and nanomagnetism communities most effectively, we are going to build a soft x-ray beamline with full polarization control operating over the 500-1600 eV energy range. The dedicated XTIP beamline will provide researchers access to a one-of-a-kind instrument. Among the potential breakthroughs are "designer" materials created from controlled assembly of atoms and molecules, and the emergence of entirely new phenomena in chemistry and physics.

2:40pm **NS+2D+AS+PC-MoA-5 Scanning Probe Microscopy Based Spectroscopy Measurement for Nanoscale Chemical Identification**, *Chanmin Su*, Bruker-Nano, Inc. **INVITED**

Scanning probe microscopy has been instrumental for physical property characterizations at the nanometer scale, primarily for mechanical, electromagnetic and thermal properties. Recent progresses were focused on chemical identification based on mid-IR spectroscopy, pushing FTIR mapping to a resolution at or beyond 10 nm. This presentation will review technology advances in both scanning near field optical microscopy and photothermal based IR spectroscopy. Each of the techniques is discussed and benchmarked by detection limit, spatial resolution and signal to noise ratio, which ultimately determines the chemical mapping efficiencies. We will highlight techniques that address correlative imaging where physical and chemical properties at the same nanoscale location being acquired either concurrently or sequentially. As an example, PeakForce tapping based chemical and physical measurements will be explained in detail with the applications ranging from 2D materials to polymer complexes. The presentation will also highlight major challenges for scanning probe based measurements to be broadly adopted as the premier tool for nanoscale chemical fingerprint mapping.

3:40pm **NS+2D+AS+PC-MoA-8 Quantifying Tip-Sample Interactions in Vacuum Using Cantilever-based Sensors: An Analysis**, *O Dagdeviren, C Zhou, E Altman, Udo D. Schwarz*, Yale University

To achieve as much quantitative information on a surface as possible, the local measurement of tip-sample interaction potentials has recently gained much popularity in particular under well-defined ultrahigh vacuum conditions, where such measurements can be carried out with great accuracy both in terms of spatial as well as force resolution. To this end, either the oscillation frequency or the oscillation amplitude and phase of the vibrating force-sensing cantilever are recorded as a function of tip-

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sample distance and subsequently converted into quantitative values for the force or interaction potential. Here, we theoretically and experimentally show that the force law obtained from such data acquired under vacuum conditions using the most commonly applied methods may deviate more than previously assumed from the actual interaction when the oscillation amplitude of the probe is of the order of the decay length of the force near the surface, which may result in a non-negligible error if correct absolute values are of importance [1]. Caused by approximations made in the development of the mathematical reconstruction procedures, the related inaccuracies can be effectively suppressed by using oscillation amplitudes sufficiently larger than the decay length. To facilitate efficient data acquisition, we propose a novel technique that includes modulating the drive amplitude at a constant height from the surface while monitoring the oscillation amplitude and phase. Ultimately, such amplitude sweep-based force spectroscopy enables shorter data acquisition times and increased accuracy for quantitative chemical characterization compared to standard approaches that vary the tip-sample distance. An additional advantage is that since no feedback loop is active while executing the amplitude sweep, the force can be consistently recovered deep into the repulsive regime.

[1] O. E. Dagdeviren et al., *Physical Review Applied* **9**, 044040 (2018).

4:00pm **NS+2D+AS+PC-MoA-9 AFM + Nanoscale Vis-IR Spectroscopy via Photo-induced Force Microscopy**, *Derek Nowak, T Albrecht, S Park*, Molecular Vista

Photo-induced Force Microscopy (PiFM) [1] combines optical spectroscopy and atomic force microscopy (AFM) via illumination of the tip-sample junction with tunable laser light and mechanical detection of forces acting on the tip in response to interaction of light with the sample. With infrared (IR) source, PiFM can map the IR absorption of the sample as a function of IR wavelength and position and achieve nm-scale resolution in displaying the locations of heterogeneous materials on the surface of a sample. Even for samples without active IR absorption band, PiFM can be used to acquire nanoscale mapping based on the dielectric constant of the sample surface; dielectric constant mapping also allows high resolution sub-surface mapping. With tunable visible and near infrared (VisNIR) laser source, PiFM can map exciton resonances with similar spatial resolution even on monolayer samples. Examples from various classes of samples including organic, inorganic, and 2D materials will be presented. We will also present PiFM spectroscopy data that show excellent correlation with bulk FTIR spectra despite the fact that PiFM acquires local chemical information from regions in the range of 10 nm in extent.

[1] D. Nowak et al., *Sci. Adv.* **2**, e150157 (2016).

## 2D Materials Focus Topic

### Room 201B - Session 2D+EM+MI+NS-TuM

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

Moderator: Johannes Jobst, Leiden University

8:00am **2D+EM+MI+NS-TuM-1 Effect of Lattice Stacking Orientation and Local Thickness Variation on the Mechanical Behavior of Few Layer Graphene Oxide**, *Teng Cui, S Mukherjee, C Cao, P Sudeep, J Tam*, University of Toronto, Canada; *P Ajayan*, Rice University; *C Singh, Y Sun, T Filleter*, University of Toronto, Canada

Investigation of few layer 2D materials is fundamentally important to bridge the gap between monolayer and bulk properties, and practically meaningful for applications as reinforcement nanofillers and layered electronic devices. Few layer introduces differences from intrinsic properties of monolayers due to the complexity of structural heterogeneities, such as lattice stacking orientation and local thickness variation. In this work [1], few layer graphene oxide (GO) with different structural heterogeneities were studied using atomic force microscopy-based deflection measurements and transmission electron microscopy (TEM). Direct TEM evidence of fracture surfaces and molecular dynamics (MD) simulations revealed decoupled and dissimilar layer crack patterns (i.e., different cracking pathway of top and bottom layers) for misaligned bilayer GO. In contrast, aligned GO bilayers generally fractured with a larger portion of common cracks shared by both layers, indicating stronger interlayer interaction than its misaligned counterpart. MD results also revealed insignificant effect of lattice alignment on the strength and toughness of GO bilayers, which is  $\sim 23.5$  GPa and  $\sim 1.71 \times 10^{-18}$  J/nm<sup>3</sup>, respectively, for both aligned and misaligned cases. Scaling up to  $\sim 5$  layers and above revealed more significant local thickness heterogeneity and consequently a  $\sim 60\%$  reduction of the normalized fracture force and toughness with respect to the average number of layers. MD simulations on partially intercalated few layer GO revealed anisotropic and heterogeneous stress distributions, as well as stress concentration near the inner edges, which may account for the significant reduction of strength and toughness.

[1] T. Cui, S. Mukherjee, C. Cao, P. M. Sudeep, J. Tam, P. M. Ajayan, C. V. Singh, Y. Sun, and T. Filleter, "Effect of Lattice Stacking Orientation and Local Thickness Variation on the Mechanical Behavior of Few Layer Graphene Oxide", *Carbon*, accepted.

8:20am **2D+EM+MI+NS-TuM-2 Out-of-Plane Mechanical Properties of 2D Hybrid Organic-Inorganic Perovskites by Nanoindentation**, *Qing Tu, I Spanopoulos, S Hao, C Wolvert, M Kanatzidis, G Shekhawat, V Dravid*, Northwestern University

2D layered hybrid organic-inorganic perovskites (HOIPs) have demonstrated improved stability and promising photovoltaic performance. The mechanical properties of such functional materials are both fundamentally and practically important to achieve both high performance and mechanically stable (flexible) devices. Here we report the static, out-of-plane mechanical properties of a series of 2D layered lead iodide HOIPs with a general formula of  $(R-NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$ , and investigate the role of structural sub-units (e.g., the length of the organic spacer molecules -R and the number of inorganic layer -n) on the mechanical properties by nanoindentation. We find that the 2D HOIPs are softer than their 3D counterparts due to the replacement of the strong inorganic layer and ionic bonds by the soft organic layers and the weak Van der Waals interactions. As n increases from 1 to 5, the relative amount of these weak factors in the crystals are decreasing and both the out-of-plane Young's modulus E and hardness H increase, approaching to the reported values of corresponding 3D crystals. DFT simulations showed a similar trend to the experimental results. Furthermore, we show that increasing the alkyl chain spacer molecule -R from -C<sub>4</sub>H<sub>9</sub> to -C<sub>12</sub>H<sub>25</sub>, E first decreases and eventually plateaus while no clear trend in H is observed. Our results reveal that the competition between the stiff inorganic layers, the soft organic layer and the weak Van der Waals interfaces determines the mechanical properties of 2D HOIPs. Finally, we compare these findings with those in other 2D layered materials such as h-BN, MoS<sub>2</sub> and MXene, and shed light on routes to further tune the out-of-plane mechanical properties of 2D layered HOIPs.

8:40am **2D+EM+MI+NS-TuM-3 Mechanical Properties of Many-layer CVD Graphene**, *Kyle Larsen, S Lehnardt, J Rowley, B Anderson, R Vanfleet, R Davis*, Brigham Young University

Graphene, a monoatomic layer of carbon atoms, has a reported Young's modulus of 1 TPa and a tensile strength of 130 GPa. These values make it both the strongest and one of the stiffest materials ever reported. The mechanical properties of multilayer graphene grown by chemical vapor deposition have been reported for films of up to 10 layers (3.35 nm). Films thicker than about 10 layers (sometimes considered graphite rather than multilayer graphene) are of interest as membranes and in MEMS applications. We have characterized CVD grown many-layer graphene films with thicknesses of about 50 nm by Raman spectroscopy, burst testing, and atomic force microscopy. The atomic force microscope was used to map the local compliance over suspended regions containing cantilevers cut out of the many-layer graphene with a focused ion beam. Analytical and finite element modeling were used in the analysis of the deflection of the many-layer graphene cantilevers to extract Young's modulus. The many-layer graphene is high quality (little or no D peak in the Raman spectrum) and has a Young's modulus in the range reported for graphene (0.5 TPa to 1 TPa).

9:00am **2D+EM+MI+NS-TuM-4 Electronic Structure and Magneto-transport Properties of Nanostructured Graphene on SiC(001)**, *Victor Aristov*, DESY Hamburg, Germany; *H Wu*, BIT, Beijing, China; *O Molodtsova*, DESY Hamburg, Germany; *A Chaika*, ISSP RAS, Russia

Graphene shows unbelievable properties that are of worth both for basic investigations and technology. The aptitude to open gap and to get graphene magnetic are principal challenges in the fields of up-to-date applications. Nanostructured graphene with an enormous amount of nanodomain boundaries and ripples becomes to be the most promising material for graphene-based electronic and spintronic applications, since nanodomain edges can completely reflect electrons over a great range of energies [1] and hold spin-polarized electronic states [2, 3]. Electrical measurements conducted at low temperatures on the vicinal SiC(001) samples demonstrate the opening of a transport gap in the nanostructured trilayer graphene up to 1.3 eV [4], which is induced by self-aligned periodic nanoboundaries. The transport gap opening produces high current on-off ratio of  $10^4$  [4, 5]. The magneto-resistance measurements disclose an exceptional big positive magneto-resistance in parallel magnetic field with strong temperature dependence [6]. It has been shown that graphene layer rippling near domain boundaries lead to one-dimensional conductivity (along the domain boundaries) at low temperatures and to accumulation of electrons with a particular spin direction at the boundaries. Moreover, nanodomain boundaries with ripples have the potential to work as a spin-filter and can result in a positive magnetoresistance at low temperature.

This work was supported by Beijing Institute of Technology Research Fund Program for Young Scholars, Science Foundation Ireland (SFI) (No. 12/IA/1264), Russian Foundation for Basic Research (Grant Nos. 17-02-01139, 17-02-01291), Marie Curie IIF grant within the 7th EC Framework Program.

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9:20am **2D+EM+MI+NS-TuM-5 Discovering and Visualizing Ferromagnetism in Intrinsic Two Dimensional Materials**, *Jing Xia*, University of California Irvine

INVITED

In this talk, I will discuss our recent results on discovering and visualizing in 2D magnetism using a unique scanning Sagnac MOKE microscope, which is based on a Sagnac interferometer technique and has achieved unprecedented nano-radian level Kerr and Faraday sensitivity even at DC. In exfoliated Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub> (CGT) atomic layers, we report the discovery of intrinsic ferromagnetism in 2D van der Waals crystals, defying the well-known Mermin-Wagner theorem. Unlike 3D magnetism, the ferromagnetic order in this 2D system is stabilized by magnetic anisotropy from the CGT structure, which is not present in graphene. As a result, changing the magnetic anisotropy with a small external magnetic field was found to strongly enhance the Curie temperature, which is a feature unique to 2D magnetism.

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11:00am **2D+EM+MI+NS-TuM-10 Onset of Buckling Folding and Slipping Instabilities in 2D Materials under Compressive Strain**, *Jaehyung Yu, E Ertekin, A van der Zande*, University of Illinois at Urbana-Champaign

Atomic membranes of monolayer 2D materials represent the ultimate limit in size of nanoelectromechanical systems. These materials have high mechanical strength, yet low bending modulus leading to high pliability. Adding in the diverse active electronic properties of different 2D materials, atomic membranes will allow new next generation technologies like highly strainable crumpled or folded electronics, or 3D origami devices based on 2D materials. In order to realize these new technologies it is important to understand how the rules of continuum membrane mechanics break down on the atomic scale and how these deformations will affect the electronic properties, including the role of compressive stress, bending, adhesion and interlayer shear.

Here, we present a combined experimental and theoretical study of the onset of instabilities such as buckling, folding and slip on the properties of 2D materials and heterostructures under compression. We generate periodic fold structures of the graphene, MoS<sub>2</sub>, and their heterostructures by introducing the compressive stresses with the pre-strained stretchable substrate. We analyzed then measured the membrane morphology using atomic force microscopy (AFM) under increasing levels of uniaxial compression up to 30%. We observed that the strain-relaxation mechanism of atomic membranes could be varied from generating and growing standing folds to collapsing to generate triple folds based on the mechanical properties including 2D modulus, bending stiffness, adhesion and interlayer shear energies. The onset of these instabilities depends on the 2D material or heterostructure making up the membranes. In graphene folds grow then collapse at compressive strain of ~5%. In monolayer MoS<sub>2</sub> standing folds grow to a fixed height of ~20 nm but do not collapse. Instead, new folds are generated in between the existing folds.

We use density functional theory (DFT) to model the morphology of the same structures under compressive slack. We find that, in multi-layer 2D materials, the onset of slip between the layers is crucial parameters to decide the bending stiffness of the material. We found that the superlubricity between the layers allows the linear scaling of bending stiffness with the number of layers, which violates the conventional cubic scaling of bending stiffness in continuum mechanics.

We unite the atomic scale simulation with the experiment through a continuum model to compare the period, shape, and transition strains extract the variations in adhesion and bending energy of different 2D materials and heterostructures to find the deformation of 2D materials under the compressive strain.

11:20am **2D+EM+MI+NS-TuM-11 Title: Spatially-Resolved Contact-Free Electrical Characterization of Transition Metal Dichalcogenide Films Grown by Chemical Vapor Deposition.**, *Miguel Isarraraz, L Bartels*, University of California, Riverside

Surface Acoustical Waves (SAWs) and Transition Metal Dichalcogenides (TMDs), separately, are topics of current research due to their present and future use in telecommunications and beyond-CMOS technology. The interaction between a SAW and a 2D electron gas has been previously studied by measuring the absorption of the SAW by GaAs and, more recently, graphene [i,ii]. Here, the interaction between a SAW and a TMD is studied using MoS<sub>2</sub> directly grown by chemical vapor deposition on 128°YX-cut LiNbO<sub>3</sub>. By focusing a 532 nm laser on the sample, the generation of electron-hole pairs is found to enhance the attenuation of the SAW as expected, and this technique can be used to spatially resolve variations inside triangular MoS<sub>2</sub> islands. Furthermore, the time dependence of the SAW attenuation with laser exposure is used to distinguish between heating and electronic effects. The induced acoustoelectric current, laser power, and SAW excitation power dependence are discussed. This technique provides a means of electrically characterizing atomically thin semiconducting film that avoids the limitations of metallic contacts.

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11:40am **2D+EM+MI+NS-TuM-12 Electronic, Thermal, and Unconventional Applications of 2D Materials**, *Eric Pop, E Yalon, C McClellan, K Smithe, C English, M Mleczo, M Muñoz Rojo, N Wang, S Suryavanshi, I Datye, C Bailey, A Gabourie, M Chen, V Chen, K Schauble, R Grady*, Stanford University

**INVITED**

This talk will present recent highlights from our research on two-dimensional (2D) materials and devices including graphene, boron nitride (h-BN), and transition metal dichalcogenides (TMDs). The results span from fundamental measurements and simulations, to devices, to system-oriented applications which take advantage of unusual 2D material properties. On the fundamental side, we have measured record velocity saturation in graphene [1,2], as well as the thermal properties of graphene nanoribbons [3]. These are important for electronic applications, which can exhibit substantial self-heating during operation [4]. Taking advantage of low *cross-plane* thermal conductance, we found unexpected applications of graphene as ultra-thin electrode to reduce power consumption in phase-change memory [5]. We have also demonstrated wafer-scale graphene systems for analog dot product computation [6].

We have grown monolayer 2D semiconductors by chemical vapor deposition over cm<sup>2</sup> scales, including MoS<sub>2</sub> with low device variability [7], WSe<sub>2</sub>, MoSe<sub>2</sub> – and multilayer TMDs MoTe<sub>2</sub> and WTe<sub>2</sub> [8]. Importantly, ZrSe<sub>2</sub> and HfSe<sub>2</sub> have native high-K dielectrics ZrO<sub>2</sub> and HfO<sub>2</sub>, which are of key technological relevance [9]. Improving the electrical contact resistance [10], we demonstrated 10 nm transistors using *monolayer* MoS<sub>2</sub>, with the highest current reported to date (>400 μA/μm), approaching ballistic limits [11]. Using Raman thermometry, we uncovered low thermal boundary conductance (~15 MW/m<sup>2</sup>/K) between MoS<sub>2</sub> and SiO<sub>2</sub>, which could limit heat dissipation in 2D electronics [12]. We are presently exploring unconventional applications including thermal transistors [13], which could enable nanoscale control of heat in “thermal circuits” analogous with electrical circuits. Overall, these studies reveal fundamental limits and new applications that could be achieved with 2D materials, taking advantage their unique properties.

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## Materials and Processes for Quantum Computing Focus Topic

### Room 203A - Session MP+EM+NS-TuM

#### High Coherence Qubits for Quantum Computing

**Moderator:** Robert Ilic, National Institute of Standards and Technology (NIST)

8:00am **MP+EM+NS-TuM-1 MBE Grown Nitride Superconductors for Quantum Circuits**, *Christopher Richardson, A Alexander, C Weddle*, Laboratory for Physical Sciences

Low microwave loss superconducting capacitors and inductors are critical circuit components of superconducting qubits. For transmon qubits, the ability to make high-quality planar resonators is an essential part of fabricating highly coherent qubits. Plasma assisted Molecular beam epitaxy (PAMBE) is used to grow niobium titanium nitride alloys (Nb<sub>x</sub>Ti<sub>1-x</sub>N) directly on silicon (111) wafers. 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. Here focus will be on the optimization of PAMBE-TiN films grown under slightly nitrogen rich conditions and high growth temperatures. Using films grown on high resistivity wafers, resonators are fabricated from coplanar waveguides with a narrow 6-μm wide center conductor and nominal 500-nm deep trench etch. Cryogenic testing at 100mK demonstrate low microwave loss that is evident from measured internal quality factors that are over 1M in the single photon regime and approach 10M at high powers. The motivation of using PAMBE to grow

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superconductors and the favorable comparison with resonators made from leading films synthesized with sputter deposition will also be discussed.

8:20am **MP+EM+NS-TuM-2 Towards Improved Coherence Times in Transmon Qubits, Sam Stanwyck**, Rigetti Computing

The depth of the circuit a quantum computer can perform depends directly on the coherence times of its qubits. There are many sources of decoherence in superconducting qubits, and identifying and minimizing dominant sources is a critical step in improving the performance of quantum computers. By measuring the internal quality factor of resonators and deliberately coupling to different loss mechanisms, we identify dominant sources of resonator loss in our systems, as well fabrication process changes to ameliorate these losses. Additionally, defects and materials present on the chip surface are correlated with process changes and coherence metrics.

8:40am **MP+EM+NS-TuM-3 Design and Fabrication for High Coherence Quantum Circuits, David Pappas, X Wu, R Lake, M Bal, J Long, C McRae, H Ku**, National Institute of Standards and Technology (NIST) **INVITED**

In this talk we focus on achieving high coherence in multi-component quantum circuits [1,13]. We will discuss geometric and electrical design strategies that mitigate energy loss while maintaining sufficient coupling to the qubit. Materials considerations -including dielectric losses in the substrate and various interfaces -play a central role in the implementation of these circuits. We will present a summary of our studies of the various participation factors and processing techniques to reduce dielectric loss in the capacitance of the qubits and resonators for readout and coupling. We also review our methods of integration for the key nonlinear component, the overlap tunnel junctions. In particular, techniques for achieving smooth surfaces for the junctions in a back-end process will be shown.

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9:20am **MP+EM+NS-TuM-5 Effect of Surface Treatment on Superconducting Qubit Coherence, Bradley Christensen**, University of Wisconsin-Madison; *P Kumar*, University of Wisconsin - Madison; *J Nelson, Y Liu, A Ballard, B Plourde*, Syracuse University; *R McDermott*, University of Wisconsin - Madison

Superconducting qubits are an attractive candidate for quantum information processing in the solid state. The fidelity of two-qubit gates for superconducting qubits is one of the more challenging limitations toward scalable quantum computing. A promising approach to perform these gates uses flux-tunable qubits to bias the qubit pairs into resonance to perform the necessary entangling operations. While this approach has many advantages over competing techniques, there are still significant issues that limit the fidelity of the gates. For example, since the two-qubit gate requires flux-biasing of a qubit, this also necessarily requires one of the qubits to operate at a flux-sensitive point, and as such,  $1/f$  flux noise will restrict the possible gate fidelity. In addition to flux noise, flux-tunable qubits also suffer from microscopic two-level system (TLS) defects that reside in the high field areas on the qubit capacitor pad. These TLS cause an enhanced decay through both resonant interactions with the qubit and Landau-Zener transitions as the qubit frequency is biased through a TLS. While one could perform spectroscopy of the TLS to map out the inoperable space, this becomes an inefficient solution for large scale systems as the TLS resonance frequencies are not stable, and will significantly drift over time.

Recent experiments on Superconducting Quantum Interference Devices (SQUID) point to adsorbed molecular  $O_2$  as the dominant contributor to magnetism in superconducting thin films, and demonstrate that improvements in the sample vacuum environment lead to significant reductions in surface spin susceptibility and magnetic flux noise power. Furthermore, TLS defects have been shown to reside in surface oxides and interfaces, where the TLS dipole couples to the qubit electric field, and experiments on microwave resonators have shown that high-temperature annealing can yield a reduction in surface TLS defects.

Here, we present our results on improving the vacuum environment of superconducting qubits with an ultra-high vacuum (UHV) bake to remove the adsorbates. We measure flux noise power spectral densities (PSD) using Ramsey-based, CPMG filtering, and dressed-dephasing techniques, allowing the flux PSD measurements to span 10 decades. Furthermore, by measuring qubit lifetime as a function of frequency (swap spectroscopy), we can map out the coupling strength, lifetime, and density of the TLS defects. We present a comparison of treated and untreated devices to demonstrate the improvement to qubit coherence through a UHV bake.

9:40am **MP+EM+NS-TuM-6 Metrology of Dielectric Loss using Lumped-Element Microwave Resonators, Corey Rae McRae, X Wu, M Bal, J Long, H Ku, D Pappas, R Lake**, National Institute of Standards and Technology

Reducing the overall concentration of TLSs in dielectric materials remains at the forefront of materials research in quantum information science. In this work, we measure a lumped element resonator fabricated from a superconductor-dielectric-superconductor trilayer to determine the TLS loss of various dielectrics of interest in superconducting quantum computing. The deposition of the trilayer prior to fabrication allows control of the metal-dielectric interfaces, and the fabrication process is generalized so that resonators containing different dielectrics can be compared easily. This lithography method enables the measurement of trilayer capacitors and junctions that have been prepared entirely in situ in an ultrahigh vacuum environment. In future work, we will interrogate a new class of low-loss dielectrics grown with epitaxial methods using the measurement capabilities developed here.

11:00am **MP+EM+NS-TuM-10 Direct Observation of Atomic Structure of Ultra Thin  $AlO_x$  Barriers in  $Al/AlO_x/Al$  Josephson Junctions for Quantum Devices, Eva Olsson**, Chalmers University of Technology, Gothenburg, Sweden **INVITED**

The atomic structure of tunnel barriers in Josephson junctions for quantum devices and the corresponding interfaces determine the properties of the junction. The thinnest region in the barrier of a junction will be the preferential tunneling channel for charge carriers and the highest current. The current increases exponentially with decreasing barrier thickness. As a consequence, a variation on the individual atom plane length scale results in inhomogeneity of the tunnel current across the barrier. There are several earlier experimental indirect indications that only a small fraction of the junction area is active.

We are using high resolution annular dark field (ADF) scanning transmission electron microscopy (STEM) imaging to obtain high resolution (better than 1 Å) and high precision (better than 1 pm) information about the local atomic structure [1]. We use ADF STEM imaging to directly determine the thickness distribution along the oxide barrier in  $Al/AlO_x/Al$  Josephson junctions [2]. The barrier thickness is about 1-2 nm. The thickness distribution shows that less than 10% of the junction area dominates the electron tunneling. We also study the influence of oxygen pressure and oxidation time on the thickness distribution. In addition, we determine the atomic structure and coordination of Al atoms within the oxide barrier layer using electron energy loss spectroscopy and nanobeam electron diffraction [3]. A lower Al coordination is observed at the metal/oxide interface compared to the interior of the oxide barrier. We also study the structure of the interfaces between the Al contact and the substrate [4,5].

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11:40am **MP+EM+NS-TuM-12 Metrology of Tunnel Junctions for Superconducting Qubits, Russell Lake**, National Institute of Standards and Technology (NIST); *X Wu, H Ku, J Long, M Bal, C McRae*, National Institute of Standards and Technology (NIST) and University of Colorado Boulder; *D Pappas*, National Institute of Standards and Technology (NIST)

Superconducting tunnel junctions make up the key non-linear circuit component in many implementations of quantum electrical circuits, including superconducting qubits. Therefore, controllable fabrication of superconducting junctions has taken a central role in the realization of quantum computers. In this talk we discuss fabrication and characterization of a wafer-scale process for nanoscale superconducting tunnel junctions (Al- $\text{AlO}_x$ -Al) [1]. We present the distribution of normal-state resistances across a wafer for different junction sizes. We have applied an analytical method of accounting for the current crowding in the junction leads [2] in order to give accurate predictions of the supercurrent from the room-temperature raw data. These corrected resistances can be input into the Ambegaokar-Baratoff formula to predict the critical current of the tunnel junctions in the superconducting state [3], and the corresponding non-linear effective inductance. These results are immediately relevant to the task of qubit frequency allocation in multi-qubit systems.

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## Nanometer-scale Science and Technology Division Room 102B - Session NS+AN+EM+MN+MP+RM-TuM

### Nanophotonics, Plasmonics, and Metamaterials

**Moderators:** Alokik Kanwal, NIST Center for Nanoscale Science and Technology, Nikolai Klimov, National Institute of Standards and Technology

8:00am **NS+AN+EM+MN+MP+RM-TuM-1 Parametric Nonlinear Interactions in Nanofabricated Silicon-based Photonics, Amy Foster**, Johns Hopkins University **INVITED**

High optical confinement waveguides on integrated platforms enable nonlinear optical interactions with low power levels. The third-order nonlinear susceptibility, a modification of a material's permittivity due to an applied optical field, exists in all materials, and is an intensity-dependent process leading to third-order parametric effects. Harnessing the high optical intensities enabled by high confinement waveguides allows standard semiconductor materials to become power-efficient parametric nonlinear optical devices that can operate with powers in the mW range. The optical confinement of a waveguide also enables control over the waveguide's dispersion, allowing for phase-matching of the parametric processes thereby improving its operating bandwidth. Using standard nanofabrication techniques, integrated photonic devices can be tailored in both geometry at the nanoscale, and in magnitude of their third-order susceptibility through modification of their material properties. In this talk, we will discuss a variety of parametric nonlinear optical demonstrations in silicon-based waveguides including optical parametric amplification and oscillation, phase-sensitive amplification, and frequency conversion and comb generation. Furthermore, we will discuss these devices for a variety of applications including optical signal processing, spectroscopy, and security.

8:40am **NS+AN+EM+MN+MP+RM-TuM-3 Ultrafast Optical Pulse Shaping using Dielectric Metasurfaces, Amit Agrawal, S Divitt, W Zhu, C Zhang, H Lezec**, NIST Center for Nanoscale Science and Technology **INVITED**

Since the invention of femtosecond pulsed lasers, the field of ultrafast optical science and technology has seen significant progress in the generation and characterization of ultrashort optical pulses. Complimentary to development in generation and characterization techniques, arbitrary temporal shaping of optical pulses has become an integral part of the field. Fourier-transform pulse shaping is the most widely adopted approach that entails parallel modulation of spatially separated frequency components to achieve the desired pulse shape. Recently, dielectric metasurfaces have emerged as a powerful technology for arbitrary control over the amplitude, phase, or polarization of light in a single, compact optical element. Here, we experimentally demonstrate shaping of sub-10 fsec ultrafast optical pulses using a centimeter-scale silicon metasurface acting as both amplitude and phase modulation mask. The deep-subwavelength silicon nanostructures, positioned with

nanometer precision, are individual optimized to provide accurate amplitude and phase modulations to each frequency component. Masks of this type offer a lower cost, larger size, higher resolution, high diffraction efficiency, high damage threshold method for controlling ultrafast pulses.

9:20am **NS+AN+EM+MN+MP+RM-TuM-5 Single-Particle Nanophotonics and Materials Investigations with Optical Microresonator Spectrometers, Erik Horak**, University of Wisconsin - Madison; *K Heylman, K Knapper, M Rea, F Pan, L Hogan, R Goldsmith*, University of Wisconsin-Madison **INVITED**

Optical microresonators have achieved impressive sensitivities in a range of experimental modalities. We leverage the exquisite sensitivity of microresonators to enable highly sensitive spectroscopic characterization of objects on the surface of the resonator. In this way, not only can single particles be detected and identified, but fundamental properties of interrogated systems can be studied, opening a path to mechanistic studies and label-free chemical identification.

Our photothermal-based technique employs a two-beam geometry. A fiber-coupled (probe) beam records the whispering-gallery mode (WGM) resonance wavelength via evanescent coupling through a tapered fiber, while a second free-space (pump) beam heats absorbing particles or molecules on the surface of the microresonator, shifting the WGM resonance. In essence we use the microresonator as a nearfield thermometer to measure dissipated heat upon optical excitation. To circumvent the photothermal background of the popular  $\text{SiO}_2$  on Si toroidal resonators, we have developed an all- $\text{SiO}_2$  microtoroidal resonator, unlocking visible wavelengths to interrogation. We further employed a double-modulation technique through simultaneous Pound-Drever-Hall locking of the probe beam and amplitude modulation of the pump beam to reach sub-100 Hz or single attometer resonance shift resolution. This corresponds to signals much smaller than that predicted from a single-molecule, and thus represents an avenue toward single-molecule absorption spectroscopy.

We demonstrate this technique by examining gold nanorods (AuNR), which validate our experimental setup with near-diffraction limited photothermal maps, Lorentzian absorption spectra with stochastic center wavelengths, and single dipole polarization dependences. Further, AuNRs in close proximity to microresonator WGMs display signatures of photonic-plasmonic interactions, a forest of Fano resonances decorating the plasmonic absorption feature. This platform offers a facile methodology to study these complex interactions, with thermal annealing of the AuNRs producing highly controllable tuning of Fano resonances. Applying our platform to conductive polymers (CP), we have begun to understand the fundamental properties that enable the high conductivity from a bottom-up nanoscale perspective. We examine the interplay between homogeneous and heterogeneous broadening, measure the long-range ordering, and determine relative surface orientation of CPs. These examples firmly demonstrate the utility of our platform to go beyond sensing allowing exploration of novel characteristics in complex systems and potentially the observation of chemical and biochemical dynamics.

11:00am **NS+AN+EM+MN+MP+RM-TuM-10 Optomechanical Interactions for Metrology and Signal Processing, Karen Grutter**, The Laboratory for Physical Sciences **INVITED**

Imprinting radio-frequency (RF) signals on optical carriers has a broad range of applications from metrology to communication and has been accomplished in bulk components using a variety of techniques. Achieving this functionality on a chip could broaden the potential application space, but the bulk frequency generation methods do not translate directly to the nanoscale. A number of methods have been proposed for on-chip frequency generation, including various sources of electro-optic modulation, comb generation via material nonlinearities in microresonators, and optomechanical/opto-acoustic interactions. In this talk, we will discuss the features of these sources, with particular focus on optomechanical interactions.

One potential phenomenon enabling opto-acoustic frequency generation is stimulated Brillouin scattering (SBS), which is essentially an interaction between propagating phonons and photons. This effect has been demonstrated in optical fibers, and recent results in on-chip waveguides show promise. One of the challenges with SBS on chip is that gain is dependent on long interaction lengths.

This interaction can be enhanced by moving to a different domain of phonon/photon interaction: cavity optomechanics. In an optomechanical cavity, the characteristics of the generated frequency are dependent on the mechanical eigenmode. We will demonstrate the relationship between



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mechanical quality factor and phase noise in ring optomechanical oscillators.

The optomechanical interaction can be optimized beyond that of ring resonators by further confining optical and mechanical modes using photonic and phononic crystals. We have designed and fabricated  $\text{Si}_3\text{N}_4$  nanobeam optomechanical crystals with  $\sim 4$  GHz mechanical breathing modes. The increased optomechanical coupling of these nanobeams confers high sensitivity to displacement, which could be exploited for various metrology applications, which we will discuss.

Further enhancement of the optomechanical coupling can be achieved by modifying the optomechanical crystal geometry to support an optical slot mode. We have designed and fabricated  $\sim 3$  GHz-frequency slot-mode optomechanical crystals in  $\text{Si}_3\text{N}_4$ . In addition to increasing the optomechanical coupling compared to the single-nanobeam device, this structure has increased versatility, enabling interaction with other stimuli and modalities. We have integrated NEMS actuators with a slot-mode optomechanical crystal, and used these actuators to tune the optical mode and lock it to an external, fixed laser wavelength. This increases the practicality of this device, enabling longer-term measurements and stabler frequency sources.

**11:40am NS+AN+EM+MN+MP+RM-TuM-12 Cold-atom based Sensors and Standards, Stephen Eckel, D Barker, J Fedchak, N Klimov, E Norrgard, J Scherschligt, National Institute of Standards and Technology INVITED**

In this talk, I will describe our recent efforts to merge nanophotonics, ultra-high vacuum, and atomic physics together to build a new generation of cold atom sensors and standards. In particular, I will focus on our recent realization of a single-beam system for cooling lithium atoms, an atomic species recently identified as an excellent candidate for a primary vacuum standard. Our system uses a triangular-shaped nanofabricated diffraction grating to produce the necessary beams for a magneto-optical trap that cools and slows the atoms. Unlike systems that use rubidium or cesium, which can be loaded from a vapor, lithium introduces additional complications because it must be produced from a thermal source requiring loading of the magneto-optical trap from behind the chip. Finally, I will conclude by talking about other trap geometries that we are pursuing, how they benefit vacuum and inertial sensors, and what the synergy of integrated nanophotonics, high-vacuum and atomic physics might be able to bring.

## Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic

**Room 202A - Session PC+AS+BI+NS+PB+SS-TuM**

### Solid-Liquid and Gas-Liquid Interfacial Processes and Characterization

**Moderators:** Stephen Nonnenmann, University of Massachusetts - Amherst, Juan Yao, Pacific Northwest National Laboratory

**8:00am PC+AS+BI+NS+PB+SS-TuM-1 Liquefied Gas Electrolytes for Electrochemical Energy Storage Devices, Y. Shirley Meng, University of California San Diego; Y Yang, University of California at San Diego INVITED**  
Electrochemical energy storage devices, such as Li-ion batteries and electrochemical capacitors, have seen little change in their electrolyte chemistry since their commercialization. These liquid electrolytes often limit the energy density and low-temperature operation of these devices, which hinder many potential applications. Our work uses electrolytes based on solvent systems which are typically gaseous under standard conditions and show excellent performance in electrochemical energy storage devices. It has demonstrated that these novel solvents have superior physical and chemical properties which are attributed to excellent performance over an extended temperature range and a wide potential window of stability with unique safety features. The use of fluoromethane as solvent for lithium batteries shows excellent low-temperature operation down to  $-60^\circ\text{C}$  with high capacity retention. The liquefied gas electrolytes also show a high coulombic efficiency for cycling dendrite-free lithium metal anodes.

**8:40am PC+AS+BI+NS+PB+SS-TuM-3 An In situ Molecular-scale View of Nucleation and Self-assembly at Solid-liquid Interfaces, James De Yoreo, Pacific Northwest National Laboratory INVITED**

Nucleation and self-assembly from solutions are seminal processes in the formation of ordered structures ranging from simple inorganic crystals to macromolecular matrices. Observations over the past fifteen years have

revealed a rich set of hierarchical nucleation pathways involving higher-order species ranging from multi-ion clusters to dense liquid droplets, as well as transient crystalline or amorphous phases. Despite their complexity, a holistic framework for understanding particle-based pathways to crystallization that extends classical concepts emerges when the coupled effects of complexity of free energy landscapes and the impact of dynamical factors that govern particle formation and interaction are considered. Here I use a series of in situ TEM and AFM studies on inorganic, organic, and macromolecular systems to illustrate that framework via the evolution in nucleation and growth processes as these complexities and dynamical factors come into play. The results show that the introduction of either size-dependent phase stability associated with the high surface-to-volume ratios of nanoparticles, or high driving force coupled with the existence of metastable polymorphs leads to two-step pathways characterized by the initial appearance of a bulk precursor phase. The creation of micro-states, which represent local minima in free energy stabilized by configurational factors associated with structural elements of molecules, can also lead to hierarchical pathways, but the intermediates are microscopic transient states that do not appear on a bulk phase diagram. However, small changes in molecular structure can eliminate these transient states, leading to a direct pathway of nucleation. Limitations on molecular mobility, either through large barriers to changes in coordination or conformation, reduced temperature, or introduction of ion-binding polymers, can freeze non-equilibrium states into place for dynamical reasons. Analysis of sub-critical cluster evolution and subsequent nucleation shows that these dynamical constraints can lead to density fluctuations in accordance with classical descriptions even when non-classical pathways dominate. The findings from these in situ studies provide a common basis for understanding the development of order in systems as diverse as simple salt crystals, branched semiconductor nanowires, and microbial membranes.

**9:20am PC+AS+BI+NS+PB+SS-TuM-5 Non-linear Surface Spectroscopy at the Aerosol Particle/Gas Interface, F Geiger, Ariana Gray Be, Northwestern University INVITED**

While the interface of the aerosol gas and particle phase is the first entity encountered by incoming gas phase species, accessing it with bond-specific methods has been hindered due to a lack of tools that can operate under ambient pressure and temperature conditions. Here, we overcome this hurdle by using nonlinear optics and demonstrate the utility of vibrational sum frequency and second harmonic generation for probing the surfaces of sea spray aerosol, secondary organic aerosol, and anthropogenic influence on them. By following the heterogeneous physical and chemical processes that drive gas-to-particle conversion, aerosol formation, their transformations and phase transitions, and reactivity, we provide the molecular origin for cloud activation.

**11:00am PC+AS+BI+NS+PB+SS-TuM-10 The Influence of Electrochemical Potential and Water Vapor on Ionic Liquid Binding Energy Shifts Examined by AP-XPS, Meng Jia, University of Delaware; A Broderick, J Newberg, University of Delaware**

Ionic liquids (ILs) have relatively high electrochemical and thermal stability, good conductivity and low volatility, making them inherently "greener and safer" compared to the conventional electrolytes. The application of ILs in the field of electrochemistry has identified many opportunities for their use as electrolytes in electrochemical devices. Due to the ubiquity of water and the hydrophilic nature of ILs, water can either be unintentionally present or often intentionally added to alter IL properties including density, viscosity, friction, and electrochemical window. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) is sensitive to both the chemical and electrical states of materials, which makes it an ideal method for studying surface potentials in electrochemical devices. In this work we examine the IL-gas interface of 1-butyl-3-methylimidazolium acetate, [BMIM][OAc], deposited on an Au foil via AP-XPS as function of electrochemical potential and surrounding water vapor pressure. The electrochemically induced binding energy shifts ( $\Delta\text{BE}/\Delta\text{E}$ ) of carbon, nitrogen, and oxygen species of the IL were analyzed. Results reveal that in the absence of water vapor there is an ohmic drop between the electrode-IL interface and the IL-vacuum interface, giving rise to a  $\Delta\text{BE}/\Delta\text{E}$  value of less than one. Upon introducing water vapor, forming an IL/water mixture, the  $\Delta\text{BE}/\Delta\text{E}$  approaches a value of one as a function of increasing pressure. We attribute this behavior to a decrease in the ohmic drop as the IL/water mixture becomes more conductive. These results suggest that the electrochemical potential of the IL-gas interface is influenced by both an external bias and by varying the surrounding relative humidity. The same is

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likely true for the IL-electrode interface where water is known to be present.

11:20am **PC+AS+BI+NS+PB+SS-TuM-11 Role of Air Gas at the Interface between Water and Graphite Surfaces**, *Ing-Shouh Hwang*, Institute of Physics, Academia Sinica, Taiwan, Republic of China; *C Yang, C Fang*, Institute of Physics, Academia Sinica, Taiwan, Republic of China, Taiwan, Republic of China; *Y Lu*, Institute of Physics, Academia Sinica, Taiwan, Republic of China; *H Ko*, Institute of Physics, Academia Sinica, Taiwan, Republic of China, Taiwan, Republic of China

The saturation concentrations of nitrogen and oxygen in water under ambient conditions are very small (~10 ppm), thus their roles have been largely ignored. Using advanced atomic force microscopy, we study the evolution of gas-containing structures at graphite/water interfaces at room temperature. Our study indicates that gas (mainly nitrogen and oxygen) molecules dissolved in water tend to adsorb onto hydrophobic/water interfaces [1]. In gas-undersaturated water, we observe gradual nucleation and growth of small two-dimensional (2D) ordered domains over time on graphite surfaces [2]. The ordered structures may eventually cover the entire interface. When water is gas-supersaturated or when fresh DI water is briefly heated, we observe cap-shaped fluid nanostructures in addition to the ordered domains [3]. The cap-shaped nanostructures are the so-called interfacial nanobubbles (INBs) or surface nanobubbles, whose nature, stability, and formation remain controversial. When water is slightly gas-supersaturated, we see evolution of the fluid-like structures. The fluid phase first appears as a circular wetting layer ~0.3 nm in thickness and is later transformed into a cap-shaped INB [4]. 2D ordered domains are nucleated and grow over time outside or at the perimeter of the fluid regions, eventually confining growth of the fluid regions to the vertical direction. We determined that INBs and the fluid layers have very similar mechanical properties, suggesting low interfacial tension with water and a liquid-like nature.

Our study suggests that, in gas-undersaturated water, dissolved gas molecules may mainly be in the dispersed monomer form. Their rearrangement with water molecules at hydrophobic/water interface may lead to gradual nucleation and growth of the ordered domains. In gas-supersaturated water, some dissolved gas molecules are well dispersed in water, but others may aggregate into clusters. Adsorption of gas clusters leads to the formation of circular fluid layers at the graphite/water interface. The work clearly shows the crucial role of gas molecules at hydrophobic/water interfaces and has broad implications in diverse research fields.

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11:40am **PC+AS+BI+NS+PB+SS-TuM-12 Probing Cluster and Nanoparticle Growth Processes with X-Ray Spectroscopy and Mass Spectrometry**, *Musahid Ahmed*, *O Kostko*, Lawrence Berkeley National Laboratory **INVITED**

Tunable synchrotron radiation (VUV and X-rays) provides a universal, yet selective scalpel to decipher molecular information in complex chemical systems when coupled to mass spectrometry and X-Ray spectroscopy. This provides profound insight into molecular growth mechanisms, solvation and electronic structure in clusters, complexes and nanoparticles. In the first part, I will describe how single photon ionization mass spectrometry may be applied to molecular beams to probe molecular growth that is mediated either by ion or neutral pathways. The association and dissociation pathways in acetylene clusters where bonding can change from van der Waals to covalent upon ionization leading to the formation of benzene will be described.<sup>1</sup> I will follow up with very recent results on association of water with "hydrophobic" naphthalene & "hydrophilic" glycerol where subtle non covalent interactions can lead to surprising results in electronic structure and its effect on the hydrogen bonding network of water.

X-ray spectroscopy provides a local probe of a sample's electronic structure with elemental and site-specificity and is thus ideally suited for probing solvation. Since X-rays can probe surfaces, interfaces and bulk, and more important penetrate matter, it provides for interrogation of buried and confined spaces. Here I will describe a new approach, Velocity Map Imaging

X-Ray Photoelectron Spectroscopy coupled to nanoparticle beams<sup>2</sup> that allows for the visualization of dynamic processes in solvation and molecular growth processes. I will describe its' implementation on aqueous arginine aerosols, where by varying the pH of the constituent solution, evidence is provided that the guanidinium groups are protonated even in a very basic solution (pH 13).<sup>3</sup> A molecular level picture of how charge and proton transport in aqueous solutions of arginine occur emerges by analyzing the energy shifts on the C and N X-ray photoelectron spectra. I will conclude by suggesting new approaches to probe gas liquid interactions and chemistry with X-Ray spectroscopy and microfluidic devices allowing access to liquids in vacuum.<sup>4</sup>

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## Surface Science Division

### Room 203C - Session SS+HC+NS+PS-TuM

#### Controlling Mechanisms of Surface Chemical Reactions

**Moderators:** Bruce D. Kay, Pacific Northwest National Laboratory, Arthur Utz, Tufts University

8:00am **SS+HC+NS+PS-TuM-1 Bond Making and Bond Breaking at Wet and Dry Surfaces**, *Angelos Michaelides*, University College London, UK **INVITED**

The making and breaking of chemical bonds at the surfaces of crystalline materials is key to an almost endless list of physical phenomena and technological processes. Increasingly computer simulation techniques are playing an important role in helping to understand such processes, acting as a complement and guide to experiments. In this talk I will discuss recent simulation work in which we are working at: (i) obtaining fundamental physical insight of chemical reactions at the surfaces of transition metal alloys; and (ii) understanding and improving the accuracy of electronic structure simulations of surface chemical processes.

8:40am **SS+HC+NS+PS-TuM-3 Stability and Reactivity of Isolated Rh<sub>1</sub> Atoms on Fe<sub>3</sub>O<sub>4</sub>(001)**, *Gareth Parkinson*, TU Wien, Austria

In this talk I will address the thermal and chemical stability of Rh adatoms adsorbed on Fe<sub>3</sub>O<sub>4</sub>(001), and discuss the reactivity of these species with a view to single-atom catalysis. Using a combination of atomic-scale imaging, spectroscopies and DFT-based calculations, I will show that Rh adatoms adsorb in a bulk-continuation cation site at room temperature on Fe<sub>3</sub>O<sub>4</sub>(001), where they remain stable upon CO adsorption and can catalyze CO oxidation via a reaction with the support at 500 K. However, at this temperature Rh begins to incorporate within the support lattice, and the higher coordination environment significantly modifies the reactivity. In addition, I will show that Rh<sub>1</sub> species efficiently dissociate water, leading to H spillover of H onto the support, and that Rh<sub>1</sub> diffusion is induced upon adsorption of O<sub>2</sub> and NO.

9:00am **SS+HC+NS+PS-TuM-4 The Mechanism of Glaser Coupling Reactions on Ag(111) and Cu(111) Surfaces: a Case for Halogen Substituted Terminal Alkyne**, *T Wang, H Lv*, University of Science and Technology of China, China; *L Feng*, University of Science and Technology of China; *J Huang, X Wu*, University of Science and Technology of China, China; *Junfa Zhu*, National Synchrotron Radiation Laboratory and Department of Chemical Physics, University of Science and Technology of China, China

Ullman and Glaser homo-couplings are the two most well-developed on-surface coupling reactions, which have been successfully employed to fabricate one-dimensional and two-dimensional nanostructures on metal surfaces. The mechanism towards surface-confined Ullman coupling has been well-established. However, the mechanism of surface-confined Glaser coupling has been poorly understood. In this presentation, we report our recent studies on the surface-confined Glaser coupling reactions on Ag(111) and Cu(111) using 1,1'-biphenyl,4-bromo-4'-ethynyl (BPBE) as the precursor molecule. By direct observations of alkynyl-Ag-alkynyl and alkynyl-Cu-alkynyl type organometallic intermediates on Ag(111) and Cu(111), respectively, we have proposed a reaction pathway initiated by

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single-molecule dehydrogenation, similar as the mechanism of on-surface Ullmann coupling. The reaction processes were further explored by density functional theory based transition state calculations. Interestingly, the dehydrogenation of terminal alkyne is revealed as a H adatom-related process on Ag(111) while a Cu adatom-related process on Cu(111). After the release of interstitial metal adatoms in the organometallic intermediates, the final C-C coupling occurs easily on Ag(111), but shows extremely low efficiency on Cu(111) due to the too strong interaction between ethynylene and the Cu(111) substrate. In addition, we have demonstrated that Glaser reaction of the molecule is prior to Ullmann reaction on Ag(111), which provides a promising approach of stepwise fabrication of sp-hybrid nanostructures. *This work is supported by the National Natural Science Foundation of China (21773222, 21473178) and the National Key R&D Program of China (2017YFA0403402).*

9:20am **SS+HC+NS+PS-TuM-5 Sulfur-driven Switching of the Ullmann Coupling on Au(111)**, Jonathan Rodríguez-Fernández, S Schmidt, J Lauritsen, Aarhus University, Denmark

Ullmann coupling reaction has been attracted great interest in the last decades due to the advantage to build 1D-2D nanostructures from bottom-up fabrication like graphene nanoribbons, polymer, etc[1]. This reaction, it is used to generate covalent molecular linked coupling, C-C, by different halogen molecule precursors. The reaction is activated by the substrate, where the precursors will be dehalogenated. Thus, the substrate plays an important role in the success of the reactions. There are several challenges, one of them is the scaling-up production of high quality nanostructures, where defects or co-adsorbates can reduce the success of this process. It has been reported two cases, where the Ullmann coupling reaction are partially inhibited[2,3]. Here, we reported for the first time the reactivation of the reaction after inhibited on Au(111) by molecular gases[4].

In this work we describe a variable temperature Scanning tunneling microscopy (VT-STM) study that allows us to identify the switch on and off of the Ullmann coupling reaction of this molecule (2,8-Dibromodibenzothiophene) on Au(111). After low temperature deposition on pristine Au(111), the results show that surprisingly Ullmann coupling mechanism happen even at 100 K. We speculate that the modification of the herringbone reconstruction due to the strong interaction between S and Au atoms can facilitate the lifting of the Au adatoms inducing the reaction even at low temperature. On the other hand, when we firstly dose sulfur atoms on the pristine gold crystal by H<sub>2</sub>S vapor and subsequently depositing DBDBT molecules, the Ullmann coupling reaction has been completely inhibited due to the formation of S-Au complexes, which is blocking the activation of the reaction due to the gold adatoms on the terrace and step-edges are not available. Dysprosium and Iodine atoms have reported similar partial inhibition on silver and copper, respectively. However, we are able to reactivate the reaction by removing the sulfur atoms from the substrate by exposing the sample to H<sub>2</sub> (gas). STM images show again the Ullmann coupling reaction has been switched on. This result shows the important of co-adsorbates on the substrate and also emphasizes the strong interaction between substrate adatoms (terraces and step edges) and the molecule precursors during the dehalogenation reaction.

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9:40am **SS+HC+NS+PS-TuM-6 The Step Sites of Ultrathin ZnO Promote Methanol Oxidation to Formaldehyde**, Xingyi Deng, D Sorescu, J Lee, National Energy Technology Laboratory

We investigated the adsorption and oxidation of methanol on ultrathin ZnO layers supported on Au(111) using temperature programmed reaction spectroscopy (TPRS) and density functional theory (DFT) calculations. In the TPRS experiments, we found that only molecular methanol-<sup>18</sup>O desorbed from the planar ZnO bilayer surface at T = 220 K and 260 K following adsorption of methanol-<sup>18</sup>O at T = 100 K, whereas a partial oxidation product, formaldehyde-<sup>18</sup>O (~95% selectivity), and a small amount of carbon dioxide (C<sup>16</sup>O<sup>18</sup>O) were produced at T = 580 K at the bilayer-trilayer step sites. Computational modeling based on the DFT calculations identified the adsorption configurations of methanol on the planar ZnO surface and at the step sites, as well as the reaction pathways to gaseous formaldehyde. The most stable adsorption configuration was found to be a

methanol molecule adsorbed at the bilayer-trilayer step sites with its C-O axis parallel to the upper terrace edge, forming a bond between its O atom and a Zn site on the lower terrace, and also a hydrogen bond between its H atom in the OH group and a lattice O anion at the upper terrace edge. Starting from the most stable adsorption configuration at the step sites, formation of gaseous formaldehyde was shown to take place preferentially via a methoxy (CH<sub>3</sub>O(ad)) intermediate, following the pathways CH<sub>3</sub>OH(ad) → CH<sub>3</sub>O(ad) + H(ad) → CH<sub>2</sub>O(g) + 2H(ad) with an overall barrier of 19.0 kcal/mol. Formation of CO<sub>2</sub> was kinetically hindered due to a much larger barrier of ~ 38 kcal/mol to produce a lattice O-bonded formaldehyde (H<sub>2</sub>COO<sub>lattice</sub>(ad)), the proposed precursor leading to CO<sub>2</sub>. These computational results suggesting the preference to produce gaseous formaldehyde from methanol oxidation at the step sites agreed well with the high selectivity toward formaldehyde observed in the TPRS experiments.

11:00am **SS+HC+NS+PS-TuM-10 Investigation of Configuration Change in Water Clusters on a Bilayer ZnO Surface**, Junseok Lee, D Sorescu, X Deng, National Energy Technology Laboratory

Adsorption of water on the nanostructured metal oxide surfaces has implications in catalysis and serves as a prototypical system in studying water-oxide interfaces. In many cases, the water molecules form hydrogen bonded clusters or extended networks on surfaces. On a bilayer ZnO/Au(111) surface, two types of cyclic triangular water clusters are found to be formed at a specific Moire domain. By using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, the behavior of the water clusters on the bilayer ZnO surface have been further interrogated. The configurations of the two types of cyclic water clusters can be converted to each other by the excitation from the STM tip at a threshold energy. In addition, another pathway for the cluster configuration change was identified at a higher electron energy where the cyclic water clusters could be turned into non-cyclic clusters reversibly. The physical origin of the configuration changes will be discussed.

11:20am **SS+HC+NS+PS-TuM-11 Oxygen Reduction Reaction on Fullerene**, Yosuke Kikuchi, J Nakamura, The University of Electro-Communications (UEC-Tokyo), Japan

It has been reported that nitrogen-doped graphene exhibits high oxygen reduction reaction (ORR) activity, while pristine graphene does not [1]. This is because that doped-nitrogen atoms provide extra electrons to graphene, leading to the stabilization of the reaction intermediates on graphene surface. On the other hand, if curvature can be given to graphene, the chemical bond nature between carbon atoms varies from pure sp<sup>2</sup> to sp<sup>3</sup>-like sp<sup>2</sup>, and then the reactivity of graphene surface is expected to increase. In this study, we evaluated the ORR activity of fullerene as an example of carbon materials with a curvature.

We investigated the ORR activity of fullerene (C<sub>60</sub>) using first-principles calculations based on the density functional theory. Electrocatalytic activities were evaluated on the basis of the computational hydrogen electrode model proposed by Nørskov *et al.* [3] We evaluated the energetics of reaction intermediates in terms of free energy of adsorption. In general, the ORR mainly proceeds in two pathways: For the two-electron pathway (2e<sup>-</sup>), oxygen molecule (O<sub>2</sub>) is reduced to hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), and for the direct four-electron pathway (4e<sup>-</sup>), the final product is water (H<sub>2</sub>O). H<sub>2</sub>O<sub>2</sub> for the 2e<sup>-</sup> pathway might corrode a carbon-based electrocatalyst material itself, causing to low durability. Therefore, we also played up the selectivity for the 4e<sup>-</sup> pathway.

It was found that the fullerene molecule has ORR activity with extremely high selectivity for the four-electron pathway, even if the nitrogen atom is not doped. On the other hand, nitrogen-doped fullerene hardly shows the ORR activity, because the reaction intermediates are overstabilized by nitrogen-doping to fullerene; the maximum electrode potentials show negative values for both the direct four-electron and two-electron pathways.

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11:40am **SS+HC+NS+PS-TuM-12 Surface Structure and Reactivity of Ni-Cu Single-Atom Alloys**, Dipna Patel, C Sykes, Tufts University

Ni is one of the most extensively used industrial catalytic metals. Utilized for steam reforming of hydrocarbons, Ni atom ensembles detrimentally catalyze the formation of graphitic carbon which leads to coking and

deactivation of the catalyst. By alloying Ni into Cu, a catalytically less active host metal, our single-atom alloy approach has the potential to greatly enhance catalytic selectivity and reduce poisoning, analogous to other systems such as Pt-Cu and Pd-Cu. First, we report characterization of the atomic-scale surface structure and local geometry of low coverages of Ni deposited on a Cu(111) single crystal, using scanning tunneling microscopy. Near room temperature, Ni preferentially alloys into the Cu host by forming Ni rich brims along ascending step edges. Next, temperature programmed desorption studies reveal that CO binds more weakly to single Ni atoms in Cu compared to larger Ni ensembles in Ni(111) which is promising for catalytic applications in which CO poisoning is an issue. This characterization of Ni-Cu surface alloys the catalytic activity and selectivity of the surface to be correlated with the atomic-scale structure of the alloy. Using this approach, the catalytic selectivity and resilience to poisoning can be tuned via both ligand and ensemble effects.

12:00pm **SS+HC+NS+PS-TuM-13 Effective Local Structure for Bottom-up Designed ORR Catalyst Using Pyridinic Nitrogen Containing Molecules, Kotarou Takeyasu, Y Shimoyama, M Furukawa, S Singh, J Nakamura, University of Tsukuba, Japan**

Nitrogen containing carbon materials have been reported to be low-cost and durable catalysts for reactions such as an oxygen reduction reaction ( $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ , ORR) in fuel cells. Among several types of nitrogen species in carbon materials, pyridinic nitrogen (nitrogen atom bound to two C atoms) was found to create ORR active sites in our previous work [1]. Recently, we also have shown that the active site is superseded by pyridinic nitrogen-containing aromatic molecules covering a carbon substrate with high density [2]. That is, bottom-up catalysts composed of pyridinic nitrogen-containing molecules and carbon supports. In the present study, we aim to investigate which local structure for pyridinic nitrogen in a molecule strongly contributes to the ORR activities and to clarify the mechanism.

For this purpose, various nitrogen-containing molecules were prepared, which were 1,10-phenanthroline, 4,7-phenanthroline, 1,7-phenanthroline, benzo[h]quinoline, phenanthridine, acridine, phenazine, quinoxaline, and dipyridophenazine. The bottom-up catalysts were prepared by simply immersing carbon black (CB) as a support material into a catalyst solution with solvent of nafion. The catalytic performances for oxygen reduction reactions (ORR) of the prepared catalysts were measured by rotating disc method in acidic electrolyte (0.1 M  $H_2SO_4$ ) at a room temperature. The prepared catalysts were also evaluated by X-ray photoemission spectroscopy (XPS) and density functional calculations.

Among the molecules, 1,10-phenanthroline, quinoxaline, and dipyridophenazine on CB showed highest activities, whose onset potentials (potentials versus RHE at a current density of  $10 \text{ mA cm}^{-2}$ ) were 0.29 V, 0.28 V, and 0.21 V, respectively. This tendency suggested that an 1,10-phenanthroline type local structure showed high ORR activities because quinoxaline and dipyridophenazine also contains the same local structure. XPS spectra after the superimposed voltage of 0.2 eV in an ORR condition for 1,10-phenanthroline showed two peaks corresponding to pyridinium N and pyridinic N. This also suggested that N-H...N structure promoted the following ORR reaction. The detail of the effect of the local electronic structure in the adsorbed molecules will be discussed.

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[1] D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, *Science*, 2016, 351, 361-365.

[2] R. Shibuya, T. Kondo, J. Nakamura, *ChemCatChem*, 2018

## 2D Materials Focus Topic

Room 201B - Session 2D+EM+MI+MN+NS-TuA

## 2D Device Physics and Applications

Moderator: Roland Kawakami, The Ohio State University

2:20pm **2D+EM+MI+MN+NS-TuA-1 Spin Relaxation and Proximity Effect in WS<sub>2</sub>/Graphene/Fluorographene Non-local Spin Valves**, *Adam Friedman*, Laboratory for Physical Sciences; *K McCreary, J Robinson, O van 't Erve, B Jonker*, US Naval Research Laboratory

The mechanisms leading to spin relaxation in graphene and its heterostructures continue to be debated. Control of the spin relaxation in graphene-based structures is necessary to achieve the envisioned utility of graphene in future spintronic devices beyond Moore's law. Proximity induced spin relaxation caused by contact to a high spin-orbit material, such as WS<sub>2</sub>, offers a promising avenue to manipulate the spin lifetime [1]. We demonstrate the operation of WS<sub>2</sub>/graphene/fluorographene non-local spin valves and extract the spin lifetimes for a range of carrier concentrations by Hanle effect measurements. Four-terminal charge transport measurements allow us to calculate the momentum relaxation time as a function of carrier concentration and compare it to the spin lifetime. These data show that the D'yakonov-Perel' mechanism is the dominant spin relaxation mechanism for WS<sub>2</sub>/graphene/fluorographene devices, while, for reference graphene/fluorographene devices, linear scaling between the spin and momentum lifetimes points to spin-flip scattering during strong elastic scattering events where the scattering event is strongly coupled to the electron spin. We attribute the change in spin relaxation type in part with the inclusion of WS<sub>2</sub> as a substrate to proximity induced spin-orbit coupling due to the adjacent WS<sub>2</sub> layer, and we compare our data to the literature.

[1] A.L. Friedman, et al. Carbon 131, 18-25 (2018).

2:40pm **2D+EM+MI+MN+NS-TuA-2 Two-dimensional Field-effect Light Emitting Transistors**, *Junyoung Kwon, H Ryu*, Yonsei University, Republic of Korea; *J Lee, C Lee*, Korea University, Republic of Korea; *G Lee*, Yonsei University, Republic of Korea

Two dimensional (2D) materials and their heterostructures hold great promises in various applications due to their unique properties and newly discovered physics. Especially, high exciton binding energy and emergence of charged excitons, *i.e.* trions, have shown that 2D semiconductors, such as transition metal dichalcogenides (TMDs), are promising candidates for new concept optoelectronics. Although lots of optoelectronic devices based on the van der Waals heterostructures of 2D materials, such as photodetectors, solar cells, and light emitting devices, have been demonstrated, development of novel optoelectronic devices is still required to fully utilize unique properties of 2D materials and enable multi-functions and versatile applications. Here we demonstrate 2D field-effect light emitting transistors (2D-FELET) consisting of monolayer WSe<sub>2</sub> (light-emitting channel layer) and graphene contacts (tunable carrier injection electrodes). We encapsulated monolayer WSe<sub>2</sub> with two pieces of hexagonal boron nitride and fabricated graphene contacts to two ends of WSe<sub>2</sub>. To selectively inject different types of charge (electrons and holes) at two graphene contacts, two separate top gates on top of WSe<sub>2</sub>-graphene overlap regions were fabricated. By independent modulation of two top gates, Schottky barrier heights for electrons and holes can be tuned, which enables the selective charge injections. When two top gates are oppositely biased, electrons can be injected from one end of WSe<sub>2</sub> channel and holes can be injected from the other end. These opposite charges are recombined at the middle of WSe<sub>2</sub> channel, leading to strong light emission. The performance of the 2D-FELETs is tunable by additional electrical field from back gate. Furthermore, the devices produced in this work can be used as polarity-tunable FETs and photodetectors, simultaneously, which are beneficial for further CMOS integration. Our study shows great potential of 2D-FELETs toward future optoelectronic applications, which request ultra-thinness, transparency, flexibility, high efficiency, multi-functions, and high integration.

3:00pm **2D+EM+MI+MN+NS-TuA-3 Quantum Devices with 2D Materials**, *H Overweg, M Eich, R Pisoni, T Ihn, P Rickhaus*, ETH Zurich, Switzerland; *Klaus Ensslin*, ETH Zurich, Switzerland

Quantum dots in graphene have been mostly realized by etching. This leads to localized states at the uncontrolled edges dominating the transport properties of these quantum devices. [1] It is well known that in bilayer graphene gaps can be opened by vertical electrical fields. [2] This approach has been used with limited success to define quantum devices [3]. The

pinch-off characteristics are typically limited by leakage currents often thought to occur at the physical sample edges [4].

Here we demonstrate that electrostatically tunable barriers can be fabricated on bilayer graphene devices with graphite as a back gate. We measure pinch-off resistances exceeding GΩ and observe quantized conduction plateaus for one-dimensional constrictions. [5] With suitable gate arrangements few carrier hole and electron quantum dots can be electrostatically defined. We measure the controlled occupation of quantum dots with single holes and electrons. Four-fold level bunching is observed in Coulomb blockade spectroscopy which is understood in terms of valley and spin states. Magnetic field dependence allows to investigate orbital and spin/valley degrees of freedom.

We further demonstrate quantum devices build on MoS<sub>2</sub>.

1. For a review see Bischoff et al., Applied Physics Reviews 2, 031301 (2015)
2. Oostinga et al., Nat. Materials 7, 151 (2007)
3. Allen et al., Nat. Comm. 3, 934 (2012)
4. [<https://www.nature.com/articles/ncomms14552#auth-1>] et al., Nat. Comm. 8, 14552 (2017)
5. Overweg et al., [<https://arxiv.org/abs/1707.09282>], [<https://arxiv.org/abs/1709.00870>]

4:20pm **2D+EM+MI+MN+NS-TuA-7 GaN Microdisk Light-emitting Diode Display Fabricated on Graphene**, *Youngbin Tchoe, K Chung, K Lee, M Song, J Park, H Kim, J Park, G Yi*, Seoul National University, Republic of Korea

Microdisplay with high resolution, brightness, and efficiency with long-term stability and reliability are highly required for advanced display technologies. Inorganic semiconductor LEDs best suits this purpose because they can emit very high density of light from a small area and they have very high efficiency and long-term stability. To use inorganic LEDs for display applications, various lift-off and transfer techniques of inorganic thin films grown on single crystal substrates, such as sapphire or Si, were developed. However, achieving display devices using inorganic semiconductor thin films is still very challenging because of the limited size and high manufacturing cost of the single crystal substrates, as well as the complicated processes required for lift-off and assembly. To resolve this problem, growths of inorganic semiconductor nanostructures and thin films on graphene substrates have recently been proposed, since graphene has great scalability and extremely thin layered hexagonal lattice structure as an excellent substrate for GaN growth. Moreover, the inorganic semiconductors prepared on large-area graphene can be transferred easily to or grown on elastic substrates to meet the flexibility demand. Here, we suggest a method of fabricating ultrathin, high-resolution inorganic microdisplay based on individually addressable GaN microdisk LED arrays grown on graphene dots.

Here, we report on the fabrication and EL characteristics of ultrathin and individually addressable GaN microdisk LED arrays grown on graphene dots for microdisplay applications. GaN microdisks were prepared by epitaxial lateral overgrowth on patterned graphene microdots on SiO<sub>2</sub>/Si substrates using MOVPE. After preparing the GaN microdisk arrays, *p*-GaN and InGaN/GaN multiple quantum well, and *n*-GaN layers were heteroepitaxially grown on the surface of the GaN microdisks. Ultrathin layers composed of GaN microdisk LED arrays on graphene dot were prepared by coating a polyimide layer and lifting-off the entire layers from the substrate. Then, single-walled carbon nanotubes (SWCNTs)/Ni/Au and SWCNTs/Ti/Au multiple electrode lines were formed on the top and bottom surface of GaN microdisk arrays in an aligned manner and crossing each other. The electrical and optical characteristics of the individually addressable GaN microdisk array on graphene dots were investigated by measuring their *I*-*V* curves and EL characteristics at various bending conditions. We also confirmed that the ultrathin micro-LED display worked reliably under flexible conditions and continuous operation mode.

4:40pm **2D+EM+MI+MN+NS-TuA-8 Room Temperature Magnetron Sputtering and Laser Annealing of Ultrathin MoS<sub>2</sub> for Transistor Device Fabrication on Flexible Polymer Substrates**, *Benjamin Sirota*, University of North Texas; *N Glavin*, Air Force Research Laboratory; *C Arnold, A Voevodin*, University of North Texas

Pulsed magnetron sputtering and subsequent laser annealing provide technologically attractive scalable route for producing two-dimensional (2D) semiconducting grade MoS<sub>2</sub> materials directly on the surface of flexible polymer substrates. In this study the room temperature magnetron sputtering was used to deposit 10 nm thick, amorphous MoS<sub>2</sub> films on flexible PDMS as well as rigid SiO<sub>2</sub>/Si substrates. This was followed by 248

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nm pulsed laser annealing to produce polycrystalline 2H-MoS<sub>2</sub> over large areas. Raman and XPS analysis confirmed that pulsed laser annealing with about 1 mJ/cm<sup>2</sup> energy density had induced film crystallization from amorphous to hexagonal, while preserving MoS<sub>2</sub> chemical composition, and avoiding formation of oxide phases or damage to the temperature-sensitive polymer surface. Electrical measurements confirmed an order of magnitude improvement in electrical conductivity of the laser annealed films as compared to amorphous MoS<sub>2</sub>. Top-gated field effect transistor (FET) devices with laser annealed sputter grown MoS<sub>2</sub> were directly fabricated on PDMS surfaces. Oxygen substitution of sulfur in sputter deposited MoS<sub>2</sub> and polycrystallinity of the laser annealed 2H-MoS<sub>2</sub> films resulted in low mobility values when compared to mechanically exfoliated and chemical vapor deposition grown single-crystal 2D MoS<sub>2</sub>. However, the described approach is intrinsically scalable and provides a direct growth route for the fabrication of 2D transition metal dichalcogenide semiconducting devices on the surface of flexible and stretchable polymers.

5:00pm **2D+EM+MI+MN+NS-TuA-9 Black Phosphorus: Fundamental Properties and Emerging Applications**, *Han Wang*, University of Southern California **INVITED**

In this talk, I will discuss our recent work in developing novel electronic and photonic devices based on the anisotropic properties of black phosphorus (BP) and its iso-electronic materials such as the monochalcogenides of Group IV elements. High mobility, narrow gap BP thin film (0.3 eV in bulk) fill the energy space between zero-gap graphene and large-gap TMDCs, making it a promising material for mid-infrared and long wavelength infrared optoelectronics. Most importantly, its anisotropic nature within the plane of the layers allow for the realization of conceptually new electronic and photonic devices. Here, I will first present our work in understanding the fundamental electronic and optical properties of black phosphorus using a newly developed scanning ultrafast electron microscopy (SUEM) technique and photoluminescence spectroscopy. Our recent study of bandgap tuning in BP and the demonstration of a polarization sensitive BP mid-IR detector will then be presented. In the second half of my talk, I will discuss our work on developing two dimensional materials based artificial synaptic devices for neuromorphic electronics, including emulating the heterogeneity in synaptic connections using the anisotropic properties of BP and a tunable memristive device as a reconfigurable synapse. I will conclude with remarks on promising future research directions of low-symmetry electronics based on anisotropic 2D materials and how their novel properties is expected to benefit the next-generation electronics and photonics technologies.

5:40pm **2D+EM+MI+MN+NS-TuA-11 Patterned Growth of Hybrid Bulk-2D Tungsten Diselenide for Transistor Applications**, *Quinten Yurek, I Liao, D Barroso, A Nguyen, N Duong, G Stecklein, L Bartels*, University of California, Riverside

As device dimensions shrink, surfaces and interfaces between materials make up a larger volume fraction of a device leading to degrading device properties in 3D materials. One solution is to use 2D materials, however these materials introduce additional challenges. For instance, high resistance Schottky barriers and a small number of free charge carriers in comparison to bulk materials. The effective mobility of field effect transistors (FETs) based on two-dimensional (2D) single-layer transition metal dichalcogenide (TMD) films is frequently limited by barriers at the contacts, as opposed to the native properties of the TMD material. Specifically, high resistance Schottky barriers form at the TMD/metal interface because of the film's thinness and resulting small number of carriers. Here we demonstrate a scalable single-step deposition method for nanoscale hybrid 2D/3D TMD structures encoded by lithographic patterning prior to deposition. By confining the metal contact to the bulk regions of WSe<sub>2</sub>, the effective mobility is increased to nearly 100 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> with an on/off ratio >10<sup>5</sup> for bottom-gated devices (through 300nm of oxide), even for comparatively long channels (>5 microns) and absent other contact optimization. Our process involves lithographic patterning of a hafnium (IV) dioxide film onto the SiO<sub>2</sub>/Si substrate prior to TMD growth. Bulk-like 3D WSe<sub>2</sub> is observed to grow at the location of the hafnia, while 2D single-layer material is grown in regions of bare SiO<sub>2</sub>. Systematic evaluation of transport data allows us to extract Schottky barrier heights and other fundamental properties of our hybrid devices. We demonstrate that this process can be used to create devices with metal/3D TMD contacts, which exhibit a reduced Schottky barrier height, while continuing to use 2D TMD channels, which result in an excellent on-off ratio.

6:00pm **2D+EM+MI+MN+NS-TuA-12 Enhanced Ionic Sensitivity in Solution-Gated Graphene-Hexagonal Boron Nitride Heterostructure Field-Effect Transistors**, *A Radadia, Nowzesh Hasan, B Hou, A Moore*, Louisiana Tech University

The charge transport in solution-gated graphene devices is affected by the impurities and disorder of the underlying dielectric interface and its interaction with the solution. This paper reports advancement in field-effect ion sensing by fabricating a dielectric isomorph, hexagonal boron nitride between graphene and silicon dioxide of a solution-gated graphene field effect transistor. Ionic sensitivity of Dirac voltage as high as -198 mV/decade for K<sup>+</sup> and -110 mV/decade for Ca<sup>2+</sup> were recorded. Increased transconductance due to increased charge carrier mobility was accompanied with larger ionic sensitivity of the transconductance due to larger ionic sensitivity of the charge carrier mobility. These findings define a standard to construct future graphene devices for biosensing and bioelectronics applications.

**Biomaterial Interfaces Division**  
**Room 101B - Session BI+AS+IPF+NS-TuA**

**IoT Session: Biofabrication, Bioanalytics, Biosensors and Diagnostics**

**Moderators:** Graham Leggett, University of Sheffield, UK, Tobias Weidner, Aarhus University, Denmark

2:20pm **BI+AS+IPF+NS-TuA-1 Functionalization of Silica Materials via Click Reaction of Surface Silanol Groups with Vinyl Sulfones**, *Fang Cheng, H Wang, W He, B Sun, J Qu*, Dalian University of Technology, China

Silica-based materials are widely used in the fields of catalysis, chromatography, biomaterials, biosensing and drug delivery due to their earth abundance and low cost. Success of these applications mostly relies on the functionalization of silica surfaces, among which covalent binding of organic molecules is preferred. Common strategies for the covalent functionalization of silica materials involve either silane treatments or Si-H reactions. Each has its share of limitations, with the former suffering from self-polymerization and multilayer modifications, and the latter being sensitive to moisture and oxygen. Herein, we proposed the 'click' reaction of silanol groups with vinyl sulfones, which enables a new and simple strategy for functionalization of silica materials. For the first time, the 'click' concept was extended to silanol groups that are abundant on the surface of silica materials, using compounds bearing vinyl sulfone groups. By simply immersing silica materials in vinyl sulfone solutions at 60°C, functionalization could be achieved in hours in the presence of catalysts. The chemical stability of vinyl sulfones and mild reaction conditions make this strategy advantageous than silane treatments and Si-H reactions. We demonstrated that silica materials with sizes ranging from microscale to macroscale could all be functionalized. Using compounds bearing multiple vinyl sulfone groups, silica materials can be further functionalized with varies of biomolecules due to the versatile reactivity of vinyl sulfone group towards thiol, amino and alcohols. Furthermore, the stability of resulting Si-O-C bond can be tuned by the properties of the vinyl sulfone compounds (e.g., hydrophobicity and surface density) as well as the environmental factors (e.g., solvents, pH and temperature). Increase in the hydrophobicity and functionalization density of the vinyl sulfone compounds could increase the stability of Si-O-C bonds. Contrast to the high stability in organic solvents, degradation of Si-O-C bond can be realized in aqueous solutions, which can be accelerated by addition of acid or base. This is rarely observed with bonds produced based of silane treatments and Si-H reactions. It could broaden the biomedical applications of functionalized silica, for example, to provide tailored release of drugs or proteins from silica surface.

2:40pm **BI+AS+IPF+NS-TuA-2 Organosilica pH Nanosensors Applied to Realtime Metabolite Monitoring**, *Kye Robinson*, Monash University, Australia; *K Thurecht*, University of Queensland, Australia; *S Corrie*, Monash University, Australia

Continuous monitoring of biomarkers in biological environments is a key challenge for the development of biosensors capable of providing real-time feedback<sup>1</sup>. These sensors promise to aid in the treatment of diseases with a highly dynamic nature however current technologies remain scarce<sup>1</sup>. Nanoparticle based "optodes" have emerged as sensitive and tuneable biosensors, using chromo/ionophores to generate analyte-specific changes in fluorescence spectra in a dynamic and reversible manner. Currently this type of sensor suffers from limitations including leaching of reagents from

the nanoparticles over time, combined with poor colloidal stability and resistance to fouling in biological fluids.

An organosilica core-shell pH sensitive nanoparticle containing a mixture of covalently incorporated pH-sensitive (shell) and pH-insensitive (core) fluorescent dyes has been developed. This platform demonstrates good long term stability (80 days), fast response time (<100 ms) and resistance to fouling in biological conditions<sup>2</sup>. This presentation will describe the modification of these pH sensing particles towards the production of a lactate responsive particle for sensing through coupling with lactate dehydrogenase. Here we will present our latest results focussed on enzyme encapsulation in addition to modulation of shell parameters including thickness and degree of crosslinking in order to tune response kinetics for application in biological tissues.

<sup>1</sup> Corrie, S. R. et al., *Analyst*, **2015**, *140*, 4350-4364

<sup>2</sup> Robinson, K. J. et al., *ACS Sensors*, **2018**

**3:00pm BI+AS+IPF+NS-TuA-3 Impact of Different Receptor Binding Modes on Surface Morphology and Electrochemical Properties of PNA-based Sensing Platforms**, *Johannes Daniel Bartl*, Walter Schottky Institut (WSI) and Physics Department, Technische Universität München, Germany; *P Scarbolo*, Dipartimento Politecnico di Ingegneria e Architettura (DPIA), Università degli Studi di Udine, Italy; *S Gremmo, G Rziga, M Stutzmann*, Walter Schottky Institut (WSI) and Physics Department, Technische Universität München, Germany; *M Tornow*, Molecular Electronics Group and Department of Electrical and Computer Engineering, Technische Universität München, Germany; *L Selmi*, Dipartimento di Ingegneria "Enzo Ferrari" (DIEF), Università di Modena e Reggio Emilia, Italy; *A Cattani-Scholz*, Walter Schottky Institut (WSI) and Physics Department, Technische Universität München, Germany

Silicon-based field-effect devices have been widely studied for label-free DNA detection in recent years. These devices rely on the detection of changes in the electrical surface potential during the DNA recognition event and thus require a reliable and selective immobilization of charged biomolecules on the device surface [1]. The preparation of self-assembled monolayers of phosphonic acids (SAMPs) on metal oxide surfaces is an efficient approach to generate well-defined organic interfaces with a high density of receptor binding sites close to the sensing surface [2,3]. In this work, we report the functionalization and characterization of silicon/silicon nitride surfaces with different types of peptide nucleic acid (PNA), a synthetic analogue to DNA [4].

Differently modified PNA molecules are covalently immobilized on the underlying SAMPs either in a multidentate or monodentate fashion to investigate the effect of different binding modes on receptor density and morphology important for PNA-DNA hybridization. Multidentate immobilization of the bioreceptors via C<sub>6</sub>-SH attachment groups at the  $\gamma$ -points along the PNA backbone provides a rigid, lying configuration on the device surface (PNA 1), whereas a monodentate immobilization by Cys-capped PNA molecules (PNA 2) results in more flexible and more accessible receptor binding sites. Our results indicate that the presented functionalization scheme can be successfully applied to produce morphologically and electrochemically different PNA bioreceptor binding sites on silicon/silicon nitride surfaces. Consequently, a well-chosen modification of the PNA backbone is a valid approach to influence the sensing properties of surface-immobilized PNA bioreceptors, which might provide an additional parameter to further tune and tailor the sensing capabilities of PNA-based biosensing devices.

[1] Ingebrandt S. and Offenhausser A., *Phys. Status Solidi A* **203** (2006), 3399–3411.

[2] Chaki N. K. and Vijayamohan K., *Biosens. & Bioelectron.* **17** (2002), 112.

[3] Stutzmann M., Garrido J. A., Eickhoff M. and Brandt M. S., *Phys. Status Solidi A* **203** (2006), 3424–3437.

[4] Nielsen P. E. and Egholm M. (ed.), *Peptide Nucleic Acids*, Horizon Scientific Press (1999).

**3:20pm BI+AS+IPF+NS-TuA-4 Biosensor for Detection of Gasotransmitter from Living Cells Employing Silver Nanorods Array**, *Shashank Gahlaut, C Sharan, J Singh*, Indian Institute of Technology Delhi, India

The detection of endogenous gases including H<sub>2</sub>S is of immense interest nowadays as it opens the way to predict some diseases as well as an early stage diagnosis. These three gasotransmitter (H<sub>2</sub>S, NO and CO) gaseous molecules transfer the information and give the signal for mainly cardiovascular diseases. Therefore, its detection has crucial importance in

bio-medical science. Here, we demonstrate H<sub>2</sub>S detection from living cells using silver nanorods arrays fabricated by glancing angle deposition method. Colorimetric and wettability properties of silver nanorods are being observed for the gaseous detection. We use the model organism *E. coli* to demonstrate the feasibility of the method for the determination of live and resistant strains of the bacteria. For the human cell, we have used HeLa cell line for the same. For the simplicity and feasibility of the technique, Android based mobile app has been developed for the colorimetric detection. Data obtained in this study show the potency of the system to identify live/dead bacteria with or without antibiotic treatment and compared with the time-consuming standard plating method, it is a simple and cost-effective method for the estimation of living and resistant microorganism. The performance of AgNRs as H<sub>2</sub>S gas sensor is investigated by its sensing ability of 5 ppm of gas with an exposure time of only 30 s. It has potential application in the area of antimicrobial resistance and bio-medical healthcare.

**4:20pm BI+AS+IPF+NS-TuA-7 Conversion of Human Stem Cells into Insulin Producing Cells Through 2D Platforms for Enhanced in-vitro Insulin Production**, *S Vishwakarma, A Khan*, Central Laboratory for Stem Cell Research and Translational Medicine, Centre for Liver Research and Diagnostics, Deccan College of Medical Sciences, India; *Marshal Dhayal*, IIT (BHU), Varanasi, India

Transplantation of whole pancreas/cadaveric islets is the most commonly acceptable treatment option for uncontrolled diabetes. However, the wider clinical applicability of these approaches is limited due to unavailability of donors and continuous need for the administration of immunosuppressant. Here we report a new strategy for efficient in-vitro trans-differentiation of human-hepatic progenitor cells (hHPCs) into insulin producing cells (iPCs) on biologically compatible micro-chips of 2D platforms. The physiological function of transdifferentiated hHPCs confirmed the activation of intracellular Ca<sup>2+</sup> signaling and activation of pancreatic transcription factors (pTFs) which triggers the insulin exocytosis during hyperglycemic challenge. The iPCs on these micro-chips showed upregulated expression of master regulator Pdx-1,  $\beta$ -cell specific marker Nkx-6.1 and more importantly C-peptide similar to human pancreatic  $\beta$ -cells during hyperglycemic challenge. These platforms may provide long-term survival and function of iPCs which could be better technology for developing effective therapeutic options for the management of diabetic.

**4:40pm BI+AS+IPF+NS-TuA-8 Polyzwitterion-modified Nanoparticles for Selective Antibody Separation**, *F Cheng, C Zhu, Wei He, B Sun, J Qu*, Dalian University of Technology, China

Antibody separation is a key biopharmaceutical process, which requires high specificity and efficiency in isolating the biomacromolecule from a complex biological fluid. Development of the separation adsorbent benefits diagnostics and therapeutics, such as point-of-care testing, treatment of cancer and autoimmune disease. In the process of antibody separation, Protein A chromatography is a commonly employed adsorbent, which could obtain antibody in high purity from serum or ascites. In the process-scale purification and therapeutic plasma exchange, safety issues, e.g. leakage and instability of the immobilized Protein A, and cross-contamination during regeneration, are overwhelmed in biopharmaceutics. An alternative approach to Protein A chromatography is using synthetic ligand, molecular weight of which is commonly less than 200 Da. The main advantages of synthetic ligand are well-controlled chemical structure, low cost, ease in clean-in-place, and repeatable regeneration capability in harsh conditions. However, it is a challenge to adsorb antibody in a highly selective manner from a complex biological fluid, which consists a variety of proteins with a broad range of concentrations.

Herein, we report a facile method to develop a quick separation adsorbent, which adsorbs antibody from a complex biological fluid with a high specificity. Two types of zwitterionic polymer-modified magnetic nanoparticles (NPs) are fabricated by conjugating pSBMA onto PEI-precoated NPs via either one-step method (1S NPs) or two-step method (2S NPs). For both methods, divinyl sulfone is used as linker molecule. Although 1S NPs were capable of resisting both IgG and BSA, 2S NPs exhibited specificity toward IgG adsorption in complex biological fluids, e.g. mixture of serums and IgG. The moderate interactions (K<sub>d</sub> ~1.2  $\mu$ M) between IgG and 2S NPs are three orders of magnitude lower than IgG binding with Protein A (K<sub>d</sub> 10nM). Through complementary characterizations and analyses, we rationalize that the surface developed herein with IgG specificity contains two key components: polyzwitterions with short chain length and sulfone groups with high density.



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5:00pm **BI+AS+HPF+NS-TuA-9 Orienting Proteins on Surfaces with Site-specific Bioorthogonal Ligations**, *Riley Bednar, R Mehl*, Department of Biochemistry and Biophysics, Oregon State University

The functionalization of material surfaces with proteins is of great importance to a number of technologies, from industrial processes to biomedical diagnostics. However, while it has been proposed that orientation may be important to the function of such biomaterials, efforts to study such roles are hampered by a lack of rapid, quantitative, and orientation-specific immobilization techniques which will reduce non-specific fouling, and allow substoichiometric attachment of proteins onto surfaces in an orientation-controlled manner. Here, Carbonic Anhydrase II (HCA)—a 30 kDA, monomeric metalloenzyme which catalyzes the interconversion of carbon dioxide to bicarbonate—is immobilized onto strained *trans*-cyclooctene (STCO)-functionalized magnetic resin in an orientation-specific manner via bioorthogonal ligation with a site-specifically installed tetrazine-containing amino acid (Tet2.0).

5:20pm **BI+AS+HPF+NS-TuA-10 High-throughput Study of the Role of Spatial Organization on the Activity of Surface-Bound Enzymes**, *Nourin Alsharif*, Boston University; *T Lawton, J Uzarski*, Natick Soldier Research, Development and Engineering Center; *K Brown*, Boston University

Many of the exceptional properties of natural materials (e.g. fracture toughness of bones, strength to weight ratio of bamboo) can be attributed to their structural hierarchy, which originates, in part, from the nanoscale organization of the enzymes that synthesize these materials. In order to best utilize such enzymes *ex vivo* to grow engineered biomaterials, the role of this multiscale organization must be understood. Here, we report a novel strategy for studying the activity of arrangements of enzymes within a multifunctional material in a high throughput manner. In particular, we use top-down patterning techniques in conjunction with small molecule self-assembly to designate enzyme-binding regions amidst a non-binding, hydrophobic background. Key to this experimental scheme is the parallel nature of both the fabrication and the characterization processes that enable the efficient study of many geometric parameters of the enzyme-binding features. These parameters include, (1) feature size, (2) density of enzyme within each feature, and (3) distance between features. This level of control can in principle allow us to separate effects of reaction kinetics and substrate diffusion. Two strategies have been explored for the immobilization of enzymes including click chemistry to non-natural amino acids and binding to poly-histidine affinity tags. Top-down lithography and enzyme assembly were verified using a variety of surface characterization techniques including atomic force microscopy, X-ray photoelectron spectroscopy, infrared spectroscopy, spectroscopic ellipsometry, and contact angle goniometry. Initially, this high throughput paradigm is used to develop a fluorimetric assay to quantify the activity of surface-bound enzymes as a function of their spatial organization. Together with the widespread utilization of high throughput techniques in synthetic biology, the ability to study spatial organization in a rapid fashion is expected to dramatically improve *ex vivo* applications of enzymes.

5:40pm **BI+AS+HPF+NS-TuA-11 Fabrication of Amino acid Contained Poly-lactic Acid Nanofibers by Electrospinning**, *C Li*, National Yang Ming University, Taiwan, Republic of China; *J Hsieh*, Ming Chi University of Technology, Taiwan, Republic of China; *P.H. Lin*, National Yang Ming University, Taiwan, Republic of China

Poly(lactic acid) (PLA,  $[C_3H_4O_2]_n$ , CAS 26161-42-2) is a biodegradable and thermoplastic polymer. PLA is naturally produced and can be extracted from many plants such as sugarcane, cornstarch or cassava roots. Typical industrial production processes for PLA are direct condensation of lactic acid monomers (~100°C - 160°C) and ring-opening polymerization of lactide with metal catalysts. For applications in bulk forms, PLA can be produced by extrusion, casting, injection molding and spin coating or even 3D printing.

In cell and tissue engineering applications, amino acids are essential ingredients for cell-tissue culture, implants/replacements, drugs and treatment tests. There are twenty amino acids appearing in human genetic codes by triplet codons and usually categorized according to their polarity, acidity/basicity.

In this study, we fabricate nanofibers by electrospinning on a spin-coated PLA film. This specially designed combination of PLA films and nanofibers is meant to have enduring interfacial adhesion between the two for biomedical applications such as implants. Both PLA nanofibers and films are mixed with selected amino acids. Five amino acids were chosen: tryptophan (Trp, ), methionine (Met, ), serine (Ser, ), glutamate (Glu, ) and arginine (Arg, ). The selection is based on the different electrical polarity of

each amino acid. The electrical polarity has profound effects on the solubility, pH acidity of amino acids in water and many other associated biochemical functions. These amino acids are representatives of certain biochemical features for potentially different influences in our applications for cell culture.

The electrospinning process is controlled by several parameters such as the voltage of power supply, feeding velocity of polymer solution through the syringe pump, electrical field strength and distance to the collection plate of nanofibers. Different combinations of these parameters are studied to determine an optimal control for fiber formation. Properties of and microstructures of deposited films and nanofibers are investigated as following: thickness and deposition rate by surface profilometer; microstructures by Fourier transform infrared spectrometer (FTIR); surface morphology by scanning electron microscope (SEM); optical properties by UV-Visible-IR spectrometer and wettability by the contact angle.

## Electronic Materials and Photonics Division Room 101A - Session EM+2D+AN+MI+MP+NS-TuA

### Solar/Energy Harvesting and Quantum Materials and Applications

**Moderators:** Yohannes Abate, Georgia State University, Nicholas Strandwitz, Lehigh University

2:20pm **EM+2D+AN+MI+MP+NS-TuA-1 Plasmonic Metasurface Electrodes for Excitonic Solar Cells**, *Deirdre O'Carroll*, Rutgers, the State University of New Jersey

**INVITED**

Excitonic organic solar cell technologies, while not currently competitive with inorganic-semiconductor analogues, can exhibit very small device embodied energies (due to comparatively low temperature and low energy-use fabrication processes), which is of interest for minimizing overall device cost and energy-payback time. To improve energy conversion efficiency in thin-film excitonic organic solar cells, light management using nanophotonic structures is necessary. Here, our recent work on improving light trapping in deeply-subwavelength excitonic organic semiconductor films using plasmonic metasurfaces will be presented. Numerous exciton-metasurface interaction phenomena, such as absorption-induced scattering, exciton-plasmon coupling and morphology-dependent surface plasmon light-trapping are observed to give rise to improved light trapping at different regions of the solar spectrum. Additionally, an approach to achieve the theoretical limits to the efficiency of excitonic organic photovoltaics (~22%) will be proposed that involves control of radiative recombination rate, and optimization of both photoluminescence quantum efficiency and photon recycling in organic semiconductor thin-films.

3:00pm **EM+2D+AN+MI+MP+NS-TuA-3 Photoemission Electron Microscopy as a New Tool to Study the Electronic Properties of an Inhomogeneous Semiconductor for Photovoltaics**, *M Berg*, Sandia National Laboratories; *J Kephart, A Munshi, W Sampath*, Colorado State University; *Taisuke Ohta, C Chan*, Sandia National Laboratories

The energy positions of the valence and conduction electronic states with respect to the vacuum level are essential parameters to evaluate how the band gaps of semiconductors or Fermi-levels of metals line up with respect to each other. Such electronic structures of materials can be determined using photoemission spectroscopy (PES). PES measurements, however, remain challenging for inhomogeneous materials with nano- to micrometer lateral dimensions due to its mesoscopic probing area, typically no less than several microns. Photoemission electron microscopy (PEEM) is a cathode lens electron microscopy technique that combines photoemission imaging with spectroscopic modes of operation to provide PES spectra from areas less than one micron in size. Here, we present PEEM studies of the electronic structure of polycrystalline cadmium telluride (CdTe) thin films, a test case to examine the applicability of this new microscopic approach to photovoltaic materials. Post-deposition CdCl<sub>2</sub> treatment of CdTe is known to increase photovoltaic efficiency. However, the precise chemical, structural, and electronic changes that underpin this improvement are still debated. In this study, PEEM was used to spatially map the vacuum level and ionization energy of CdTe films, enabling the identification of electronic structure variations between grains and grain boundaries. *In vacuo* preparation and inert environment transfer of oxide-free CdTe surfaces isolated the separate effects of CdCl<sub>2</sub> treatment and ambient oxygen exposure. Qualitatively, grain boundaries displayed lower work function and downward band bending relative to grain interiors, but

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only after air exposure of CdCl<sub>2</sub>-treated CdTe. This study highlights the importance of probing the spatially varying electronic structure, elucidating the concurrent impacts of processing steps ( CdCl<sub>2</sub> treatment and oxygen exposure ) to develop a comprehensive picture of local electronic structure in an inhomogeneous semiconductor.

The PEEM work was performed at the Center for Integrated Nanotechnologies, an Office of Science User Facility (DE-AC04-94AL85000). M. B. & C. C. were supported by a U.S. DOE-EERE SunShot BRIDGE award (DE-FOA-0000654 CPS25859). T. O. was supported by the CINT user program and Sandia LDRD. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. The views expressed in the article do not necessarily represent the views of the US DOE or the US Government.

**3:20pm EM+2D+AN+MI+MP+NS-TuA-4 Modification of Bandgap for Lead-Free Double Perovskite Cs<sub>2</sub>AgInCl<sub>6</sub> with Bi Doping, *Hassan Siddique*, University of Science and Technology of China; *H Da, X Wang*, University of Science and Technology of China, China; *R Dai, Z Wang*, University of Science and Technology of China; *Z Ding, Z Zhang*, University of Science and Technology of China, China**

Lead halide perovskites have the excellent luminescent properties but exist some vital disadvantages such as instability and Pb toxicity. Lead-free double perovskites draw attention due to a possible candidate for environment-friendly materials. Direct bandgap lead-free halide of Cs<sub>2</sub>AgInCl<sub>6</sub> is one of them. [1] In this work Bi doping Cs<sub>2</sub>AgInCl<sub>6</sub> (CAIC) was successfully prepared. Bi dopant above 15% CAIC can restrict the parity forbidden transition responding to sub absorption peak around 600 nm.[2] On the other hand, the intensity of photoluminescence enhances with the increasing Bi dopant and touches the maximum around 30% doping, then gradually loses its intensity with further doping due to the mechanism of the concentration quenching at room temperature. Bi doping in CAIC can also modify the band gap. The absorption spectra indicate that the band gap reduces from 3.10eV without Bi doping to 2.68eV for Cs<sub>2</sub>AgIn<sub>0.30</sub>Bi<sub>0.70</sub>Cl<sub>6</sub>. PL decay life time reveals the good intrinsic excitonic feature with less defect trappers [3]. Average life time for Cs<sub>2</sub>AgIn<sub>0.70</sub>Bi<sub>0.30</sub>Cl<sub>6</sub> is 490 ns which is least among all other Cs<sub>2</sub>AgIn<sub>(1-x)</sub>Bi<sub>x</sub>Cl<sub>6</sub> doping. Thermogravimetric analysis (TGA) result reveals thermal stability of Cs<sub>2</sub>AgIn<sub>0.30</sub>Bi<sub>0.70</sub>Cl<sub>6</sub> for the high-temperature 506°C. The Bi doping can decrease the band gap, restrict defect states, enhance PL and improve stability; these good performances make Cs<sub>2</sub>AgIn<sub>(1-x)</sub>Bi<sub>x</sub>Cl<sub>6</sub> more suitable for optoelectronic properties.

**4:20pm EM+2D+AN+MI+MP+NS-TuA-7 Optimized (Quantum) Photonics, *Jelena Vuckovic*, Stanford University** **INVITED**

Photonics has numerous applications ranging from optical interconnects, classical and quantum computing, to sensing (such as LIDAR and AR), and imaging. However, the state of the art photonics is bulky, inefficient, sensitive to environment, lossy, and its performance is severely degraded in real-world environment as opposed to ideal laboratory conditions, which has prevented from using it in many practical applications. Therefore, it is clear that new approaches for implementing photonics are crucial.

We have recently developed a computational approach to inverse-design photonics based on desired performance, with fabrication constraints and structure robustness incorporated in design process [1,2]. Our approach performs physics guided search through the full parameter space until the optimal solution is reached. Resulting device designs are non-intuitive (see Figure), but are fabricable using standard techniques, resistant to temperature variations of hundreds of degrees, typical fabrication errors, and they outperform state of the art counterparts by many orders of magnitude in footprint, efficiency and stability. This is completely different from conventional approach to design photonics, which is almost always performed by brute-force or intuition-guided tuning of a few parameters of known structures, until satisfactory performance is achieved, and which almost always leads to sub-optimal designs.

Apart from integrated photonics, our approach is also applicable to any other optical and quantum optical devices and systems. In recent years, color centers in diamond and silicon carbide (SiC) have emerged as a possible platform for implementation of quantum circuits [3,4]. We demonstrate how such quantum hardware can also be optimized to be robust, efficient, and scalable.

## References

[1] A. Piggott et al, *Nature Photonics* 9, 374–377 (2015)]

[2] L. Su et al, *ACS Photonics* ASAP (2018)

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[4] M. Radulaski et al, *Nano Letters* 17 (3), 1782-1786 (2017)

**5:00pm EM+2D+AN+MI+MP+NS-TuA-9 Optical Properties of Single Silicon Vacancies in 4H-SiC, *H Banks*, National Research Council Postdoc residing at the Naval Research Laboratory; *O Soykal*, Sotera Defense Solutions, Inc, residing at the Naval Research Laboratory; *S Pavunny, R Myers-Ward, D Gaskill, Samuel Carter*, U.S. Naval Research Laboratory**

Defects in wide bandgap materials have generated substantial interest as promising systems for quantum information and quantum sensing due to bright, stable optical emission that is often coupled to long-lived spin states. One promising defect system is the silicon monovacancy in SiC (V<sub>Si</sub>), which has a spin-3/2 ground state that can be optically polarized and maintain long spin coherence times even at room temperature. SiC is an attractive material in terms of mature growth and fabrication technology and also has a low natural abundance of nuclear spins, which reduces spin dephasing. While significant work has been performed to study the spin properties of V<sub>Si</sub> for ensembles and even single defects, the optical properties and their connection to the spin system are less developed. Here we report on high resolution optical spectroscopy of single V<sub>Si</sub> defects, specifically V<sub>2</sub> defects, at low temperatures. Using laser excitation spectroscopy, the zero phonon line (ZPL) transitions corresponding to the m<sub>s</sub>=±1/2 and m<sub>s</sub>=±3/2 spin states are resolved, with a linewidth down to 70 MHz and a splitting of 1 GHz. While there is significant variation in the transition energies from one defect to another, the splitting of these lines is very uniform. We also find that emission from the V<sub>2</sub> defect under resonant excitation of these lines rapidly decays on two very different timescales. Slow decay on a 10 ms timescale is attributed to photoionization of V<sub>Si</sub> and can be prevented by periodically exciting the defect with a second laser at 745 nm. Fast decay on a μs or shorter time scale occurs due to a combination of intersystem crossing and spin polarization of the ground state. A significant difference in the decay rates of the two transitions is observed, which gives rise to spin-dependent photoluminescence intensity and non-resonant optical spin polarization. These results further our understanding of the connection between the optical and spin properties of this defect system that are necessary to optically control and readout the spin system as well as to develop a spin-photon quantum interface.

**5:20pm EM+2D+AN+MI+MP+NS-TuA-10 Photoluminescence Studies on Patterned Silicon Vacancy Defects in Li Ion Implanted 4H-SiC for Scalable Quantum Device Applications, *Shojan Pavunny*, U. S. Naval Research Laboratory; *S Carter, H Banks, R Myers-Ward, P Klein*, U.S. Naval Research Laboratory; *E Bielejec*, Sandia National Laboratories; *M DeJarld, A Bracker, E Glaser, D Gaskill*, U.S. Naval Research Laboratory**

Recently, silicon vacancy defect centers (V<sub>Si</sub>) in the CMOS compatible wide bandgap semiconductor SiC hexagonal polytypes have drawn great research interest for future applications in scalable quantum information and quantum sensing mainly due to their high electronic spin (S = 3/2) with a long coherence time at room temperature. Realization of future densely integrated quantum devices will greatly benefit from the ability to deterministically induce the desired V<sub>Si</sub> density at the optimal location in the three-dimensional solid-state matrix with nanometer accuracy and excellent optical properties. With this motivation, we demonstrate targeted formation of arrays of V<sub>Si</sub> ensembles as well as single defects in high-quality 4H-SiC epilayers by a direct, maskless focused ion beam implantation technique with a designed lateral separation of ~5 μm and a ~25 nm spot size. We have carried out high-resolution optical spectroscopy studies (E<sub>L</sub>c and E<sub>||</sub>c) on these arrays, in which lithium ions are implanted at doses varying from 10<sup>12</sup> – 10<sup>15</sup> Li/cm<sup>2</sup> at a fixed energy of 100 keV to a depth of ~400 nm from the surface. Photoluminescence intensity and defect conversion yield with dose, photostability, fluorescence saturation, and V<sub>1</sub>:V<sub>1'</sub> intensity evolutions with temperature and excitation power were investigated. Results obtained from temperature dependent photoluminescence studies can provide key insights in the design and fabrication of scalable and reproducible three dimensional SiC quantum hybrid devices including photonic crystal cavities.

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5:40pm **EM+2D+AN+MI+MP+NS-TuA-11 Processing of Cavities in SiC Material for Quantum Technologies, Rachael Myers-Ward, K Hobart, K Daniels, A Giles, M Tadjer, L Luna, F Kub, S Pavunny, S Carter, H Banks, E Glaser, U.S. Naval Research Laboratory; P Klein, Sotera Defense Solutions; K Qiao, Y Kim, J Kim, Massachusetts Institute of Technology; K Gaskill, U.S. Naval Research Laboratory**

Silicon carbide is a material of interest for quantum computing and sensing applications owing to deep point defect centers with long spin coherence times (which characterizes the lifetime of the qubit), specifically the  $V_{Si}$  [1], divacancies [2] and nitrogen-vacancy centers [3]. These spin qubits have been isolated and coherently controlled, where  $V_{Si}$  have  $T_2$  coherence times up to 100  $\mu s$  [4] and divacancies to 1 ms [2], making these two defects of most interest to date. While the current spin coherence times have been shown to be as long as 1 ms, further improvements are needed to fully realize the potential of SiC for quantum applications. In this work, we create  $V_{Si}$  in epitaxial SiC and investigate fabricating the layers into microstructures suitable for using the  $V_{Si}$  photoluminescence (PL) emission. We have found 4H-SiC epitaxial layers grown under standard growth conditions and with varying doping densities from  $10^{14}$  to  $10^{18}$   $cm^{-3}$  have no measurable  $V_{Si}$  present, as determined by confocal PL. To introduce  $V_{Si}$ , we used 2 MeV electron irradiation in doses ranging from 0.75 to 75 kGy. This results in  $V_{Si}$  PL ranging from single to ensemble emission within the confocal volume. Hence, we are able to tune the vacancy concentration.

In order to improve the indistinguishable photons from the  $V_{Si}$  and/or divacancies for real applications, photonic crystal cavities (PCC) are used to tune the emission energy [4]. Our PCC design consists of a planar array of cylindrical holes approximately 220 nm wide in a slab of SiC, ~300-500 nm thin having an area  $50 \times 50 \mu m^2$ , similar to [4]. To maximize the PCC quality factor, the slab should have a large index of refraction difference on the top and bottom; i.e., an air gap is desired under the slab. To achieve this goal, we have identified four fabrication methods to create the PCC. One of these techniques is to use remote epitaxy as an innovative approach which entails growing epitaxial graphene on a SiC substrate by means of Si sublimation. Silicon carbide is then grown on a monolayer of graphene to the desired film thickness [5]. This thin SiC layer is then transferred, facilitated by the weak van der Waal forces at the graphene/SiC substrate interface, to a substrate more amenable to cavity fabrication. All four fabrication methods will be presented in detail.

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6:00pm **EM+2D+AN+MI+MP+NS-TuA-12 Investigation of Localized Electronic structures of PbSe Quantum Dot Superlattice on a Highly Oriented Pyrolytic Graphite (HOPG), Il Jo Kwak, S Ueda, University of California at San Diego; A Abelson, C Qian, M Law, University of California, Irvine; A Kummel, University of California at San Diego**

Lead-Chalcogenide quantum dots are of interest due to the facility of adjustment of their electrical and optical properties. Using a colloidal self-assembly technique, extended arrays of nanocrystal QDs superlattices can be generated. The quantum confinement within individual QDs in the superlattice is relaxed and delocalization of wave functions occurs due to coupling of the QDs. In the QD solids, bulk-like electronic bands with a bandwidth of 100~200 meV are expected to form which yield much higher carrier mobility and diffusion length compared to weakly-coupled QDs; however, the electronic properties of such highly ordered QD arrays are not fully understood. The local density of state of a highly ordered monolayer PdSe superlattice was investigated by low temperature scanning tunneling microscopy.

A monolayer of PbSe QDs was prepared using the Langmuir Schaefer deposition technique. First, oleate-capped PbSe QDs dispersed in hexane were drop casted onto diethylene glycol surface. After the hexane was evaporated, a (111) in-plane oriented polycrystalline FCC superlattice was formed on the diethylene glycol surface.  $NH_4SCN$  solution was applied onto the oleate-capped PbSe superlattice film. The injection of  $NH_4SCN$  initiates the ligand exchange and phase transformation from an FCC to a simple cubic structure superlattice. A monolayer QD superlattice was prepared on a HOPG substrate. Afterward, the HOPG sample was loaded into a commercial UHV scanning tunneling microscopy chamber with a base

pressure of  $1 \times 10^{-10}$  torr. The sample was annealed to remove hydrocarbons and ligands from the surface. The topography of the QDs was observed with a tungsten tip. The STM images were acquired in constant current mode.

STM imaging showed the PbSe QD monolayer had 4-fold symmetry with an average inter QD spacing of 7nm. It is also found the height fluctuation of the QDs was 1nm indicating size variation of the QDs and imperfect crystal structure of the superlattice. Scanning tunneling spectroscopy was performed to investigate the electronic structure of the PdSe QDs using a variable z-mode with an external lock-in amplifier in the bias range of -2 to 2V. Single site STS showed resonant peaks from molecular orbitals of QDs before the ligand exchange process; however, the peaks were not observed after the ligand exchange due to necking between the QDs in the superlattice. In addition, the size of band gap was decreased as increasing the number of nearest neighboring QDs due to necking between QDs. Layer 2 QDs showed more p-type behavior than layer 1 QDs possibly due to the band bending effect at the interface of HOPG and QD superlattice.

## Nanometer-scale Science and Technology Division Room 102B - Session NS+AM+MI+MN+SS+TR-TuA

### SPM – Probing and Manipulating Nanoscale Structures

**Moderators:** Renu Sharma, NIST Center for Nanoscale Science and Technology, Carl Ventrice, Jr., SUNY Polytechnic Institute

2:20pm **NS+AM+MI+MN+SS+TR-TuA-1 Building Artificial Quantum Matter with Dopant Atoms, Sven Rogge, University of New South Wales, Australia**  
**INVITED**

Atomic-scale engineering reached the level of control where single-atom devices can be reproducibly fabricated with high yield. This talk focuses on the progress of single dopant atom placement in the context of engineered quantum matter. Silicon offers a particularly interesting platform for single dopants because when isotopically purified it acts as a “semiconductor vacuum” for spins. This leads to extraordinary coherence that is used to realise donor atom based qubits. Spatially resolved tunnelling experiments reveal the spectrum and quantum state image of single atoms and tunnel coupled arrangements of atoms. These measurements grant access to the wavefunction of donors in the silicon lattice that makes it possible to pinpoint the dopants to their exact position in the lattice that is essential in the evaluation of engineered quantum matter. A first step towards engineered Hamiltonians for Fermionic systems in the form of atomic chains was taken where interacting dopants were employed to simulate a two-site Hubbard Hamiltonian at low effective temperatures with single-site resolution. Quasi-particle tunnelling maps of spin-resolved states with atomic resolution reveal interference processes from which the entanglement entropy and Hubbard interactions are quantified. We will present dopant based multi-electrode devices fabricated by the scanning probe hydrogen depassivation and decoration technique where the quantum state of the device can be manipulated and imaged in situ. The aim of this work is to build a two dimensional array of up to 30 spins in the solid state to implement complex highly correlated systems.

3:00pm **NS+AM+MI+MN+SS+TR-TuA-3 Scanning Tunneling Microscopy Study of Structure Control of a Nanocarbon Catalyst through a Surface-Activated coupling Reaction, Jeremy Schultz, P Whiteman, N Jiang, University of Illinois at Chicago**

In order to optimize nanocarbon materials for metal-free catalysis, the structure must be controlled and characterized at the nanoscale. One method for the bottom-up assembly of nanocarbon catalysts is through an Ullmann-type coupling reaction induced by a metal substrate, where a halide leaving group allows covalent intermolecular coupling. Scanning tunneling microscopy has been applied to a fundamental study of 3,6-dibromo-phenanthraquinone (DBPQ), a molecule selected for its catalytically active diketonic groups. Conjugated polymers formed from DBPQ have been found to be capable of catalyzing alkane oxidative dehydrogenation (ODH) reactions as well as nitrobenzene (NB) reduction reactions.

Different surfaces were investigated for their role in the surface-activated coupling reaction. Intact monomer molecules were found to self-assemble through hydrogen and halide interactions on Ag(100), resulting in well-packed molecular islands which impacted the organometallic structure ultimately formed after reaction. On Au(100), two competing intermediate dimers were observed resulting from a chiral covalent bond between base DBPQ molecules. Cis dimers were found to result in reaction products that

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became stuck as tetramers without the potential for further polymerization. Utilization of increasing coverage and a new surface identity that arose from the leaving Bromide resulted in selective formation of longer conjugated polymer chains composed of trans dimers. This study characterizes the ability of initial self-assembly and leaving groups to steer reaction dynamics and control the structure of a nanocarbon catalyst.

3:20pm **NS+AM+MI+MN+SS+TR-TuA-4 Detecting the Tip Shape Dependence of the Plasmonic Photon Emission under STM**, *Songbin Cui*, Pohang University of Science and Technology, Republic of Korea; *U Ham*, Institute for Basic Science (IBS), Republic of Korea; *T Kim*, Pohang University of Science and Technology, Republic of Korea

Photon signal can be enhanced significantly by modifying the plasmonic nanocavity. This enhancement becomes an important issue in super-resolution microscopy and high resolution spectroscopy, such as scanning tunneling microscopy (STM) electroluminescence [1], surface enhanced Raman spectroscopy, tip enhanced Raman spectroscopy [2], and so on. Low temperature STMs can allow us to achieve less than 1nm tip-sample gap stably. This gap-mode plasmonic nanocavity between an STM tip and surface realizes sub-molecular photon spectroscopy [1]. A few works demonstrated that light emission signal can be effectively enhanced by certain resonant plasmonic spectral peaks, which can be modified by tip indentation [2] and showed theoretically that the larger tip aperture causes a blue shift and the shaper apex curvature results in higher intensity in a photon spectrum [3]. However, the tip shape dependence of the plasmonic nanocavity remains unclear. In this work, we experimentally present the role of tip shape in surface plasmonic light emission. We have used Ag tips and a Ag(100) substrate, and photon signals have been measured from both side of the STM tip simultaneously. We dipped STM tips into the substrate with controlling the dipping depth and the lifting speed in order to change the tip shape, and then, the tip shape subsequently was checked through STM profiles. We found that changing small parts of tip apex (<3nm tip direction) can differ the photon spectrum significantly. Furthermore, the plasmonic photon emission from different direction from a STM tip could be quite different due to tip shape asymmetry. This finding can help us to tune the plasmonic photon emission spectra more efficiently.

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4:20pm **NS+AM+MI+MN+SS+TR-TuA-7 Advances in SPM Methods for Energy-relevant Materials**, *Marina Leite*, University of Maryland College Park

**INVITED**

The scientific understanding of nanoscale materials and devices is continuously growing ever since atomic force microscopy (AFM) has enabled us to image these systems at similar length scale. Specifically, there is a pressing need for functional imaging as energy-relevant technologies are becoming dominated by nano- and mesoscale constructs. In this presentation I will review my group's recent research discoveries based on new AFM methods to measure and determine how the electrical, chemical, and/or optical properties influence overall photovoltaic device behavior [1,2]. We realize novel functional imaging AFM-based methods to elucidate the driving forces for the dynamic response of the perovskites upon and post-illumination [3], and polycrystalline materials for solar cells [4,5]. We map nanoscale variations in open-circuit voltage  $V_{oc} > 300$  mV under 1-sun illumination, not revealed by conventional AFM tools. Using fast-KPFM (16 seconds/scan) while maintaining high spatial sensitivity, we map, in real-time, the dynamics of the  $V_{oc}$  in perovskite solar cells with spatial resolution  $< 100$  nm. Unexpectedly, we identify a 'residual  $V_{oc}$ ' post-illumination, attributed here to iodine ion migration, a process that takes place in a time scale of several minutes. We foresee our functional imaging tool to be implemented in the identification of stable perovskite compounds, ranging from lead-free and non-toxic alternatives to new options for tandem designs.

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5:00pm **NS+AM+MI+MN+SS+TR-TuA-9 Coherent Electrical Contact to Semiconducting Graphene Nanoribbon**, *Chuanxu Ma*, *L Liang*, Oak Ridge National Laboratory; *Z Xiao*, North Carolina State University; *A Puzetky*, *K Hong*, Oak Ridge National Laboratory; *W Lu*, *J Bernholc*, North Carolina State University; *A Li*, Oak Ridge National Laboratory

High quality electrical contact to low-dimensional semiconductor channel materials is the key to unlocking their unique electronic and optoelectronic properties for fundamental research and device applications. Inappropriate contacts create interfacial states that can pin the Fermi level and form a large Schottky barrier. For 2D transition metal dichalcogenides (TMDs), a route to a high-performance contact has recently been proposed by using a phase transition that converts a hexagonally packed semiconductor (2H) phase into a distorted octahedrally packed metallic (1T') phase. However, a similar approach is not available for 1D materials. Conceptually, an ideal contact would be a metal-semiconductor interface formed with native covalent bonds without introduction of any structural or electronic boundaries. Realization of such a seamless contact in 1D materials such as graphene nanoribbons (GNRs) requires atomically precise development of a heterostructure from well-defined atomic or molecular precursors.

Here we report on a successful approach for making seamless contacts in 1D materials through the formation of GNR staircase heterostructure. The coherent staircase is made of GNRs with widths varying from 7, 14, 21 and up to 56 carbon atoms. The graphitic heterostructures are synthesized by a surface-assisted self-assembly process with a single molecular precursor. While the 7-atom-wide GNR is a large-gap semiconductor, the conjugated wide GNRs are either quasi-metallic or small-gap semiconductors, similarly to the 2D metals. Our study, which combines STM and Raman measurements with DFT calculations, reveals that the heterointerface consists of native  $sp^2$  carbon bonds without localized interfacial states. Such a seamless heterostructure offers an optimal electrical contact to the wide-gap 1D semiconductor.

5:20pm **NS+AM+MI+MN+SS+TR-TuA-10 Visualizing Coordination Structures of Small Gas Molecules to Metallo-porphyrin on Au(111) Using Scanning Tunneling Microscopy**, *MinHui Chang*, Korea University, Republic of Korea; *Y Chang*, *N Kim*, Korea Advanced Institute of Science and Technology (KAIST); *U Jeon*, *H Kim*, Korea University, Republic of Korea; *Y Kim*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea; *S Kahng*, Korea University, Republic of Korea

Binding reaction between small molecules and metallo-porphyrins play crucial roles in functional processes of biological systems such as oxygen delivery, muscle contraction, and synaptic transmission. Their geometrical structures such as tilted binding of NO to metallo-porphyrin have been recently confirmed by high-resolution scanning tunneling microscopy (STM) images at the single molecule level. Here, we present STM images of further systems, di, tri, and quadra-atomic small molecules, coordinated to metallo-porphyrin on Au(111). We observed square ring, rectangular ring, and center-bright structures for three different small molecules. With the help of density functional theory (DFT) calculations, we reproduce the experimental STM images in the simulated images. Thus, our study shows that geometric structures of small molecules coordinated to metallo-porphyrins can be probed with STM combined with DFT methods.

5:40pm **NS+AM+MI+MN+SS+TR-TuA-11 Effects of Dimensionality on the Reactivity of Carboxylic-Acid-Terminated Monolayers**, *Dominic Goronzy*<sup>1</sup>, *E Avery*, *N Gallup*, University of California, Los Angeles; *J Staněk*, *J Macháček*, *T Baše*, Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic; *K Houk*, Chemistry and Biochemistry, University of California, Los Angeles; *P Weiss*, University of California at Los Angeles

Self-assembled monolayers (SAMs) are an advantageous construct to modify surfaces and thereby to tune material properties. Three major determinants affect the spontaneous assembly of monolayers: the substrate-monolayer interface, the interactions between the adsorbate molecules, and the monolayer-environment interface. By controlling the exposed functional groups in the SAM, this interface between the surface and the environment can be probed and manipulated. To examine how exposed carboxyl functional groups modulate the properties of SAMs, we have tethered thiol-functionalized carborane cage molecules with and without a carboxyl group to Au{111} surfaces. Using scanning tunneling microscopy (STM), visualization of the *para*-functionalized carboxylic acid carboranethiol was only possible in the form of a mixed monolayer of functionalized and unfunctionalized molecules. These experiments demonstrated that the functionalized molecule adopted the same nearest-

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

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neighbor spacings on the surface as the unfunctionalized *para*-carboranethiol, approximately 7.2 Å. By comparison, in our study of carboranethiols with a carboxylic acid functional group attached in the *meta* position, we have been able to image pure functionalized monolayers *via* STM with these molecules showing nearest-neighbor spacings of 8.4 Å, approximately 1 Å larger than the unfunctionalized carboranethiols. Studies of two different isomers of *meta*-carboranethiolate carboxylic acids yielded similar results. In order to examine the effects of changing dimensionality from a 3D solvent system to a 2D thin film, we applied contact angle titration to probe the reactivity of the carboxylic acid head group. These experiments demonstrated a substantial shift from a  $pK_a$  of 3-3.2 in solution (3D) to an apparent surface  $pK_a$  of approximately 6.5-7.5. Density functional theory calculations were performed to test the effects of desolvation by 2D confinement and showed shifts in  $pK_a$  consistent with the experimental data. Together, these results support the concept that the confinement in a 2D environment induces significant changes in reactivity in the molecules, as evidenced by the  $pK_a$  shift. Thus, precise positioning of functional groups in SAMs is an important tool to investigate the behavior of surface-confined molecules. This system may also serve as a model to explore dimensionality effects in biological systems, including proteins confined within membranes.

## Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic

Room 202A - Session PC+AS+BI+EM+NS+PB+SS-TuA

### Progress in Industrial Processes and Characterization of Interfaces and Gas-Solid Interfacial Processes and Characterization

**Moderators:** Jeffrey Fenton, Medtronic, Inc., Xiao-Ying Yu, Pacific Northwest National Laboratory

2:20pm **PC+AS+BI+EM+NS+PB+SS-TuA-1** Near Ambient Pressure XPS as a Standard Tool for True Non-destructive High-throughput Surface Chemical Analysis in Industrial Applications, *Andreas Thissen, P Dietrich, SPECS Surface Nano Analysis GmbH, Germany; M Kjaervik, W Unger, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany* **INVITED**

Since many decades X-ray excited Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA) is a well-accepted standard method for non-destructive chemical analysis of solid surfaces. Over the last years it has been possible to develop XPS instrumentation, that can work far beyond the standard conditions of high or ultrahigh vacuum: Near Ambient Pressure (NAP)-XPS, or ESCA under environmental conditions has become a method, that enters the field of standard surface chemical analysis and thus also the industrial sector. The main reason for this is the extremely fast solid surface analysis of any (degassing or non-degassing) material. Furthermore the environmental conditions around the sample avoid strong surface degradation due to vacuum or photon stimulated desorption. Even during the analysis the sample stays under its equilibrium conditions. Last, but not least the surrounding gas pressures of a couple of mbar acts as built-in charge neutralization on any type of material. This Environmental Charge Compensation (ECC) also decreases the negative influences of the characterization on the sample constitution. All this considered, NAP-XPS is capable of true non-destructive high throughput analysis of sample surfaces. The influence of the ambient conditions on quantification in XPS will be demonstrated and discussed.

After a short summary of the relevant development steps in NAP-XPS instrumentation over the last forty years, this presentation summarizes results of surface chemical analysis on insulating polymer samples, showing the spectroscopic resolution for C1s, F1s and O1s emission lines as a comparison for PET and PTFE. Using this, the application of ECC to bulk insulators (polymeric materials, ceramics), food samples, pharmaceuticals, and different biological materials is demonstrated. The unique ability to measure liquids, like water or aqueous solutions allow for studies of drying processes of liquid containing materials, like paper or absorber materials and finally also opens the field to medical applications, especially to studies of drug uptake into gram-negative bacteria embedded in biofilms.

The last part summarizes methods to analyze materials and device under working conditions. As examples reduction and reoxidation of catalytically active compounds and operando electrochemistry will be presented. An outlook to future industrial applications will be given.

**ACKNOWLEDGEMENTS:** This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

3:00pm **PC+AS+BI+EM+NS+PB+SS-TuA-3** Surface Modifications in the Medical Device Field – Understanding of Methods to Control Adhesion and Reactions That Materials Undergo, *Jeffrey Fenton, B Theilacker, A Belu, B Tischendorf, Medtronic*

**INVITED**

Advances in materials chemistry have increased the need for deep understanding of process-material interactions and their role in device or component longevity. In the medical device industry advances are due in part to operating in a federally regulated environment where it may be necessary to understand not only what is the surface chemistry, but how various chemistries interact with the body, what is clean, or where does a foreign material originate. This presentation will highlight case studies where microscopy and surface characterization techniques were successfully applied to help further understand materials performance and interactions with the body.

Polymers used in the medical industry often undergo numerous clinical trials, laboratory testing, and development to understand the body and polymer interactions. The interactions these materials often undergo may potentially be at odds with the bulk material properties. For example, it may be desirable to modify surface properties of PTFE for polymer adhesion or modify a surface chemistry to improve bio compatibility. Methods of polymer surface modification will be presented that either enable or hinder the adhesion of a material to the surface.

Lithium ions generated during battery discharge may undergo interactions with components in or near the battery forming chemistries that may degrade battery performance or material stability. For example, lithium ions are known to interact with silica containing glass to form lithium silicide. The formation of these silicides can degrade the hermetic seal of feedthroughs. One method of studying these interactions is in-situ interfacial reactions characterization. This facile method of generating ions in-situ can be leveraged to understand what reactions may occur at a substrate surface.

The application of surface characterization techniques such as X-ray photoelectron spectroscopy (XPS), Time of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS), and Scanning Electron Microscopy (SEM) provide unique insights into surface modifications and can help ensure the reliability of medical devices. These techniques support the development and manufacturing of Medtronic products such as packing and perfusion devices to improve processing conditions, understand failure modes, and surface-tissue interactions.

4:20pm **PC+AS+BI+EM+NS+PB+SS-TuA-7** Ambient Pressure X-Ray Photoelectron Spectroscopy Studies of Catalytically Active Interfaces using Electron Transparent Graphene Membranes, *R Mom, L Frevel, Fritz-Haber Institute of the Max Planck Society, Germany; J Velasco-Velez, MPI CEC Mülheim, Germany; T Jones, M Plodinec, Fritz-Haber Institute of the Max Planck Society, Germany; R Schlögl, MPI CEC Mülheim, Germany; Axel Knop-Gericke, Fritz Haber Institute of the Max Planck Society, Germany* **INVITED**

Green production of hydrogen will be an important building block in the transition to a carbon-balanced economy and could be realized by electrolytic water splitting powered by cheap renewable energy sources. Water electrolysis is currently limited by the oxygen evolution reaction (OER) and development of the associated catalysts is proceeding slowly, mainly due to missing descriptors for activity and stability of working OER catalysts. Herein, we contribute to that emerging field with in situ XPS and NEXAFS on iridium anodes. In our in situ cell the catalyst is probed through a graphene layer, which traps an electrolyte layer around the catalyst and provides electrical contact for separated iridium nanoparticles. In this way we enhance spectroscopic signal from the active surface relative to the bulk of the catalyst and reduce mass transport problems. In taking advantage of these benefits, we found that the two well-known oxidation waves occurring before the OER onset are connected to the development of two different types of electron deficient oxygen species, which are bound to one ( $\mu_1$ ) or two ( $\mu_2$ ) iridium atoms. It appears that oxygen is not only a "non-innocent ligand", but rather a protagonist in the catalysis of the OER.

During the electrochemical reduction of oxygen, platinum catalysts are often (partially) oxidized. While these platinum oxides are thought to play a crucial role in fuel cell degradation, their nature remains unclear. We studied the electrochemical oxidation of Pt nanoparticles using in situ XPS. By sandwiching the particles between a graphene sheet and a proton

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exchange membrane that is wetted from the rear, a confined electrolyte layer was formed, allowing us to probe the catalyst under wet electrochemical conditions. We show that the behavior at the onset of Pt oxidation is influenced by the choice of proton exchange membrane, yet universally involves PtO<sub>2</sub> formation. The oxidation process is fast: even bulk oxide growth occurs on the sub-minute timescale. Thus, our observations indicate that PtO<sub>2</sub> may take part in the transient processes that dominate Pt electrode degradation.

**5:00pm PC+AS+BI+EM+NS+PB+SS-TuA-9 The Influence of Density and Chemical Bonding on Atomic and Molecular Structures of Alcohols, Water and Oxides, Gabar A. Somorjai, University of California at Berkeley** INVITED

Alcohol oxidation reaction over platinum nanoparticles with size ranging from 2 to 8 nm deposited on mesoporous silica MCF-17 was studied in the gas and liquid phases. Among methanol, ethanol, 2-propanol, and 2-butanol oxidations, the turnover frequency increased as the nanoparticle size became large in both reaction phases. The activation energy in the gas phase was higher than that in the liquid phase. Water co-adsorption decreased the turnover rate of all the gas and liquid phase oxidations except for the gas-phase 2-butanol case, while certain amount of water promoted 2-propanol oxidation in the liquid phase. Sum frequency generation vibrational spectroscopy (SFG) study and DFT calculation revealed that the alcohol molecules pack horizontally on the metal surface in low concentration and stand up in high concentration, which affects the dissociation of  $\beta$ -hydrogen of the alcohol as the critical step in alcohol oxidation.

Ice surfaces have water layers with thickness ranging from one monolayer at 100K to 30 layers of 273K. At the interfaces of two ice cubes, ice layers grow at the disappearing water interfaces (regelation). SFG studies of water surfaces show three peaks in the vibrational spectrum; "free OH", liquid like hydrogen bonded water, with half bilayer termination, and ice-like water, with bilayer termination, with more hydrogen bonds.

Most nanocatalysts are composed of highly dispersed transition metal nanoparticles on oxides. The interface between the metal nanoparticles and the oxides plays a crucial role in determining the catalytic performance of nanocatalysts. Due to non-adiabatic electronic excitation, energetic electrons in metals can be generated during exothermic chemical processes. The energy barrier formed at the metal-oxide interfaces leads to the irreversible transport of energetic, or hot, electrons. The dopants and impurities present on the oxides can generate additional charge carriers or oxygen vacancies that affect the catalytic activity. The accumulations or depletion of hot electrons on the metal nanoparticles, in turn, can also influence the catalytic reactions. In this talk, we outline recent studies of the role of metal oxide interfaces and characteristics of fast charge transfer between metals and oxides that lead to ionization of molecules at the interface. The molecular ions produce so-called acid-base reactions. The electronic configuration of metal-oxide nanocatalysts during catalytic reactions will be introduced and its influence on heterogeneous catalysis will be outlined.

**5:40pm PC+AS+BI+EM+NS+PB+SS-TuA-11 Atomic Scale Observation of Oxidation and Reduction of Palladium Surface, Takehiro Tamaoka, H Yoshida, S Takeda, Osaka University, Japan**

Reaction processes on metal surfaces under gas environment have been investigated in various research fields such as catalysis, gas sensing, and many more. Palladium is a well-known material which is used for hydrogen storage, hydrogen sensing, and exhaust catalysis. Therefore, the phase transition of palladium in hydrogen or oxygen has been extensively investigated by means of environmental transmission electron microscopy (ETEM). However, the oxidation and reduction process of palladium surface at the atomic scale remain poorly understood.

Here, we investigated the surface structure of a wedge-shaped palladium specimen in both hydrogen and oxygen by means of in-situ atomic resolution ETEM. Under ambient condition the surface of palladium is oxidized by several nanometers. After introducing hydrogen (100 Pa) in ETEM, the native oxide layer (PdO) was reduced to metallic fcc palladium even at room temperature. After exposure and exhaustion of hydrogen, we introduced oxygen (100 Pa) in ETEM. The palladium oxide was reproduced and the ETEM results show that the oxidation started from step edges and terraces and proceeded until the palladium surface was completely covered by the palladium oxide.

We also show that oxidation of palladium is dependent on the history of hydrogen exposure. When the duration of hydrogen exposure was over 90 min., we found that the surface was not oxidized. This was not due to bulk hydrogenation as demonstrated by our electron energy loss spectroscopy  
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(EELS) results. We performed similar studies for the surface of platinum in oxygen after prolonged hydrogen exposure. However in platinum, the oxidation of the surface was not suppressed. This suggests that the process for suppression of oxidation, after prolonged hydrogen exposure, exists for palladium and not for platinum.

From these results, we hypothesize possible processes that explain how the prolonged hydrogen exposure suppresses the oxidation of palladium surface. We will also present atomic-scale in-situ movies on the surface dynamics in palladium and platinum in various processing.

**6:00pm PC+AS+BI+EM+NS+PB+SS-TuA-12 Polymorphism of Hydrogen-Bonded Clusters at the Vacuum-Solid Interface, Angela Silski, J Petersen, University of Notre Dame; R Brown, Clarkson University; S Corcelli, S Kandel, University of Notre Dame**

Molecular self-assembly is an attractive bottom-up approach to nanostructure fabrication. Using molecules as building blocks and carefully tuning the non-covalent intermolecular interactions, unique nanostructured architectures can be designed. Given the structure/function relationship on the nano- and meso-scale, this bottom-up approach to designing new architectures is critical in the careful design of novel materials with desired chemical properties. In this study, the role of hydrogen bond donor/acceptor position in metastable cluster formation is explored using scanning tunneling microscopy (STM) with complementary density functional theory (DFT) calculations. We observe a metastable cyclic pentamer for isatin (1H-indole-2,3-dione) with DFT providing support for a cyclic structure stabilized by both NH...O and CH...O hydrogen bonds between neighboring molecules. The CH...O hydrogen bond is made between the 7-position proton acting as the hydrogen bond donor and the 3-position carbonyl as the hydrogen bond acceptor, and calculations indicate that the isatin pentamer structure is 12 kJ/mol more stable than the dimer on the per molecule basis. To probe the importance of the CH...O hydrogen bond in stabilizing the isatin pentamer, we compare to isatin derivatives: we replace the 3-position carbonyl with a methyl group (3-methyl 2-oxindole), the 7-position proton with a fluorine (7-fluoroisatin), systematically move the location of the hydrogen bond donor/acceptor by one position, (phthalimide), and remove of the primary hydrogen bond donor (1,2-indandione and 1,3-indandione). We show that cyclic pentamer formation is either altered or precluded as a result of these substitutions. Additionally, the importance of CH...O bonding in forming isatin pentamers is supported by electrospray ionization mass spectrometry (ESI-MS) measurements, which include a magic-number isatin pentamer peak, whereas the derivative molecules show little clustering under the same conditions. This work is significant in understanding the role that the position of the hydrogen bond donor/acceptor groups has on the resulting 2D supramolecular assemblies.

## Plasma Science and Technology Division Room 104A - Session PS+EM+NS+SS-TuA

### Plasma Processing of Challenging Materials - II

**Moderators:** Michael Gordon, University of California at Santa Barbara, Wei Tian, Applied Materials Inc.

**2:20pm PS+EM+NS+SS-TuA-1 Self-limiting Growth of III-nitride Materials via Hollow-cathode Plasma-ALD: Structural and Chemical Analysis, Necmi Biyikli, A Mohammad, D Shukla, University of Connecticut** INVITED

Plasma-assisted/enhanced atomic layer deposition (PALD) provides an alternative route for the low-temperature synthesis of III-nitride thin films with sub-monolayer precision thickness control, ultimate three-dimensional conformality, and large-area uniformity. On the other hand, PALD synthesis of AlN, GaN, and InN films required relatively long plasma co-reactant exposure durations (40 - 120 sec) to achieve self-limiting surface saturation with minimal carbon impurities which directly correlates the effectiveness of the ligand-removal process. During such extensive plasma half-cycles, the plasma source itself is exposed to elevated temperatures and along with energetic hydrogen radicals, which resulted in etching of conventional quartz-based inductively coupled plasma (ICP) sources. We have mitigated this problem by using a stainless-steel based capacitively-coupled hollow-cathode plasma (HCP) source, which reduced the oxygen impurity levels at least two orders of magnitude in GaN films while increasing the average film grain/crystallite size of AlN films by one order of magnitude.

Using HCP-assisted ALD (HCP-ALD), we have grown the entire III-nitride wide bandgap semiconductor family (AlN, GaN, InN) at  $\leq 200^\circ\text{C}$  substrate

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temperatures with single-phase hexagonal poly-crystalline material quality. However, there is still plenty of room and need for improvement in material properties before we can use these layers as active device layers. A careful systematic study needs to be carried out to achieve device quality III-nitride films via HCP-ALD. In this talk, we will present an overview of our HCP-ALD efforts including our recent materials characterization results obtained with a custom-design HCP-ALD reactor. A particular focus will be devoted to the structural and chemical properties of the III-nitride films and how they correlate with reactor parameters and plasma conditions.

3:00pm **PS+EM+NS+SS-TuA-3 Electrostatic Charge of Solution-droplet in Plasma-coupled Micro Reactor**, *Tae Hwan Kim, S Lee*, National Fusion Research Institute, Republic of Korea

Plasma-liquid interaction research has increased because of emerging technological applications such as material synthesis, plasma bio-applications, environmental applications, and agriculture/food applications. Recently, an important scientific breakthrough in the understanding of the liquid reaction at the plasma-liquid interface that an electron transfer reaction at the plasma-liquid interface that leads to electrochemical reactions, which is referred to as the plasma electrochemical reaction [1]. Further evidence of plasma electron reaction (PER) was observed that the electrons in plasma can be solvated in a plasma electrochemical system [2].

In this talk, we present a new reaction pathway in which plasma-liquid interaction can cause an electrostatic charge in a liquid and the electrostatically charged solution can produce an electrochemical reaction. The experiments were performed with our newly designed plasma-coupled-microreactor (PCM), which can control the ambient gas and initiate a rapid plasma electrochemical reaction. Helium(He)-droplets and liquid-droplets were formed, and microplasma-droplets were ignited by dielectric barrier discharge (DBD). The generated microplasma-droplet can induce not only PER but also an electrostatic charge in a solution. The charge of the solution by microplasma-droplet and liquid-droplet interaction can be affected by the type and amount of stabilizer, the acidity of the solution, and the length of the electrodes used to form microplasma-droplets.

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[2] P. Rumbach, David M. Bartels, R. Mohan Sankaran, David B. Go, The solvation of electrons by an atmospheric-pressure plasma. *Nat. Commun.* 6, 7248 (2015).

3:20pm **PS+EM+NS+SS-TuA-4 Surfactant-free and Stable Colloidal Metal Oxide Ultra-small Quantum Dots via Plasma-liquid Electrochemistry**, *Dhillibabu Padmanaban, D Carolan, R McGlynn, T Velusamy, P Maguire, D Mariotti*, Nanotechnology & Integrated Bio-Engineering Centre, Ulster University, UK

Metal oxides are materials of great importance and interest with exceptional chemical stability, tunable optical and electrical properties and, importantly, meeting cost and environmental requirements for a sustainable future. For these reasons metal oxides nanoparticles are being investigated for a very wide range of applications that include energy harvesting and solar conversion and for exploiting nanoscale effects. However, due to synthesis challenges, the properties of ultra-small and quantum confined metal oxide nanoparticles, or quantum dots (QDs), are still very little understood while expected to offer exciting opportunities. Here we demonstrate that the synthesis of metal oxide QDs can be achieved by plasma-liquid electrochemistry with exceptional control of the size distribution even for particles well below 2 nm in diameter. Plasma-induced chemistry initiated at the plasma-liquid interface allows for rapid and simple production of highly stable colloidal suspension in ethanol of surfactant free metal oxide QDs, where a solid metal foil acts as the metal precursor. We provide an overview of these capabilities for a range of metal oxides that include Cu, Ni, Co, Mo and Zn oxides. We then study in detail the synthesis mechanisms leading to cupric oxide (CuO) QDs providing a range of experimental evidence that clarifies chemical reaction pathways due to the plasma interacting with ethanol. For a better understanding of the plasma chemistry, the process was also studied with different electrodes so to assess the impact of QDs formation in the overall plasma-ethanol chemistry. We have carried out extensive material characterization for the QDs and we have also analysed liquid products at different conditions by Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, nuclear magnetic resonance, mass-spectroscopy etc. Our work points at the role of different species in the synthesis of QDs. We

believe that some of these chemical pathways may be general and applicable to the formation of other metal oxide QDs, however in some cases (e.g. for Mo-oxide) we expect some deviations. Overall our work discloses important general aspects of plasma-liquid interactions, in particular when ethanol is used. The study of the properties of our metal-oxide QDs uncovers quantum confinement effects that can become particularly useful in many application and suggest exciting opportunities in the control of defects and achieving phases that are difficult to produce with other methods.

4:20pm **PS+EM+NS+SS-TuA-7 From Organometallic Precursors to Bimetallic Nanocatalysts using Atmospheric-pressure Plasma Processes**, *Joffrey Baneton, J Mertens, M Smiljanic, S Cauchies, T Segato*, Université Libre de Bruxelles, Belgium; *Y Busby*, Université de Namur, Belgium; *G Caldarella*, Université de Liège, Belgium; *V Debaille, S Godet*, Université Libre de Bruxelles, Belgium; *J Pireaux*, Université de Namur, Belgium; *N Job*, Université de Liège, Belgium; *M Gordon*, University of California at Santa Barbara; *M Sankaran*, Case Western Reserve University; *F Reniers*, Université Libre de Bruxelles, Belgium

Developing new technologies to produce energy while respecting the environment is one of the important challenges in materials science. One of the possible routes is the use of hydrogen fuel cells. Unfortunately, some limitations remain such as the electrocatalysis of the reduction of dioxygen which requires a rare and expensive metal: platinum [1]. Therefore, minimizing its amount at the cathode while maximizing its accessibility, electroactivity and stability constitutes one of the main goal of current research. An interesting way consists in the synthesis of platinum-based alloys. Indeed, it is well known in the literature that combining two metals leads to the production of durable materials with higher activity [2].

Different routes can lead to the formation of bimetallic nanostructures including wet-chemistry, ultrasound processes or thermal evaporation. In this catalogue of methods, atmospheric-pressure plasma techniques are very attractive due to their versatility, rapidity and ease of use. In the present research, two different kinds of reactors, a microplasma device [3] and radio-frequency plasma torch [4], have been used to study the synthesis of bimetallic nanoparticles from acetylacetonate precursors. A complete chemical and morphological characterization is provided thanks to the combined use of X-ray photoelectron spectroscopy, transmission electron microscopy, UV-visible spectroscopy and X-ray crystallography.

Different experimental parameters can play a crucial role is the reduction process of the organometallic precursors. For example, concerning the microplasma system, the initial concentrations have a direct influence on the size distribution and agglomeration while, concerning the RF plasma torch treatment, the nature of the plasma gas mixture can limit the production of nanoparticles or favor their anchoring at the surface of a carbon support [5]. After optimization of the processes, electrochemical measurements were conducted to evaluate their activity, stability and performances as catalysts for hydrogen fuel cells.

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4:40pm **PS+EM+NS+SS-TuA-8 Synthesis of Hydrogenated Amorphous Carbon Nanoparticles using High-Pressure CH<sub>4</sub>+Ar Plasmas and Their Deposition**, *Kazunori Koga, S Hwang, K Kamatani, N Itagaki*, Kyushu University, Japan; *T Nakatani*, Okayama University of Science, Japan; *M Shiratani*, Kyushu University, Japan

Nanostructure fabrication such as nanoparticles through bottom-up processes is important in nanotechnologies due to their size-related properties [1]. Plasma is a powerful tool to produce nanoparticles. To control their size, pulsed discharge plasmas are commonly employed, but the plasmas have the limitation of the throughput. To realize continuous production, we have developed a multi-hollow discharge plasma chemical vapor deposition (MHDP-CVD) method. We have succeeded in producing crystalline Si nanoparticles of 2 nm in size using hydrogen diluted silane plasmas [2, 3]. Here we applied the method to synthesis carbon nanoparticles. The experiments are carried out by CH<sub>4</sub>+Ar MHDP-CVD. CH<sub>4</sub> and Ar were injected into the reactor, flowed through hollows of 5 mm in diameter in the electrode. The gas flow rate ratio of CH<sub>4</sub> and Ar was 1:6.



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The total gas flow rate was 10 to 200 sccm . The pressure was kept at 2 Torr. Discharges were generated in hollows by applying rf power of 40 W at 13.56 MHz. Nanoparticles are nucleated and grow in the discharges. They are transported outside of the discharges by the fast gas flow and the growth of the nanoparticles are stopped. They deposited on TEM mesh grids set on the substrate holder 50 mm far from the electrode. From TEM measurements, spherical nanoparticles were deposited on the grid. The mean size decreases from 270 nm for 10 sccm to 20 nm for 120 sccm . The gas residence time for 120 sccm is 1/12 of that for 10 sccm . The size for 120 sccm is 1/13.5 of that for 10 sccm . The results indicate that the size of carbon nanoparticles are controlled by gas residence time of nanoparticles in plasmas. Above 125 sccm, No nanoparticle is observed on the TEM mesh. It suggests that deposition of nanoparticles depends on gas flow velocity and direction on the substrate.

[1] M. Shiratani, et al., J. Phys. D 44 (2011) 174038.

[2] T. Takeya, et al., Thin Solid Films 506 (2006) 288.

[3] K. Koga et al., ECS Transactions 77 (2017) 17.

5:00pm **PS+EM+NS+SS-TuA-9 Antimony-doped Tin Oxide Nanocrystals Synthesized by Low Temperature Plasma**, *Qinyi Chen, E Thimsen*, Washington University in St. Louis

For electrochemical applications, metal-oxide materials are attractive as electrodes for reactions occurring at positive potentials in the presence of water. Often, these metal-oxide materials function as an electrically-conductive support for a noble metal catalyst, and therefore must have very high specific surface area. Among conductive metal-oxide materials, antimony-doped tin oxide (ATO) stands out with its combination of: 1) high chemical stability over a wide range of pH values and reduction potentials, 2) high electrical conductivity, and 3) abundant constituent elements. Synthesis of ATO nanocrystals has been developed in liquid phase using sol-gel and colloidal methods. However, post-synthesis heat treatments are required to activate the electron donors and increase the conductivity of ATO nanocrystal assemblies prepared using liquid-phase techniques, which may adversely affect the surface area and pore structure of the material. In this work, we report on our efforts to synthesize monodispersed, conductive ATO nanocrystals through a single-step low temperature plasma growth method without any post treatments. Precursor vapors of tin and antimony were fed into a radiofrequency, flow-through low temperature plasma reactor. The precursor vapors reacted to nucleate ATO nanocrystals. Thin films comprised of ATO nanocrystals were then immediately deposited by supersonic impact deposition of the aerosol resulting from plasma synthesis. The resulting materials were characterized by a variety of methods to determine film thickness, porosity, nanocrystal size, and elemental composition. Local electron concentration and mobility within the nanocrystals were assessed by Fourier-transform infrared absorption spectroscopy. Hall effect was used to characterize longitudinal electrical transport in the film. The nanocrystal growth mechanism in the plasma will be discussed with a focus on antimony dopant incorporation. The effects of nanocrystal size on the transport properties of ATO thin films will be presented.

5:20pm **PS+EM+NS+SS-TuA-10 Femtosecond Laser Texturing of Plasma-immersed Ti to Create TiN**, *Chisung Ahn, E Barlaz, D Ruzic*, University of Illinois at Urbana-Champaign

Pulsed femtosecond lasers have been used as a functionalization method for metal surfaces due to their ability to produce nanostructures uniformly with easily controlled user inputs such as spot size and exposure repetition. Laser assisted nitriding of Ti in ambient nitrogen has previously been demonstrated in our group to significantly reduce native oxides. A major challenge to the current process is the limited ability of the laser to produce nitrogen radicals.

In this study, we investigate the effects of increased nitrogen radical concentration on surface topography and chemical composition for textured Ti metal. A secondary DC plasma is generated along the path length of the laser close to the sample surface in ambient nitrogen and under vacuum. The surface topography and chemical compositions of the resultant Ti coupons are analyzed by SEM and XPS respectively. Changes to hydrophilicity are quantified using contact angle measurements.

5:40pm **PS+EM+NS+SS-TuA-11 Modeling Chemical Reactions in Contact Glow Discharge Electrolysis**, *Bocong Zheng, M Shrestha, K Wang, T Schuelke, Q Fan*, Michigan State University

Contact glow discharge electrolysis is becoming attractive for nanomaterials manufacturing and surface engineering. In this discharge electrolysis, an electrode is submerged in a liquid electrolyte and a plasma

is formed in a vapor layer around the electrode. The process combines the characteristics of electrolysis and plasma discharges, creating high-energy-density plasmas that lead to intensive physical processes and chemical reactions on the working electrode. The authors have found that the physical processes and the chemical reactions could be decoupled under certain conditions. In that case, a textured electrode surface could be created through a chemical-reaction-dominated process instead of an irregular porous surface produced by the physical-reaction-dominated interactions. The mechanisms are not clearly understood yet. This study aims to elucidate the plasma characteristics and the chemical reactions in contact glow plasma electrolysis. A plasma fluid model is established to predict the discharge process with constraint conditions obtained from the experiments. The modeling reveals that the plasma is highly electronegative, and the dominant neutral species are H<sub>2</sub> and O<sub>2</sub> dissociated from water vapor. The formation of textured surface is attributed to the anisotropic chemical etching by the reactive species generated in the plasmas.

6:00pm **PS+EM+NS+SS-TuA-12 Effects of Light Ion Beam Irradiation in Plasma Etching Processes**, *Kazuhiro Karahashi, T Ito, H Li, M Isobe, K Mizotani, S Shigeno*, Osaka University, Japan; *M Fukasawa, A Hirata, T Tatsumi*, Sony Semiconductor Solutions Corporation, Japan; *S Hamaguchi*, Osaka University, Japan

Gases containing hydrogen are widely used in microfabrication processes of electronic devices using plasma etching. For example, HBr gas is used for silicon etching, hydrofluorocarbon gases are used for silicon oxide etching, and Hydrocarbon-based non-corrosive gases are used for transparent conducting oxides etching. Unlike other atoms, hydrogen is lighter in weight, smaller in atomic radius, and chemically reactive, so it has various effects in the etching process. In order to precisely control the etching reaction and realize nanometer order microfabrication processes, it is necessary to clarify the effect of hydrogen. In this study, by comparing various effects on etching processes between hydrogen and helium incident ions using molecular dynamics (MD) simulation and ion beam experiments, physical and chemical effects by such light ion injection on etching processes were evaluated.

We have shown in this study based on MD simulation and ion beam experiments that, when a Si surface exposed to an O radical flux is simultaneously irradiated by an H<sup>+</sup> or He<sup>+</sup> ion beam, diffusion of oxygen atoms into the Si film is promoted. Since the enhanced diffusion occurs in a similar manner in both cases of H<sup>+</sup> and He<sup>+</sup> ion injections, it is clear that the enhanced diffusion is essentially caused by knock-on effects by incident light ions. On the other hand, in the case of etching of ZnO, which is an ionic crystal, our beam experiments have shown that its crystal size decreases by light ion irradiation using in-plane X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) measurements. The reduction of grain sizes seems correlated with the reduction of the physical sputtering yield of the ZnO film.

The results above show the following two physical effects by irradiation of a substrate with light ions such as H<sup>+</sup> and He<sup>+</sup>: 1) enhancement of diffusion of heavy atoms deposited on the substrate surface into it's the bulk of the film and 2) decrease of grain sized of ionic crystalline substrate due to amorphization and recrystallization. The decrease of grain sizes, which induce the increase in grain boundary areas may contribute to an increase in sputtering yield of the substrate.

## Reconfigurable Materials and Devices for Neuromorphic Computing Focus Topic

Room 203A - Session RM+EM+NS-TuA

### IoT Session: Reconfigurable Materials and Devices for Neuromorphic Computing

**Moderators:** Gina Adam, National Institute for R&D in Microtechnologies (IMT Bucharest), Brian Hoskins, National Institute of Standards and Technology (NIST)

2:20pm **RM+EM+NS-TuA-1 Non-volatile Memories for Neuromorphic Computing**, *Alec Talin*, Sandia National Laboratories **INVITED**

Inspired by the efficiency of the brain, CMOS-based neural architectures and memristors are being developed for pattern recognition and machine learning. However, the volatility, design complexity and high supply voltages for CMOS architectures, and the stochastic and energy-costly switching of memristors complicate the path to achieve the interconnectivity, information density, and energy efficiency of the brain

# Tuesday Afternoon, October 23, 2018

using either approach. In my talk, I will review the latest advances in neuromorphic computing architectures based on deep neural networks implemented using CMOS and memristors and describe the challenges in achieving both high accuracy and energy efficiency using these devices. I will then discuss an alternative approach based on the non-volatile redox memory (NVRM): a device with a resistance switching mechanism fundamentally different from existing memristors, involving the reversible, electrochemical reduction/oxidation of a material to tune its electronic conductivity. The first type of NVRM that I will describe is based upon the intercalation of Li-ion dopants into a channel of  $\text{Li}_{1-x}\text{CoO}_2$ . This Li-ion synaptic transistor for analog computing (LISTA) switches at low voltage (mVs) and energy, displays hundreds of distinct, non-volatile conductance states within a 1V range, and achieves high classification accuracy when implemented in neural network simulations<sup>1</sup>. The second type of NVRM I will describe operates on a similar principle but is based on the polymer system PEDOT:PSS, and which we call the electrochemical neuromorphic organic device (ENODE)<sup>2</sup>. Plastic ENODEs are fabricated on flexible substrates enabling the integration of neuromorphic functionality in stretchable electronic systems. Mechanical flexibility makes ENODEs compatible with three-dimensional architectures, opening a path towards extreme interconnectivity comparable to the human brain.

- 1) E. J. Fuller et al., *Advanced Materials* 29, 1604310 (2017).
- (2) Y. B. van de Burgt et al., *Nature Materials* 16, 414 (2017).
- (3) S. Agarwal et al., *IEEE 2017 Symposium on VLSI Technology Digest of Technical Papers*, DOI: 10.23919/VLSIT.2017.7998164.

## 3:00pm **RM+EM+NS-TuA-3 Anionic and Protonic Transfer Materials for ReRAM and Neuromorphic Computing, Jennifer Rupp, Massachusetts Institute of Technology** **INVITED**

The next generation of information memories and neuromorphic computer logics in electronics rely largely on solving fundamental questions of mass and charge transport of oxygen ionic defects in materials and their structures. Here, understanding the defect kinetics in the solid state material building blocks and their interfaces with respect to lattice, charge carrier types and interfacial strains are the prerequisite to design new material properties beyond classic doping. Through this presentation basic theory<sup>1</sup> and model experiments for solid state oxides their impedances and memristance<sup>2</sup>, electro-chemo-mechanics and lattice strain<sup>3-5</sup> modulations is being discussed as a new route for tuning material and properties in ionic conducting oxide film structures up to new device prototypes based on resistive switching. Central are the making of new oxide film materials components, and manipulation of the charge carrier transfer and defect chemistry (based on ionic, electronic and protonic carriers)<sup>1-2, 5-6</sup>, which alter directly the resistive switching property and future computing performances. A careful study on the influence of microstructure and defect states vs. the materials' diffusion characteristics is in focus. For this, we suggest novel oxide heterostructure building blocks and show in-situ spectroscopic and microscopic techniques coupled with electrochemical micro-measurements to probe near order structural bond strength changes relative to ionic, protonic and electronic diffusion kinetics and the materials integration to new optimized device architectures and computing operation schemes.

- 1) Memristor Kinetics and Diffusion Characteristics for Mixed Anionic-Electronic  $\text{SrTiO}_3$ - $\delta$ : The Memristor-based Cottrell Analysis Connecting Material to Device Performance F Messerschmitt, M Kubicek, S Schweiger, JLM Rupp *Advanced Functional Materials*, 24, 47, 7448 (2014) >
- 2) Uncovering Two Competing Switching Mechanisms for Epitaxial and Ultra-Thin Strontium Titanate-based Resistive Switching Bits M Kubicek, R Schmitt, F Messerschmitt, JLM Rupp *ACS Nano* 9, 11, 10737 (2015) >
- 3) Designing Strained Ionic Heterostructures for Resistive Switching Devices S Schweiger, R Pfenninger, W Bowman, U Aschauer, JLM Rupp *Advanced Materials*, (2016) >
- 4) The Effect of Mechanical Twisting on Oxygen Ionic Transport in Solid State Energy Conversion Membranes Y Shi, AH Bork, S Schweiger, JLM Rupp *Nature Materials*, 14, 721 (2015) >
- 5) A Micro-Dot Multilayer Oxide Device: Let's Tune the Strain-Ionic Transport Interaction S. Schweiger, M. Kubicek, F. Messerschmitt, C. Murer, J.L.M. Rupp *ACS Nano*, 8, 5, 5032 (2014) >
- 6) How does Moisture affect the Physical property of Memristance for Anionic-Electronic Resistive Switching Memories? F Messerschmitt, M Kubicek, JLM Rupp *Advanced Functional Materials*, 25, 32, 5117 (2015) >

## 4:20pm **RM+EM+NS-TuA-7 Memristor Neural Networks for Brain-Inspired Computing, Qiangfei Xia, University of Massachusetts Amherst** **INVITED**

As CMOS scaling approaches its limits, it becomes more difficult to keep improving the speed-energy efficiency of traditional digital processors. To address this issue, computing systems augmented with emerging devices particularly memristors, offer an attractive solution. Memristors use conductance to represent analog or digital information. The dynamic nature of memristor with both long-term and short-term memories, together with its small effective size contributes to the energy efficiency in weight updating (training). The in-memory computing scheme in a crossbar breaks the 'von Neumann bottleneck' as the weights are stored locally in each device during computing. The read out (inference) is finished in one clock cycle regardless of the array size, offering massive parallelism and hence high throughput. The capability of using physical laws for computing in a crossbar enables direct interfacing with analog signals from sensors without energy-hungry analog/digital conversions.

We developed a Ta/hafnium oxide memristor with stable multilevel resistance, linear current voltage characteristics in chosen conductance ranges, in addition to high endurance and long retention. We further integrated the memristors with foundry-made transistors into large arrays. We demonstrated that the reconfigurable memristor networks are capable of analog vector matrix multiplication, and successfully implemented a number of important applications including signal processing, image compression and convolutional filtering. We also built a multilayer memristor neural network, with which we demonstrated in-situ and self-adaptive learning capability with the MNIST handwritten digit dataset. The successful demonstration of analog computing and in-situ online training suggests that the memristor neural network is a promising hardware technology for future computing.

## 5:00pm **RM+EM+NS-TuA-9 Indium Phosphide Synaptic Device on Silicon for Scalable Neuromorphic Computing, Jun Tao, D Sarkar, R Kapadia, University of Southern California**

Inspired by the superior capability of the brain, neuronal spiking, and synaptic behavior have been mimicked by the CMOS-based neuronal cell in hardware, which contains 6-12 transistors depending on specific functionality and the robustness of the design. However, the higher energy consumption and physical area have led researchers to look for architectures based on single device and novel materials.

In our work, utilizing thin-film vapor-liquid-solid growth method, we fabricated scalable Indium phosphide (InP) channel transistors directly on Si/SiO<sub>2</sub> wafer, which can emulate significant synaptic characteristics such as elasticity, short- and long-term plasticity, metaplasticity, spike number dependent plasticity and spike timing dependent plasticity, by modeling gate electrode as the pre-synaptic axon terminal, the drain electrode as the post-synaptic dendrite, and the gate oxide-semiconductor channel as the synapse junction, in which we also interpreted the FET channel conductance as the synaptic weight.

We also demonstrated that by controlling the charging and discharging of interfacial traps at the gate oxide-semiconductor stack, we can essentially engineer hysteresis of the synaptic device to customize the synapse behavior and modify the synapse weight non-linearly. It underpins optimal selectivity of signal transduction and satisfies the key neuromorphic architecture characteristic—training and learn. Tuning hysteresis in a family of transfer characteristics in spike timing dependent plasticity (STDP) emulation, we attain maximum potentiation (depression) for the minimum positive (negative) interval time, which gradually decays down to elasticity, as we expected, indicating the scalable InP channel transistors on silicon as promising devices and platform for neuromorphic computation.

## 5:20pm **RM+EM+NS-TuA-10 Ultra-low Power Microwave Oscillators based on Phase Change Oxides as Solid-State Neurons, Boyang Zhao, J Ravichandran, University of Southern California**

Voltage or current controlled oscillators are well-established candidates for solid-state implementations of neurons. Metal to insulator transition (MIT) based phase change electrical oscillators are one of the many candidates for solid-state neurons, but current implementations are far from the ideal performance limits of energy and time necessary to induce the transition. We propose the use of nanoscale, epitaxial heterostructures of phase change oxides such as VO<sub>2</sub>, NbO<sub>2</sub> and oxides with metallic conductivity as a fundamental unit of a low power electrical oscillator, capable of operating as neurons for neuromorphic computing architectures. Our simulations such that such oscillators can operate in the microwave regime and overcome many of the power consumption issues plagued by phase change electrical oscillators.

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5:40pm **RM+EM+NS-TuA-11 Leveraging Nanodevice Volatility for Low Energy Computing Inspired from Nature**, *Alice Mizrahi*, NIST/University of Maryland; *T Hirtzlin*, Centre de Nanosciences et Nanotechnologies; *B Hoskins*, NIST Center for Nanoscale Science and Technology; *A Fukushima*, AIST; *A Madhavan*, NIST Center for Nanoscale Science and Technology; *H Kubota*, *S Yuasa*, AIST; *N Zhitenev*, *J McClelland*, *M Stiles*, NIST Center for Nanoscale Science and Technology; *D Querlioz*, Centre de Nanosciences et Nanotechnologies, France; *J Grollier*, UMR CNRS/Thales

**INVITED**

Artificial neural networks are performing tasks, such as image recognition and classification, that were thought only accessible to the brain. However, these algorithms run on traditional computers and consume orders of magnitude more energy more than the brain does at the same task. One promising path to reduce the energy consumption is to build dedicated hardware to perform cognitive tasks. Nanodevices are particularly interesting because they allow for complex functionality with low energy consumption and small size. I discuss two nanodevices. First, I focus on stochastic magnetic tunnel junctions, which can emulate the spike trains emitted by neurons with a switching rate that can be controlled by an input. Networks of these tunnel junctions can be combined with CMOS circuitry to implement population coding to build low power computing systems capable of processing sensory input and controlling output behavior. Second, I turn to different nanodevices, memristors, to implement a different type of computation occurring in nature: swarm intelligence. A broad class of algorithms inspired by the behavior of swarms have been proven successful at solving optimization problems (for example an ant colony can solve a maze). Networks of memristors combined with CMOS circuitry can perform swarm intelligence and find the shortest paths in mazes. These results are striking illustrations of how matching the functionalities of nanodevices with relevant properties of natural systems open the way to low power hardware implementations of difficult computing problems.

## Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic

Room Hall B - Session PC+AS+BI+EM+NS+PB+SS-TuP

## Processing and Characterization of Gas-Liquid, Solid-Liquid, and Gas-Solid Interfaces

**PC+AS+BI+EM+NS+PB+SS-TuP-1 Operando Photoelectron Spectroscopic Study of Copper-based Oxide Semiconductor Interface with Water,** *Pitambar Sapkota, S Ptasinska*, University of Notre Dame; *A Cabrera*, Instituto de Física, Pontificia Universidad Católica de Chile, Chile

The quest for suitable semiconductor photoelectrodes to build efficient and stable photoelectrochemical (PEC) cells for solar water splitting is continually growing in the material sciences and solar energy community. Along with good stability in aqueous media, such photoelectrodes should have suitable band-edges and band-gap energies properly matching both the water oxidation-reduction potential and the solar spectrum, respectively. Copper-based oxide semiconductors are promising candidates fulfilling these criteria, but little is known about the interfacial properties of these compounds with H<sub>2</sub>O under operational conditions. Therefore, knowledge of their surface dynamics and interfacial reactions under realistic conditions is essential to improve our understanding of water-splitting mechanism, as well as to increase the stability and efficacy of PEC devices. Ambient pressure X-ray photoelectron spectroscopy was used to characterize the semiconductor surface and study the chemical reactions occurring at the interface under the reaction conditions. In this study, thin films of CuFeO<sub>2</sub> and CuFe<sub>1-x</sub>Ga<sub>x</sub>O<sub>2</sub> composites were exposed to various H<sub>2</sub>O pressures and temperatures. Water interactions with the Cu-based oxide surface and the electronic structures of the surface atoms were evaluated from the Cu 2p, Fe 2p, C 1s and O 1s photoemission spectra to identify surface species newly formed.

**PC+AS+BI+EM+NS+PB+SS-TuP-2 Interfacial Water in Silicon-based Catalytic Motors,** *Jordi Fraxedas, K Zhang, B Sepulveda, M Esplandiu*, Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Spain; *X Garcia, J Llorca*, Institute of Energy Technologies, Department of Chemical Engineering and Barcelona Research Center in Multiscale Science and Engineering. Universitat Politècnica de Catalunya, Spain; *V Perez-Dieste, C Escudero*, Alba Synchrotron Light Source, Spain

Self-propelled motors that can harvest chemical energy from their surroundings to convert it in mechanical energy are at the cutting edge of nanotechnology for their appealing applications in e.g., environmental remediation and nanobiomedicine. A full understanding of the propulsion mechanism is crucial to improve their performance and controllability. Recently, a simple motor made of silicon and a noble metal that can operate with visible light has been developed [1]. The photoactivation mechanism and consequent motion is essentially based on the formation of electron/hole pairs. The holes are strong oxidizing agents for the species in the fluid producing protons and the electrons can diffuse towards the metal surface and participate in the counterpart reduction reaction. As a result, a gradient of proton concentration is formed in the fluid which builds-up an electric field driving the motion of the fluid through electro-osmosis. A mechanism that competes with the electro-osmotic process is based on diffusion-osmosis and is triggered by the redox decomposition exclusively at the metal surface and is not light responsive. We have recently shown that it is possible to enhance/suppress one mechanism over the other by tuning the surface roughness of the micromotor metal. Thus, the actuation mechanism can be switched from light-controlled electrokinetics to light-insensitive diffusio-osmosis by only increasing the metal surface roughness [2].

We have recently performed near ambient pressure photoemission studies of Pt/Si micromotor surfaces activated by oxygen plasma in water atmosphere at the NAPP endstation of the CIRCE beamline at the ALBA synchrotron near Barcelona. We have used p-type silicon substrates with one half covered with a Pt film with a thickness of about 50 nm grown by both e-beam and sputtering deposition. The results reveal a chemical gradient at the Si/Pt edge with a reduction of the Pt species. The analysis has to carefully consider the photochemical reactions induced by the combined action of the impinging beam and the water condensed at the surfaces. The beam induced damage evolves in two regimes: an initial preferential reduction of Pt<sup>4+</sup> species and then the reduction of Pt<sup>2+</sup> species, which increases the metallic character of the surface.

[1] M.J. Esplandiu, A. Afshar Farniya, A. Bachtold, ACS Nano, 9, 11234 (2015).

[2] K. Zhang, J. Fraxedas, B. Sepulveda, M. J. Esplandiu, ACS Appl. Mater. Interfaces 9, 44948 (2017).

**PC+AS+BI+EM+NS+PB+SS-TuP-3 Chiral Modification of Oxide-Supported Pt Surfaces: An in-situ ATR-IR Study,** *Yufei Ni, F Zaera*, University of California, Riverside

The synthesis of enantiopure compounds is of great significance to the designing of pharmaceuticals and agro products. Possible methods for the manufacture of enantiopure chemicals include the separation of racemic product mixtures and reactions with other chiral chemicals, but perhaps the most promising procedure is the use of enantioselective heterogeneous catalysis. Chiral modification of catalytically active metals such as Pt and Ni is believed to be the most feasible approach to produce chiral heterogeneous catalysts. In this context, the use of cinchona alkaloids-modified Pt for the hydrogenation of activated ketones has drawn particular attention in the past few decades. A better understanding of how these chiral modifiers work to bestow enantioselectivity is still a prerequisite for the design of such catalysts.

In this project, we have used attenuated total reflection infrared absorption spectroscopy (ATR-IR) to investigate the details of the adsorption of such cinchona-alkaloid chiral modifiers on the Pt surfaces of supported catalysts in situ at the liquid-solid interface. It was determined that adsorption can be only observed after H<sub>2</sub> pretreatment of the catalyst. A comparison study in terms of adsorption strength was carried out using not only cinchona alkaloids such as cinchonidine and cinchonine but also simpler alternatives such as (R)- or (S)-(-)-1-(1-naphthyl) ethylamine (NEA), naphthylmethyl amine, and dimethyl naphthyl ethylamine. The adsorption strength of the different modifier molecules was found to be quite different among those compounds. This is illustrated by the fact that quinoline can displace s-NEA from Pt but not vice versa, for instance, and by the observation that when Pt is exposed to a solution containing both quinoline and s-NEA only the quinoline's signature peaks can be detected by ATR-IR spectroscopy. The ordering of the modifiers studied in terms of adsorption strength was found to correlate with their ability to chirally modify the Pt catalyst during the hydrogenation of unsaturated aldehydes.

Finally, it was found that NEA bonds to the metal through the nitrogen atom of its amine moiety, and not through the aromatic ring as commonly believed.

**PC+AS+BI+EM+NS+PB+SS-TuP-4 Wettability Behaviour of Synthesized Carbon Nanospheres and its Application as a Photocatalyst,** *Sonal Singhal, A Shukla*, IIT Delhi, India

Superhydrophobic and superhydrophilic surfaces have been widely investigated due to their diverse range of applications such as self-cleaning, microfluidic application in biotechnology, corrosion, Anti-reflecting coatings and microelectronic mechanical system etc. Here, a facile chemical vapour deposition method is reported for the synthesis of carbon nanospheres (CNSs). Henceforth, the morphology of as-synthesized sample is characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray diffraction (XRD), Raman spectroscopy and FTIR spectroscopy are used to determine the phase purity, chemical composition and presence of chemical bonds on the surface of synthesized CNSs. TEM and SEM results reveal the presence of CNSs with a diameter ranging from 50 nm to 400 nm. Raman spectroscopy confirms the presence of disordered carbon and low graphitization, which are also confirmed by TEM and XRD results. Optical properties of as-synthesized CNSs is investigated by UV-Vis spectroscopy and photoluminescence. Wettability behaviour of as-synthesized carbon nanospheres is investigated by contact angle measurements. CNSs shows a water contact angle of 152°, which confirms the fabrication of superhydrophobic carbon nanosphere surface. After the proper explanation of wettability behaviour, it also discusses the application of as-synthesized CNSs as a photocatalyst. As it is well known, catalyst enhances the chemical reaction rate without changing its properties. Therefore, various kind of catalysts has been developed for the purpose to enhance the catalysis for environmental applications. Among different materials, carbon-based materials are widely used as a catalyst support due to their excellent properties. Considering these facts, the degradation of an organic pollutant under UV light is discussed here using CNSs.

# Tuesday Evening Poster Sessions, October 23, 2018

**PC+AS+BI+EM+NS+PB+SS-TuP-5 Thermally Driven Solid-solid Li<sup>+</sup> Transfer into Nanostructured TiO<sub>2</sub>, *Tiffany Kaspar, T Varga*, Pacific Northwest National Laboratory; *D Shapira*, Advanced Light Source, Lawrence Berkeley National Laboratory; *A Martinez, Y Shin, K Han, M Lee, S Thevuthasan, V Murugesan*, Pacific Northwest National Laboratory**

Due to their good chemical stability, strong oxidation capability, and desirable lithium electrochemical activity, nanostructured titanium dioxide (TiO<sub>2</sub>) anode materials have received considerable attention recently. Decreasing the particle size to 10-20 nm can increase the electrochemical capacity to 200-300 mAhg<sup>-1</sup>. Furthermore, nanostructured TiO<sub>2</sub> anodes are non-toxic and would be suitable for cost effective mass production. Among the rutile, anatase, and brookite polymorphs of TiO<sub>2</sub>, anatase nanoparticles have shown the best Li ion insertion properties and maximum reduction, indicating increased Li ion intercalation into the material. Here, we have synthesized 10-20 nm anatase TiO<sub>2</sub> nanoparticles and contacted them with solid Li- bis(trifluoromethanesulfonyl)imide (LiTFSI) as a function of temperature to understand the chemical and structural effects associated with thermally driven solid-solid Li<sup>+</sup> transfer to, and intercalation in, TiO<sub>2</sub> nanoparticles. We have used a combination of x-ray photoelectron spectroscopy (XPS), Ti L-edge scanning transmission x-ray microscopy (STXM), Raman spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy to gain a fundamental understanding of the structural evolution of TiO<sub>2</sub> nanoparticles during Li<sup>+</sup> intercalation. Our results indicate that thermally driven solid-solid Li<sup>+</sup> transfer to TiO<sub>2</sub> has occurred, and altered the TiO<sub>2</sub> structure at the edges of the agglomerated nanoparticles.

## 2D Materials Focus Topic

### Room 201B - Session 2D+AM+EM+NS-WeM

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

Moderator: Eric Pop, Stanford University

8:00am **2D+AM+EM+NS-WeM-1 Carbon Doping of 2D Transition Metal Dichalcogenides by Plasma Enhanced CVD**, *Yanfu Lu, F Zhang, S Sinnott, M Terrones*, The Pennsylvania State University

Doping of 2D transition metal dichalcogenides has been discovered to be an effective way to tune the electronic structure and modify the lattice structure at the surface. The n-type and p-type doping of monolayer MoS<sub>2</sub>/WS<sub>2</sub> heterostructures may enable the fabrication of field-effect transistors of ultra-low thickness. Plasma enhanced chemical vapor deposition provides a stable and controllable approach for introducing carbon dopants to monolayer WS<sub>2</sub>. Photoluminescence measurement indicates that the band gap of C-doped WS<sub>2</sub> decreases by 0.17 eV.

Corresponding first principles calculations provide the correlation between the position and chemical saturation of the carbon dopants and the electronic structure of the system. To verify covalently bonded dopants, we use Raman spectroscopy, X-ray photoelectron spectroscopy, and scanning transmission electron microscopy to examine the pristine sample and carbon-doped samples. Subsequent I-V characteristics measurements prove p-type doping and the energy band diagram. Finally, the mechanism associated with and, more importantly, the structure-property relationship of chalcogen doping are analyzed. The resulting new insights of transition metal dichalcogenide-based heterostructures and alloys are discussed.

8:20am **2D+AM+EM+NS-WeM-2 Methoxy Formation Induced Defects on MoS<sub>2</sub>\***, *Duy Le*, University of Central Florida; *P Evans*, University of Nebraska - Lincoln; *Z Hooshmand*, University of Central Florida; *T Rawal*, Oak Ridge National Laboratory; *L Bartels*, University of California, Riverside; *P Dowben*, University of Nebraska-Lincoln; *T Rahman*, University of Central Florida

Defects are known to play an important role in determining the chemical properties of otherwise inert MoS<sub>2</sub> basal plane. Here we report our joint experimental and theoretical study of the adsorption and reaction of methanol on the MoS<sub>2</sub> basal plane to determine the factors that control system reactivity. We find that exposure of the MoS<sub>2</sub> basal plane to methanol leads to the formation of adsorbed methoxy and coincides with sulfur vacancy generation and that the methoxy moieties bind to molybdenum, not sulfur, while some adsorbed methanol is readily desorbed near or slightly above room temperature. Our calculations also suggest that the dissociation of methanol via O-H bond scission occurs at the defect site (sulfur vacancy), followed subsequently by formation of a weakly bound H<sub>2</sub>S species that promptly desorbs from the surface with creation of a new sulfur vacancy, in great agreement with photoluminescence and scanning tunneling microscopy data that show clear evidence of the sulfur vacancy creation on the MoS<sub>2</sub> surface, after exposure to methanol [1].

[1] P. Evans et al, *J. Phys. Chem. C* (2018). DOI: 10.1021/acs.jpcc.8b02053

\* Work supported in part by DOE grant DE-FG02-07ER15842

8:40am **2D+AM+EM+NS-WeM-3 Defect Engineering of 2D Materials for Advanced Electronic Devices**, *Gwan-Hyung Lee*, Yonsei University, Republic of Korea

INVITED

Two-dimensional (2D) materials have brought a great deal of excitement to nanoscience community with their attractive and unique properties. Such excellent characteristics have triggered highly active researches on 2D material-based electronic devices. New physics observed only in 2D semiconductors allow for development of new-concept devices. Assembly of 2D blocks for van der Waals heterostructures also provide a big playground for engineers and physicists to investigate unprecedented properties of 2D materials and fabricate multi-functional electronic devices. However, atomically thin 2D materials, such as graphene and transition metal dichalcogenides (TMDs), have only two surfaces at top and bottom without a bulk so that they are very sensitive to environment. In other words, properties of 2D materials can be altered easily by surface modification. In this talk, I will show novel approach to fabricate high performance 2D electronic devices by utilizing various surface treatments, such as fluorination and hydrogenation of graphene and layer-by-layer oxidation of MoS<sub>2</sub>. When different types of defects, such as sp<sup>3</sup> bonds and vacancies, are induced on the surface of graphene, the electrical properties of graphene can be tuned. With mild plasma treatment, MoS<sub>2</sub> can be oxidized layer-by-layer and monolayer MoS<sub>2</sub> can be fabricated from the

multilayer MoS<sub>2</sub>. These surface treatment techniques can be used for fabrication of high performance graphene devices and MoS<sub>2</sub> optoelectronic devices. Defect engineering of 2D materials holds a great promise in engineering the 2D materials and fabricating advanced electronic devices of 2D materials.

9:20am **2D+AM+EM+NS-WeM-5 Modeling Defects and Electron-electron Interactions in Low-dimensional Materials**, *Daniel Gunlycke, C Ekuma*, U.S. Naval Research Laboratory

While each nanoscale structure in a low-dimensional material can exhibit a variety of properties, the odds are that it will be (1) sensitive to defects and (2) strongly influenced by electron-electron interactions. The ratio of defect sites to pristine sites naturally increases, as structures become smaller.

Electron localization can furthermore dramatically magnify the role of defects. In low-dimensional materials, dielectric screening is generally less effective, reducing the tendency for electronic interactions to become uniform across the sites in the materials. Despite the importance of both defects and electron-electron interactions, the properties of low-dimensional materials are often investigated in the absence of one or the other. This not only creates uncertainty over the predictions but could entirely miss certain physical phenomena, including insulator-to-metal transitions. In this presentation, we will discuss a general first-principles-based approach to explore realistic low-dimensional structures that explicitly accounts for both defects and electron-electron interactions [1]. It is based around a generalized Anderson Hamiltonian and applies density functional theory, as well as dynamical mean-field theory. We will also present electronic and optical properties of two-dimensional materials obtained using our method and discuss the potential for using defect engineering for improved solar cell performance.

[1] C. E. Ekuma, V. Dobrosavljevic, and D. Gunlycke, *Physical Review Letters* **118**, 106404 (2017)

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9:40am **2D+AM+EM+NS-WeM-6 Post-Synthesis Modifications of Two-Dimensional MoSe<sub>2</sub> or MoTe<sub>2</sub> by Incorporation of Excess Metal Atoms into the Crystal Structure**, *Paula Mariel Coelho*, University of South Florida; *H Komsa*, Aalto University, Finland; *H Coy Diaz*, Y Ma, University of South Florida; *A Krasheninnikov*, Institute of Ion Beam Physics and Materials Research, Germany; *M Batzill*, University of South Florida

Modifications of MoSe<sub>2</sub> and MoTe<sub>2</sub> with metallic mirror twin grain boundaries (MTB) in films grown by molecular beam epitaxy have been previously reported [1,2]. The goal of the study presented here has been to understand the formation-mechanism of MTB networks and apply this gained knowledge for controlled modifications of these 2D materials. In a combined scanning tunneling microscopy and density functional theory approach we demonstrate that excess Mo can easily diffuse into the pristine MoSe<sub>2</sub> or MoTe<sub>2</sub> (but not into MoS<sub>2</sub>) layer and cause crystal modifications into Mo-rich twin grain boundaries. Vapor deposited Mo atoms are first incorporated by diffusing into interstitial (or split-interstitial) sites. Then, further Mo-atoms incorporate into the crystal structure to form triangular, Mo-rich grain boundary loops. Only after a critical density of MTBs is reached, Mo is no-longer absorbed by the 2D-crystal sheet and Mo-clusters start to form at the surface. The energetics and barriers for Mo-incorporation is calculated by DFT and shows that the formation of twin grain boundaries in the presence of excess Mo is favorable for MoTe<sub>2</sub> and MoSe<sub>2</sub>, but not for MoS<sub>2</sub> - in agreement with the experiment. The achievable dense networks of MTBs constitute a new Mo-rich metallic phase that may be used for controlled electric contacts or creation of active sites in electro-catalysis [4] and thus adding new functionalities into transition metal dichalcogenide-based materials and devices. Moreover, DFT simulations suggest that this mechanism for incorporation of transition metals is not limited to Mo. This enables modification of the materials properties by heteroatom dopants and initial experimental work demonstrates the incorporation of both Ti and V. V-interstitials in MoTe<sub>2</sub> are predicted to have a magnetic moment and magnetic hysteresis curves indicate the induction of ferromagnetism in MoTe<sub>2</sub> by doping the material with less than 1% of V interstitials.

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- [1] Ma Y, et al. (2017) Metallic Twin Grain Boundaries Embedded in MoSe<sub>2</sub> Monolayers Grown by Molecular Beam Epitaxy. *ACS Nano* **11**, 5130-5139.
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11:00am **2D+AM+EM+NS-WeM-10 Dry Cleaning and Doping of MX<sub>2</sub> for Contact Engineering**, *Daniil Marinov*, IMEC, Belgium; *J Ludwig*, IMEC & KU Leuven, Belgium; *D Chiappe*, IMEC, Belgium; *E Voronina*, T Rakhimova, Skobel'syn Institute of Nuclear Physics, Lomonosov Moscow State University; *J de Marneffe*, *I Asselberghs*, IMEC, Belgium; *S De Gendt*, IMEC, KU Leuven, Belgium

Two-dimensional transition metal dichalcogenides (e.g. MoS<sub>2</sub>, WS<sub>2</sub>) are promising materials for a number of electronic and optoelectronic applications. Wafer-scale integration of these materials into sophisticated devices requires atomic-scale control of the processing steps such as deposition, etch, clean and doping. Reduction of the contact resistance is a major roadblock towards demonstration of high-performance devices. Significant Schottky barrier at the metal-MX<sub>2</sub> interface as well as surface contamination (e.g. by polymer residues) are the main factors contributing to the high contact resistance in fabricated MX<sub>2</sub> devices. In this study, a fully dry cleaning and doping technique is developed with a particular focus on contact engineering.

We demonstrate that a remote H<sub>2</sub> plasma is efficient for removal of organic residues from MX<sub>2</sub> surfaces. However, sulfur can be also stripped from the topmost layer by reactive H atoms. The main challenge is thus to precisely control the sulfur loss while maintaining the cleaning efficiency. At high substrate temperature, a 200 nm PMMA layer can be fully removed selectively to a single layer of WS<sub>2</sub> without damaging the 2D material (as confirmed by photoluminescence measurements). At low substrate temperatures significant S-vacancy formation was observed. Surface temperature is therefore the key parameter for controlling the reactivity of H atoms on WS<sub>2</sub>.

Controllable formation of sulfur vacancies opens routes for substitutional doping. After H<sub>2</sub> plasma strip, WS<sub>2</sub> and MoS<sub>2</sub> samples were exposed to a flow of molecular gases (Cl<sub>2</sub>, CO, OCS) without igniting the plasma. It is shown that Cl<sub>2</sub> and OCS can react with H<sub>2</sub> plasma treated MX<sub>2</sub> forming stable surface groups. Ex-situ conductive AFM measurements confirm that molecular doping prevents the loss of conductivity (that is observed after H<sub>2</sub> plasma alone). Moreover, OCS and Cl<sub>2</sub> exposure enhances electrical current injection in the material through grain boundaries and edges. The latter effect is beneficial for contact resistance reduction on MX<sub>2</sub>.

To gain a deeper insight in the observed surface phenomena, DFT simulation of the interaction of atomic (H, Cl, F) and molecular (OCS, Cl<sub>2</sub>) species with MX<sub>2</sub> surface was performed. S-vacancy creation by atomic hydrogen via formation of gas phase H<sub>2</sub>S was observed in simulations, in qualitative agreement with the experiments. Moreover, dissociative adsorption of Cl<sub>2</sub> and OCS in S-vacancy sites is predicted by the DFT model.

Dr D. Marinov has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 752164.

11:20am **2D+AM+EM+NS-WeM-11 Deep Learning for Atomically-Resolved Scanning Transmission Electron Microscopy Experiments on 2D Materials**, *Maxim Ziatdinov*, *S Kalinin*, Oak Ridge National Laboratory

Understanding fundamental atomic-scale mechanisms behind solid state reactions and phase transformations is critical for optimizing functional properties of technologically relevant materials. Recent advances in scanning transmission electron microscopy (STEM) have allowed to visualize dynamic processes in solid state systems, induced by thermal or chemical stimuli or electron beam, on the level of individual atoms and single atomic defects. However, while there have been multiple STEM studies on materials structure evolution, the materials-specific knowledge on the kinetics and thermodynamics of these processes and atomic potentials is almost non-existent, which is mainly due to the inherent limitations of the current (semi-)manual image analysis techniques. Here we demonstrate an approach based on deep convolutional neural networks for automated analysis of dynamic STEM data from 2-dimensional materials, such as monolayer WS<sub>2</sub>, under e-beam irradiation. Our approach allows to create a library of atomic defects, explore subtle atomic distortions around the defects of interest and map chemical transformation pathways on the atomic level. We specifically show how the developed framework can be used for extracting diffusion parameters

of sulfur vacancies in WS<sub>2</sub> and for studying transformation pathways for Mo-S complexes, including detailed transition probabilities.

11:40am **2D+AM+EM+NS-WeM-12 Magnetic Doping in 2D MBE-grown MoSe<sub>2</sub>/graphene Heterostructures Studied by Photoelectron Spectroscopy and Band Structure Imaging**, *Maxime Gay*, *O Renault*, CEA-LETI, France; *M Dau*, *C Vergraud*, *M Jamet*, CEA-INAC-SPINTEC, France

2D TMDCs present a unique combination of electronic and mechanical properties such as a direct bandgap, strong spin-orbit coupling and K-valley inequivalence, with an atomic-scale thickness [1]. Introducing magnetic phases into these materials opens exciting perspectives towards spin control in magnetic tunnel junctions. To date, magnetism in 2D systems was mostly studied by theoretical calculations. Within the diluted magnetic semiconductors model, transition metal atoms from the monolayer are substituted by a few Mn, Fe or Co atoms [2-4].

Our study focuses on Mn-doped-MoSe<sub>2</sub> monolayers, grown by molecular beam epitaxy on graphene, and characterized by photoemission techniques (XPS, kPEEM) coupled with observations at different scales (DRX, TEM). Before doping, we found that the in-plane lattices of graphene and MoSe<sub>2</sub> are aligned with each other and that a bandgap opens in the graphene around the Fermi level [5-6]. After Mn doping, the obtained Mn insertion is measured up to 15% by XPS. The influence of Mn doping on the band structure of MoSe<sub>2</sub>/graphene heterostructure will be presented and discussed.

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- [2] Mishra, R., et al. Phys. Rev. B - Condens. Matter Mater. Phys. 88, 1-5 (2013).
- [3] Zhang, K., et al. Nano Lett. 15, 6586-6591 (2015).
- [4] Singh, N. & Schwingschögl, U. ACS Appl. Mater. Interfaces 8, 23886-23890 (2016).
- [5] Dau, M. T., et al. Appl. Phys. Lett. 110, 11909 (2017).
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## Extending Additive Manufacturing to the Atomic Scale Focus Topic

### Room 102B - Session AM+NS+SS-WeM

#### Nanofabrication with Focused Electron Beams (8:00-10:00 am)/Atomic Scale Manipulation with Focused Electron Beams (11:00 am-12:20 pm)

Moderator: *Ondrej Dyck*, Oak Ridge National Laboratory

8:00am **AM+NS+SS-WeM-1 3D Nano-Printing via Focused Electron Beams: An Emerging Technology for Novel Applications**, *Harald Plank*, *R Winkler*, *J Sattelkow*, Graz University of Technology, Austria; *J Fowlkes*, Oak Ridge National Laboratory; *P Rack*, University of Tennessee Knoxville **INVITED**

3D-printing of functional structures has emerged as an important technology in research and development. While being reliable on the micro and sub-micron scale, the extension to the nanoscale is still a challenging task. Among the very few direct-write techniques on that scale, focused electron beam induced deposition (FEED) is one of the promising candidates as this technology allows fabrication of functional nano-structures on almost any material and substrate morphology in a single-step process. Based on strong fundamental progress in recent years, FEED was demonstrated to be capable of fabricating complex, freestanding 3D nano-architectures with individual branch diameters down to 20 nm. Together with the increasing availability of precursors with different functionalities, FEED is advancing from a versatile research tool into a predictable and reliable 3D nano-printer, which opens up new opportunities for advanced applications.

In this contribution, we start with the basic principles of 3-dimensional printing via FEED, complemented by simulations for deeper insight into the fundamental processes that are operative. In the following, we present a variety of FEED based proof-of-principle studies to demonstrate the capabilities of this direct-write technology. This ranges from scientifically oriented applications, such as plasmonics, magnetism and nano-mechanics toward industrially relevant concepts for scanning probe microscopy related tip fabrication, such as electrical, thermal and optical 3D nano-

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probes. Finally, we overview some of the remaining challenges and provide an outlook on future activities.

**8:40am AM+NS+SS-WeM-3 3D Nanoprinting using an Electron Beam: Simulations and Computer-aided Design, Jason Fowlkes**, Oak Ridge National Laboratory; *R Winkler*, Graz Centre for Electron Microscopy, Austria; *B Lewis*, Carl Zeiss Microscopy, LLC; *A Fernandez-Pacheco*, *L Skoric*, *D Sanz-Hernandez*, University of Cambridge; *M Stanford*, *E Mutunga*, *P Rack*, University of Tennessee; *H Plank*, Graz University of Technology, Austria

**INVITED**

The deposition of complex 3D nanoscale objects with prescribed geometry and function constitutes a major goal of nanoscience. Additive assembly is the ideal approach to efficiently deposit 3D materials. Focused electron beam induced deposition (FEBID) is a resist-free, direct-write method suitable for the additive deposition of materials on both planar and nonplanar surfaces. During FEBID, a focused electron beam is scanned along the substrate surface inducing the deposition and condensation of absorbed precursor molecules, often an organometallic, delivered locally by an in-situ gas injector. Until recently, 3D deposition using FEBID was mostly a trial-and-error exercise lacking a reliable framework to deposit a wide range of geometries.

A design environment specific to beam induced deposition will be presented that has enabled the deposition of complex, 3D nanoscale mesh style objects spanning nanometer to micrometer length scales. A complementary 3D simulation of FEBID provides a predictive capability that aids in the design of more complex 3D deposits. The purpose of this design/simulation capability is to generate the primary electron beam coordinates and beam exposure dwell times necessary for the experimental deposition of 3D mesh objects, with a reduced fill factor, i.e., geometries required for the design of metamaterials, high-aspect ratio sensors/actuators and/or nanomagnetic/optical lattices.

The simulation reveals that precursor surface diffusion and electron beam induced heating, in particular, can impose unwanted mesh object distortions if not properly accounted for. This general rule applies for several precursors under picoampere, millisecond beam exposure using typical local precursor fluxes consistent with high vacuum scanning electron microscope operation. Compensation for these influences can be applied in either the CAD phase, as geometric distortions, or through the introduction of exposure pulsing which acts to mitigate the development of transient mass/heat gradients. The role of simulation in design will also be explained in the context of the proximity effect due to scattered electrons, specifically their role in inducing unwanted deposition. Simulation results are limited to cases where complementary experiments converge with simulated predictions in terms of the final deposit geometry and the electrical current collected dynamically during deposition.

**9:20am AM+NS+SS-WeM-5 2D/3D Nano-printed Functional Structures for Application and Device Development using Focused Electron Beams, Michael Huth**, Institute of Physics, Goethe University, Frankfurt am Main, Germany

**INVITED**

Focused electron beam induced deposition (FEBID) is a direct-write method for the fabrication of nanostructures whose lateral resolution rivals that of advanced electron beam lithography but is in addition capable of creating complex three-dimensional nano-architectures even on non-standard materials and surfaces. In FEBID, a precursor gas adsorbed on a substrate surface inside of a scanning electron microscope is dissociated in the focus of the electron beam. This implies a conceptual similarity to „conventional“ 3D printing. However, more than anything else it is the intrinsic material properties of FEBID structures which give this technique its particular strength and relevance when compared to other nano-fabrication approaches. In this regard, the realization of novel, custom-tailored sensor concepts is exemplary for the various developments in FEBID that led to a growing number of scientific contributions in solid state physics and materials science over the last decade.

In this talk an overview is given of the application of FEBID structures for nano-sensing of force and strain, dielectric changes or charge accumulation in the environment of the sensor element, as well as magnetic stray fields.

Single-electron charging and proximity to a metal-to-insulator transition form a common ground from which the design and realization of a desired sensor functionality are accomplished, as is the possibility to finely tune the sensor's signal-to-noise ratio *in situ*.

The essential part of the sensor functionality based on FEBID structures is the microstructure that results if metal-organic precursors are used in the writing process. In many instances, *nano-granular metals* result, i.e., nanometer-sized metallic particles are formed that are embedded in an

insulating matrix. Charge transport in nano-granular metals is dominated by tunneling. From this it is apparent that they might be suitable materials for strain-sensing since the tunnel coupling has an exponential dependence on the inter-grain distance which is altered under strain. However, charge transport in nano-granular metals does not only depend sensitively on the inter-grain distance. The average grain size and the dielectric properties of the insulating matrix as well as the material properties in close proximity to the nano-granular metal are equally important. The corresponding electronic parameters that determine the charge transport regime are the inter-granular tunnel coupling, the charging energy of a single grain and the dielectric function of the matrix material. It is the interplay of these parameters and their tunability that leads to the large application domain of FEBID-based sensing.

**11:00am AM+NS+SS-WeM-10 Single Atom Scale Manipulation of Matter by Scanning Transmission Electron Microscopy, Stephen Jesse**, *O Dyck*, *S Kalinin*, Oak Ridge National Laboratory

**INVITED**

Fabrication of atomic scale structures remains the ultimate goal of nanotechnology. The reigning paradigms are scanning probe microscopy (SPM) and synthesis. SPM assembly dates to seminal experiments by Don Eigler, who demonstrated single atom manipulation. However, stability and throughput remain issues. The molecular machines approach harnesses the power synthetic chemistry to build individual functional blocks, yet strategies for structural assembly remain uncertain.

In this presentation, I discuss research activity towards a third paradigm — the use of the atomically focused beam of a scanning transmission electron microscope (STEM) to control and direct matter on atomic scales. Traditionally, STEM's are perceived only as imaging tools and beam induced modifications as undesirable beam damage. Our team and several groups worldwide have demonstrated that beam induced modifications can be more precise. We have demonstrated ordering of oxygen vacancies, single defect formation in 2D materials, and beam induced migration of single interstitials in diamond like lattices. What is remarkable is that these changes often involve one atom or small group of atoms, and can be monitored real-time with atomic resolution. This fulfills two out of three requirements for atomic fabrication. I will introduce several examples of beam-induced fabrication on the atomic level, and demonstrate how beam control, rapid image analytics, better insight through modelling, and image- and ptychography based feedback allows for controlling matter on atomic level.

This research is supported by and performed at the Center for Nanophase Materials Sciences, sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, BES DOE.

**11:40am AM+NS+SS-WeM-12 Single Atom Modification of 2D Materials: Fabrication and Electronic Structure, Demie Kepaptsoglou**, *F Hage*, SuperSTEM Laboratory, UK; *T Susi*, *J Kotakoski*, *J Meyer*, University of Vienna, Austria; *Y Lin*, *K Suenaga*, National Institute of Advanced Industrial Science and Technology (AIST), Japan; *T Hardcastle*, University of Leeds, UK; *U Bangert*, University of Limerick, Republic of Ireland; *J Amani*, *H Hofsaess*, University of Göttingen, Germany; *Q Ramasse*, SuperSTEM Laboratory, UK, United Kingdom of Great Britain and Northern Ireland

**INVITED**

The past decade has seen incredible progress in the ability to isolate and manipulate two-dimensional crystals. Due to their unique structure and dimensionality, it is possible to confine charge carriers in two dimensions, resulting in peculiar physical, chemical and electronic properties. Such novel properties can be further controlled and tuned through defects such as single atom dopants, interfaces, etc. This defect engineering takes place quite literally at the atomic level, where a combination of low voltage scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS) and *ab-initio* calculations provides not only the most powerful means of characterization, but also a unique tool for manipulating the single atom structures and engineer their electronic interaction with the host matrix. This approach was recently used to demonstrate that low energy ion implantation (of dopants such as N and B) can be successfully implemented to introduce single substitutional defects with excellent retention rates and without affecting the structural integrity of the surrounding graphene matrix. Atomically-resolved EELS experimental data reveals the bonding signature of the dopants themselves and their impact on the surrounding lattice. *Ab initio* calculations, in excellent agreement with the experiment, confirm the nature of the excited states being probed by the EELS experiments and the electronic structure reconfiguration of the doped material around the single atom dopants. Results directly confirm the possibility of tailoring the plasmonic



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properties of graphene in the ultraviolet waveband at the atomic scale, a crucial step in the quest for utilizing its properties toward the development of plasmonic and optoelectronic devices. The gentle STEM observation conditions can also be used to controllably drive the diffusion of substitutional dopants through single layer graphene, one atomic jump at a time. Atomically precise manipulation with STEM relies on recent advances in instrumentation that have improved the instruments' stability and their beam positioning abilities. While momentum transfer from highly energetic electrons often leads to atom ejection, interesting dynamics can be induced when the transferable kinetic energies are comparable to bond strengths in the material. For instance, a combined experimental and theoretical study revealed that for Si dopants manipulated in the STEM by 60keV electrons these jumps are not due to impacts on the Si atom, but to sub-threshold impact events on the surrounding C atoms. This approach suggests that STEM could emerge as an alternative method for the direct assembly of nanostructures.

## Applied Surface Science Division

### Room 204 - Session AS+NS+SA-WeM

#### Beyond Traditional Surface Analysis

**Moderators:** Mark Engelhard, EMSL, Environmental Molecular Sciences Laboratory, Kathryn Lloyd, DuPont

8:00am **AS+NS+SA-WeM-1 Solar Wind Interaction with Carbonate Deposits on Asteroid (1) Ceres' Surface: The Role of Surface Analysis in Laboratory Planetary Science, Catherine Dukes, G Rodriguez Lopez, C Bu, University of Virginia**

Bright deposits of anhydrous carbonates across the dark background of dwarf-planet Ceres have been identified by Dawn's VIR spectrometer with a composition that varies from natrite with minor amounts of ammonium bicarbonate within the Cerealia and Vinalia Faculae to magnesite, calcite, and dolomite in other high-albedo regions [1]. These deposits are expected to derive from the aqueous alteration of volatile-containing silicates, forming a viscous brine below Ceres' solid crust. Hydrated salts from this reservoir are deposited on the planetary surface by extrusion through vents or co-ejected by jets of sub-surface water ice. Water loss in the material occurs with exposure to the low pressure environment on Ceres' surface as a function of exposure time, even at temperatures < 240 K [2].

Unprotected from the impacts of solar particles, cosmic rays, and meteorites, anhydrous salts undergo chemical and physical change (space weathering), which can be remotely identified by optical reflectance. The effect of solar-wind ions on carbonates can be simulated in the laboratory, and the correlation between surface composition and morphology with optical change can be used to infer physical processes occurring on airless planetary bodies. We investigate the stability of carbonates and measure systematic darkening with 4 keV He-ion fluence, a potential geologic chronometer for Ceres' bright deposits.

Carbonate powders are pressed into pellets, then introduced into vacuum ( $10^{-9}$  Torr) and cooled to  $\sim 110/200$  K.

An external-beam from an FT-IR is used to perform *in-vacuo* reflectance measurement. Spectra were acquired at varied fluence, equivalent to solar irradiation of  $\sim 300 - 30,000$  years at 2.8 A.U. Changes in surface composition and molecular chemistry were investigated by *in-situ* X-ray photoelectron spectroscopy (XPS).

Blueish luminescence of sodium carbonates with He<sup>+</sup> is observed. Vis-NIR darkening ( $\sim 80\%$ ) of natrite (Na<sub>2</sub>CO<sub>3</sub>) occurs after  $10^{18}$  He cm<sup>-2</sup>, with reddening of the visible spectral slope. Similar darkening is noted for 1.3 - 5  $\mu$ m, along with attenuation of carbonate overtones. Concomitant XPS measurement shows a reduction of carbon and oxygen, with enhancement of sodium. Exposure of the darkened sample to 10,000 L H<sub>2</sub>O-vapor results in brightening to > 80%.

Ion-induced darkening of Ceres' natrite deposits is expected to occur on a time-scale of 100 - 1000 years, and can be reversed by exposure to water vapor. For deposits of varied albedo, this suggests that the brightest areas are the most recent deposits or the most recently exposed to water.

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[2] Bu et al. (2017) Icarus doi.org/10.1016/j.icarus.2017.12.036

8:20am **AS+NS+SA-WeM-2 Looking Deeper and Smaller: Enhancing XPS by Hard X-ray Probes and High-resolution Imaging, Olivier Renault, CEA/LETI-University Grenoble Alpes, France; C Zborowski, University of Southern Denmark, Denmark; J Rueff, Synchrotron SOLEIL, L'orme des Merisiers, France; Y Yamashita, S Ueda, NIMS, Japan; G Grenet, Lyon Institute of Nanotechnology, France; S Tougaard, University of Southern Denmark, Denmark**

X-ray photoelectron spectroscopy (XPS) has become a mature technique with a widespread use spanning from fundamental research to R&D labs. In parallel, the intrinsic complexity of materials and systems to be analyzed by XPS has increased. Some of the limitation of XPS are of concern if a non-destructive, non-invasive analytical protocol is the key issue. These are, especially, the poor lateral resolution and the poor bulk sensitivity, making impossible the analysis of microscopic features and buried interfaces in a reliable way.

In this contribution, we review the capabilities of current and novel techniques to get into: (i) high lateral resolution and quantitative micro-analysis using spectroscopic imaging implemented by X-ray PhotoElectron Emission Microscopy (XPEEM); (ii) high depth sensitivity offered by Hard X-ray Photoelectron Spectroscopy (HAXPES), coupled or not with inelastic background analysis to further enhance information depth up to nearly 100 nm.

We will highlight the capabilities of each techniques by different practical examples in the field of 2D materials [1] and device technology [2, 3], emphasizing particularly the perspectives offered by novel laboratory hard X-ray sources [4].

[1] H. Kim, O. Renault et al., Physical Review B, 2016. 94(8): p. 081401.

[2] P. Risterucci, O. Renault et al., Applied Surface Science, 2017, 402: p. 78-85.

[3] C. Zborowski, et al., Applied Surface Science, 2018. 432(Part A): p. 60-70.

[4] O. Renault, E. Martinez, et al., Surf. Interface Anal. 2018 (in press).

8:40am **AS+NS+SA-WeM-3 Reenvisioning Amphiphilicity: Translating Cell Membrane Design Principles to Synthetic 2D Materials, Shelley Claridge, Purdue University**

2D materials such as graphene exhibit unique electronic and mechanical properties that promise substantial advantages in applications ranging from nanoelectronics to human health. Such interfaces are often functionalized noncovalently with lying-down phases of functional molecules to avoid disrupting electronic structure within the basal plane. Interfacial structures have commonly been characterized down to sub-nm scales using scanning probe techniques such as STM, either in vacuum, or at a solid-liquid interface with a nonpolar liquid (e.g. octadecene). However, molecules used in this approach are often structurally similar to amphiphiles such as fatty acids and phospholipids found in biological cell membranes, suggesting possible utility in *aqueous* environments. At the same time, the overall surface chemistry is strikingly different than that of the cell membrane -- in essence, the surface chemistry is that of a repeating cross-section of a lipid bilayer, with both hydrophilic and hydrophobic components exposed, forming a striped amphiphilic structure with sub-10-nm periodicity.

As 2D materials are integrated into hybrid materials and devices, this noncovalent amphiphilic interfacial structure raises two classes of significant questions requiring interfacial analysis: **(1) How do noncovalent lying-down ligand layers respond to solution or thermal processing?** What are the best ways to probe controlled *disordering* across scales from nm to  $\mu$ m at an interface with a polar liquid? If ligand dynamics vary with structure, to what extent can design principles from the cell membrane be invoked to control chemical functionality and reactions at the interface? **(2) Can noncovalently-adsorbed layers be patterned to template further interactions with the environment?** Lying-down phases of phospholipids and fatty acids present 1-nm-wide stripes of ordered chemical functional groups, suggesting the possibility of controlling processes such as crystallization, phase segregation, or analyte binding. We examine these questions, again developing approaches to characterize interface structure across the range of relevant length scales, and invoking structural design principles from the cell membrane.

9:20am **AS+NS+SA-WeM-5 Microstructural Effects on Surface Potential of Amorphous Solid Water, Caixia Bu, C Dukes, University of Virginia**

Amorphous solid water (ASW) formed by vapor deposition on substrates <math>\sim 130 K is of interest for its abundance in Earth's upper atmosphere, icy planetary bodies, and throughout the interstellar medium, as well as its use

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as model material in many disciplines. Two crucial characteristics of ASW are a self-induced negative surface potential and formation of nanopores [1]. Here, we examine the role of microstructure, including nanopores, on the spontaneous surface potential of ASW, and describe the complementary experimental techniques used, which have application for other microporous solids.

ASW films were deposited by directed vapor beams onto a He-cooled quartz-crystal microbalance (QCM) under ultra-high vacuum. The integrated pore volume (porosity) was calculated by combining the areal mass measured via QCM and thickness measured by UV-visible interferometry. The integrated surface area was indicative by the abundance of incompletely coordinated surface water molecules (H<sub>2</sub>O) on the pores, using the O-H dangling bonds (DBs) measured by FT-IR spectroscopy. An *in-situ* Kelvin probe measured film surface potential. A long-distance optical microscope monitored film morphology *in vacuo*. Annealing effects were investigated by heating the film at 1.8 K/min.

The magnitude of the negative surface potential ( $|V_s|$ ) increased linearly with film thickness at rates ( $|\Delta V_s/\Delta L|$ ) that decreased with increasing growth temperature ( $T_g = 10\text{--}110\text{ K}$ ), keeping deposition angle at  $\theta = 0^\circ$  (angle between vapor beam and QCM normal); at  $T_g = 30\text{ K}$ , the  $|\Delta V_s/\Delta L|$  decreased with increasing  $\theta$  ( $= 10\text{--}75^\circ$ ). ASW porosity showed no dependence on  $T_g$  at  $\theta = 0^\circ$ , but increased significantly with increasing  $\theta$ . The H<sub>2</sub>O DBs decreased/increased with increasing  $T_g/\theta$ , showing similar trends as the  $|\Delta V_s/\Delta L|$ . Upon heating, the most striking result was that the DB at  $\sim 3720\text{ cm}^{-1}$  (from two-coordinated H<sub>2</sub>O) and the  $|V_s|$  had similar temperature-dependent evolutions. By correlating all measurements, we propose that the observed intrinsic ASW surface potential results from aligned incompletely-coordinated H<sub>2</sub>O on the pore surfaces [2].

The  $|V_s|$  decreased abruptly when ASW thickness exceeded a critical value ( $L_c$ ), and cracks appeared in the optical images of the films. The  $L_c$ ,  $\sim 1\text{--}5\text{ }\mu\text{m}$  ( $T_g = 10\text{--}50\text{ K}$ ;  $\theta = 0\text{--}55^\circ$ ), increased with  $T_g$  and  $\theta$ , suggesting dependences on the microporous structure. We explain such dependences of  $L_c$  in the context of Griffith theory and estimate the tensile strength of ASW to be  $\sim 25\text{--}40\text{ MPa}$  [3].

We acknowledge support from the NASA LASER Program.

[1] Raut et al., *J. Chem. Phys.* **127**, 204713 (2007); [2] Bu et al., *J. Chem. Phys.* **143**, 074702 (2015); [3] Bu et al., *Appl. Phys. Lett.* **109**, 201902 (2016).

9:40am **AS+NS+SA-WeM-6 Speciation and Reactivity of Organic Matter in Uranium Mine Wastes from Laguna- New Mexico: An Application of Surface Sciences in Environmental Systems.**, *Carmen A. Velasco*, *A Ali*, University of New Mexico; *C Osburn*, North Carolina State University; *K Artyushkova*, *J Cerrato*, University of New Mexico

The co-occurrence of organic matter and uranium in the Jackpile Morrison formation, New Mexico was investigated using spectroscopy, microscopy, and water chemistry techniques to better understand the effects of organic matter on uranium (U) binding from abandoned U mine wastes. Samples were collected from the Jackpile Mine (JP)- New Mexico. The mean concentration of acid extractable content for mine waste from the JP was  $2.61 \pm 0.09\%$  U. Results from microprobe mapping suggest that U particles are surrounded by carbon (C) inclusions, while results from XRF analyses showed 2.78% (JP) carbon (C). Loss on ignition (LOI) analysis showed that  $19.90 \pm 0.95\%$  of organic carbon within the samples. Thermal gravimetric analysis (TGA) show the maximum weight loss between  $105^\circ\text{C}$  and  $505^\circ\text{C}$ , confirming that change on mass after the LOI is likely due to the loss of organic content of the samples. Analyses using XPS suggest that changes occur on the C binding and U oxidation state after modifying the pH in batch experiments. Emission Matrix (EMM) identified humic-acid and fulvic-acid like components present in the organic matter comprised in the mine waste, which is consistent with the organic functional groups detected by XPS. These findings suggest that uranium minerals are possibly complexed carboxylic functional groups from humic-and fulvic like substances. This study identified the relevance of considering the binding of U and C in mine wastes to better understand U mobilization in the environment.

\*This work was awarded the best talk award at the 2018 NMAVS Symposium (Albuquerque-May2018)

11:00am **AS+NS+SA-WeM-10 Optical Constants Measured for Iridium and Samarium by Reflection Electron Energy-loss Spectroscopy Spectra**, *LiHao Yang*, *H Xu*, University of Science and Technology of China; *A Sulyok*, *M Menyhard*, Institute for Technical Physics and Materials Science Centre for Energy Research, Hungarian Academy of Sciences (MTA); *K Tokesi*, Institute for Nuclear Research, Hungarian Academy of Sciences (ATOMKI), Hungary; *Z Ding*, University of Science and Technology of China, China

The optical properties, as one of the most important physical properties of materials, arouse a continuous interest of researchers. Accurate measurement of optical data by optical methods in a photon energy range up to 100 eV is still insufficient as special experimental conditions are required during the measurements in vacuum ultraviolet region (20-50 eV). In recent years a well-established technique based on the reflection electron energy loss spectroscopy (REELS) has been developed to obtain optical constants in a rather wide range of electron energy loss. The REELS method does not require a complicated process for preparation of samples and the incident electron energy is usually around a few keV. However, the REELS spectrum usually contains not only bulk excitation but also surface excitation. To remove the surface excitation effect from the REELS spectrum in data analysis, Da et al. [1] have developed a reverse Monte Carlo (RMC) method for the derivation of the energy loss function (ELF) which is directly related to optical constants of a solid.

In the present work, reflection electron energy loss spectra of Ir and Sm were measured at several primary energies ranging from 0.5 keV up to 2 keV and in a wide energy-loss range. Polycrystalline Ir and Sm samples were cleaned by Ar<sup>+</sup> ion bombardment. To minimize the surface roughening and damage, glancing incidence angle of  $80^\circ$  with respect the surface normal and low projectile energy of 1 keV were applied with the rotated sample during the sputtering. Cleanliness of surface was checked by continuous detection of main Auger peaks of C and O. A reverse Monte Carlo simulation was performed to extract ELFs of these metals from experimental REELS spectra. All the ELFs have produced REELS spectra in a good agreement within the experimental uncertainty. The reliability of the obtained optical data has been confirmed by applying the Thomas-Ritchie-Kuhn (f-sum rule) and the perfect-screening sum rules (p-sum rule). The good agreement indicates that RMC treats accurately the surface excitation effect which is well removed from the final ELF. Comparisons of our data with other sources from experimental measurements are given.

The work was support by the National Natural Science Foundation of China (No. 11574289) and Special Program for Applied Research on Super Computation of the NSFC-Guangdong Joint Fund (2nd phase) under Grant No. U1501501.

## Reference:

[1] B. Da, Y. Sun, S. F. Mao, Z. M. Zhang, H. Jin, H. Yoshikawa, S. Tanuma, and Z. J. Ding, *J. Appl. Phys.* **113**, 214303 (2013).

11:20am **AS+NS+SA-WeM-11 X-Ray Photoelectron Spectroscopy and Electrical Modeling of Electrowetting on Dielectric Devices**, *Pinar Aydogan Gokturk*, Bilkent University, Turkey; *B Ulgut*, *S Suzer*, Bilkent University, Turkey

Electrowetting on dielectrics (EWOD) is a process of changing the contact angle of a droplet sitting on the dielectric covered electrode by the application of external electric field. In majority of the electrowetting experiments reported in the literature, water or aqueous salt solutions are used and ambient medium is either the air, or another immiscible liquid like oil. In this study, for the first time two non-aqueous liquids; (i) polyethylene glycol with an average molecular weight of 600 Da, and (ii) DEME-TFSI ionic liquid, both with low vapor pressure and volatility, are used as droplets in the UHV chamber of an x-ray photoelectron spectrometer (XPS) with traditional electrowetting on dielectric device geometry. With the experimental determination on tracing the electrical potential developments on and around the droplet, using the shifts in the binding energy positions of peaks coming from the liquid and/or the substrate, under imposed AC and DC electrical fields, we are aiming to shed light on the numerous models employed for simulating the electrowetting phenomenon. Additionally, using XPS and incorporating real capacitors and resistors, we mimic and check on the commonly used models used for simulating the electrical behavior of the EWOD systems. Possible and accepted electrical circuit models are also used to simulate the XPS data.

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11:40am **AS+NS+SA-WeM-12 Near Ambient Pressure XPS Study of Oxygen Binding to the Surface of Transition Metal-nitrogen-carbon Electrocatalysts for Oxygen Reduction**, *K Artyushkova, Yechuan Chen, P Atanasov*, University of New Mexico

The most promising class of platinum group metal-free materials for oxygen reduction reaction (ORR) is based on graphene-like carbon containing nitrogen and transition metal (MNC). It is well established that nitrogen coordination with metal in the carbon network of MNC materials is directly related to ORR activity; however, the exact nature of the active sites is still debated even after over 50 years of research.

The mechanism of oxygen reduction reaction in metal-nitrogen-carbon (MNC) catalysts has been studied by a combination of spectroscopic and theoretical structure-to-activity studies. Using inhibitors that have unique spectral signatures and have strong binding to the active sites allows elucidating the relationship between the chemistry of active sites and its activity.

We will report laboratory-based and near ambient pressure (NAP-XPS) analysis for series of electrocatalysts belonging to Fe-N-carbon families. X-ray photoelectron spectroscopic analysis of the interaction of complexing agents based on phosphonate and *in situ* monitoring of oxygen binding to metal-free active sites provides an important insight into the reaction mechanism. The effect the nitrogen chemistry and the type of iron on the oxygen binding was investigated by NAPXPS under an oxygen environment at operating temperature of the fuel cell. Preferential oxygen binding to different types of nitrogen and iron moieties in presence and absence of inhibitor was followed by spectroscopic changes in high-resolution nitrogen photopeak.

12:00pm **AS+NS+SA-WeM-13 Surface Chemistry of Scandium**, *Michael Brumbach, D Casalnuovo, E Barnat, C Winters, D Robinson Brown, C Snow, A Grillet*, Sandia National Laboratories

Manipulation of metal surface chemistry through vacuum gas dosing has been demonstrated for many years. Additionally, ex situ preparation methods, ion sputtering, and/or in vacuo thermal treatment are all known to change surface properties through oxidation, removal of oxide, change in microstructure, altering contaminants, or other mechanisms. While these studies have been performed for decades, there are few examples of these experiments for pure scandium films. Furthermore, few examples of dosing clean scandium surfaces under vacuum have been published. In this work, scandium films were treated with UV/ozone ex situ cleaning, ion sputtering, and thermal treatment under UHV. These surfaces were then exposed to different gases in the millitorr pressure range for extended periods of time. An optical emission spectrometer was used to monitor the composition of the dosing gas. Surfaces were analyzed before and after dosing. In concert with the gas analyses, the changes in surface chemistry of scandium could be correlated to the dosing species. This work discusses the X-ray photoelectron peak fitting of scandium and the changes in chemistry that can be observed through surface exposures.

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Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

## Industrial Physics Forum

### Room 101B - Session IPF+AS+BI+NS-WeM

#### IoT Session: Bioanalytics, Biosensors and Diagnostics

**Moderators:** Anna Belu, Medtronic, Inc., Sally McArthur, Swinburne University of Technology, Australia

8:40am **IPF+AS+BI+NS-WeM-3 Harnessing Bacteria for Fabrication of Photoelectrodes and Pressure Sensors**, *Y Feng, K Marusak, Y Cao, E Ngaboyamahina, J Glass, L You, Stefan Zauscher*, Duke University **INVITED**  
Conventional methods for material fabrication often require harsh reaction conditions, have low energy efficiency, and can cause a negative impact on the environment and human health. In contrast, structured materials with well-defined physical and chemical properties emerge spontaneously in diverse biological systems. However, these natural processes are not readily programmable. By taking a synthetic-biology approach, we demonstrate a method for the fabrication of semiconducting, transition metal nanoparticles (NPs) with tunable bandgap and useful photoelectric properties, through bacterial precipitation. Surface analytic measurements revealed that our bacterially precipitated CdS NPs are agglomerates of

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quantum dots (QDs) in a carbon-rich matrix. We discovered that the precipitation conditions of the bacteria can be tuned to produce NPs with bandgaps that range from quantum-confined to bulk CdS. We determined the photoelectrochemical properties and energy band structure of thin films prepared from these NPs by electrochemical measurements. By taking advantage of the organic matrix, which is residual from the biosynthesis process, we fabricated a prototype photo-charged capacitor electrode by incorporating the bacterially precipitated CdS with a reduced graphene oxide sheet. Furthermore, we show the programmable, three-dimensional (3D) material fabrication using pattern-forming bacteria growing on top of permeable membranes as the structural scaffold. When the bacteria are equipped with an engineered protein that enables the assembly of gold (Au) nanoparticles into a hybrid organic-inorganic dome structure, the resulting hybrid structure functions as a pressure sensor that responds to touch. We furthermore show that the response dynamics are determined by the geometry of the structure, which is programmable by the membrane properties and the extent of circuit activation. By taking advantage of this property, we demonstrate signal sensing and processing using one or multiple bacterially assembled structures. Our work provides the first demonstration of using engineered cells to generate functional hybrid materials with programmable electronic properties and architectures for energy conversion, energy storage, and for signal sensing and transduction.

9:20am **IPF+AS+BI+NS-WeM-5 Surface Chemistry and Surface Analysis: Their Importance and Application in Industrial Genomics**, *Fiona Black*, Illumina Inc. **INVITED**

Understanding the genome has the power to revolutionize health.

However, building robust and scalable tools to interrogate single base variants with high robustness requires a system level approach to integrate surface patterning and activation, biosensing, and imaging. This talk will review how micro-patterning, bioanalytical controls, surface analytical techniques and measurement tools are applied in an industrial setting to develop and manufacture cutting edge systems for sequencing and genotyping applications

11:00am **IPF+AS+BI+NS-WeM-10 Design and Evaluation of Organosilica Nanosensors for Continuous Molecular Monitoring in Complex Biological Environments**, *Simon Corrie*, Monash Univ., Melbourne AU, Australia **INVITED**

Continuous monitoring of biomarkers in biological environments is a key challenge for the development of biosensors capable of providing real-time feedback. Sensors capable of continuous pH monitoring have already found applications in detection of bacterial infections and have potential for aiding in treatment of dynamic diseases. Nanoparticle based "optodes" have emerged as sensitive and tuneable biosensors, using chromo/ionophores to generate analyte-specific changes in fluorescence spectra in a dynamic and reversible manner. Current key limitations of these materials include leaching of reagents from the nanoparticles over time, combined with poor colloidal stability in biological fluids.

Organosilica is a promising material for developing stable biosensors, allowing simple control over size, interfacial chemistry and porosity. This presentation will describe the development of a core-shell nanoparticle containing a mixture of covalently incorporated pH-sensitive (shell) and pH-insensitive (core) fluorescent dyes. Attachment of anti-fouling polymers is used reduce aggregation and biofouling in biological media. Fluorescence analysis of the nanoparticles reveals that the shell/core fluorescence ratio is highly sensitive to pH over a physiological range with the response time <1s. The sensitivity and dynamic range can be tuned by varying material properties of the shell (primarily thickness and porosity). We will present our latest results on the application of these nanosensors for continuous, real-time monitoring, including in bacterial cultures, subcutaneous mouse "tattoos," and in 3D hydrogel scaffolds.

11:40am **IPF+AS+BI+NS-WeM-12 Optoregulated Biointerfaces**, *Aránzazu del Campo*, INM-Leibniz Institute for New Materials, Germany **INVITED**

Cells interact with their microenvironment by engaging membrane receptors with complementary partners at the surrounding matrix or at other neighbouring cells. These receptor complexes, often associated to cytoskeletal structures, allow exchange of biochemical and mechanical information. The ability to quantify this exchange is crucial for our understanding of cellular behavior and responses to external factors. Using model bionterfaces with optoregulated interaction possibilities, selective membrane receptors in living cells can be addressed in situ, i.e. on a sensor surface, while quantifying specific cellular responses. Light-

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regulated tools to apply and sense cell biochemical and mechanical interactions will be presented.

## MEMS and NEMS Group

### Room 202B - Session MN+NS+PS-WeM

#### IoT Session: Multiscale Manufacturing: Enabling Materials and Processes

**Moderators:** Susan Burkett, The University of Alabama, Roya Maboudian, University of California at Berkeley

#### 8:00am MN+NS+PS-WeM-1 Miniaturizing 3D Printed Microfluidics: State-of-the-Art and Outlook, *Greg Nordin*, Brigham Young University INVITED

While there is great interest in 3D printing for microfluidic device fabrication, the challenge has been to achieve feature sizes that are in the truly microfluidic regime ( $<100\ \mu\text{m}$ ). The fundamental problem is that commercial tools and materials, which excel in many other application areas, have not been developed to address the unique needs of microfluidic device fabrication. Consequently, we have created our own stereolithographic 3D printer and materials that are specifically tailored to meet these needs. We show that flow channels as small as  $18\ \mu\text{m} \times 20\ \mu\text{m}$  can be reliably fabricated, as well as compact active elements such as valves and pumps. With these capabilities, we demonstrate highly integrated 3D printed microfluidic devices that measure only a few millimeters on a side, and that integrate separate chip-to-world interfaces through high density interconnects (up to 88 interconnects per square mm) that are directly 3D printed as part of a device chip. These advances open the door to 3D printing as a replacement for expensive cleanroom fabrication processes, with the additional advantage of fast (30 minute), parallel fabrication of many devices in a single print run due to their small size.

#### 8:40am MN+NS+PS-WeM-3 A Novel Inkjet Printing Technology Based on Plasma Conversion of Metal-Salt Based Inks for the Fabrication of Microfabricated Sensors, *Y Sui, M Sankaran, Christian Zorman*, Case Western Reserve University

Inkjet printing is a leading additive manufacturing method to produce patterned metal thin films on flexible substrates. The most commonly-used inks consist of colloidal nanoparticle suspensions that employ organic molecules to stabilize the nanoparticles from agglomeration and precipitation. High temperature ( $>200^\circ\text{C}$ ) treatment is used after printing to remove the insulating organics and sinter the nanoparticles. The thermal step can limit printing on polymers such as PDMS, paper, and other temperature-sensitive substrates. Moreover the selection of metals is limited by those available in nanoparticle suspensions, with the most popular being Ag.

In this paper, we present the development of an ink-jet printing process that uses a particle-free, stabilizer-free ink and low-temperature plasma to produce electrically conductive metallic patterns on temperature-sensitive substrates. The inks are comprised of a metal salt, a solvent, and a viscosity modifier tailored to enable printing using a Dimatix DMP3000 series printer. The as-printed structures are treated with a low-pressure argon plasma which serves to convert the metal salt-based structures to metal structures with conductivities that approach bulk values. To date, we have demonstrated the process for Sn, Pb, Bi, Cu, Pt, Ag, Pd, and Au-based inks. The plasma-treated structures exhibit a high degree of porosity that can be as high as 70%, making them particularly well suited for use as active elements in microfabricated sensors. The extended paper will present details pertaining to the printing process, material characterization and testing of mechanical, chemical and biological sensors fabricated by this printing process.

#### 9:00am MN+NS+PS-WeM-4 Full Wafer Thickness Through Silicon Vias for MEMS Devices, *Andrew Hollowell, E Baca, D Dagel, M Jordan, L Menk, K Musick, T Pluym, J McClain*, Sandia National Laboratories

A significant amount of development has been achieved integrating TSVs with standard silicon (Si) substrates; however, there are unique challenges associated with integrating TSVs with MEMS substrates. Industry has achieved TSV integration through a dependence on substrate thinning, a TSV reveal approach. However, often these MEMS devices depend on the thickness of the substrate for controlling the radius of curvature of the substrate, such as throughout Sandia's ultra-planar multilevel MEMS technology (SUMMIT™). TSV filling relies on tight control of the fluid kinetics during the electroplating process and the ability to balance the

diffusion of  $\text{Cu}^{2+}$  and organic suppressor molecules throughout the depth of the via in order to realize a void-free fill of the TSV. In this work we have extended the filling model for  $60\ \mu\text{m}$  deep TSVs, developed by Tom Moffatt and Dan Josell, up to  $675\ \mu\text{m}$  deep TSVs.

In addition to the thickness constraints for MEMS integration, often MEMS devices are realized through unique release processes and are dependent on high temperature anneals. The most common release process is a hydrofluoric acid (HF) based release to selectively remove supporting oxide films and preserve the Si features that make up the MEMS components. The necessity to release structure in selective etchants presents additional challenges for integrating TSVs with MEMS components. We have overcome this challenge through the integration of additional capping layers which are selectively removed after the MEMS release. In order to accommodate the need for high temperature anneals we have removed the use of metal in the MEMS device and instead used doped silicon. The Cu TSVs are then integrated with the device after all the high temperature anneals are complete, making direct electrical contact to the doped Si. In this work, we present our integration approach for mating Cu TSVs with doped Si MEMS contacts and our plating approach for superfilling  $675\ \mu\text{m}$  deep,  $100\ \mu\text{m}$  wide TSVs.

This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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#### 9:20am MN+NS+PS-WeM-5 Scaling from Die Level to Full 150 mm Wafer TSV Filling through Fluid Dynamics Modeling and Current Controlled Deposition, *Ehren Baca, M Jordan, L Menk, K Musick, P Yeh, A Hollowell*, Sandia National Laboratories

In this work we have developed a novel methanesulfonic acid (MSA) based electrolyte with a single suppressor additive for filling  $100\ \mu\text{m}$  diameter  $675\ \mu\text{m}$  deep through silicon vias (TSVs). Contrary to conventional three-additive systems we have achieved bottom up super filling of these large TSVs with a single suppressor additive. This bottom up super filling mechanism is dependent on a strict balance between applied potential and diffusion of both suppressor molecules and  $\text{Cu}^{2+}$  ions. The bottom up deposition was developed through die level plating experiments on sample sizes approximately  $1\ \text{in}^2$ . We control the solution replenishment by connecting the sample, both electrically and mechanically, to an aluminum rod and rotating the sample in solution. The rotation rate is directly correlated to the velocity of solution moving across the opening of the vias and therefore related to the solution replenishment inside the TSVs. At first a potentiostatic approach was used to supply a sufficient potential to break down the suppressor with a reference electrode in our plating cell.

Mapping the current, during deposition allowed us to develop a galvanostatic plating process.

Experiments were performed to scale this plating process to be compatible with production level electroplating tools. The fluid dynamics and applied current are significantly different on production plating tools. The tools do not come equipped with reference electrodes and in some cases, they have multiple anodes for current partitioning to control the uniformity of the electric field. Further, the wafer rotates about the center of the wafer and baffles are integrated into the tool to control the uniformity of a fountain type fluid replenishment system. With the wafer rotated about its center, there is a large variance in the velocity of fluid at different radii along the wafer. In this work, we present a set of scaling experiments performed on die with incremental increases in sample size to clearly map the die level plating parameters to a full wafer plating tool and achieve uniform TSV filling across a  $150\ \text{mm}$  wafer.

This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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9:40am **MN+NS+PS-WeM-6 Batch Level Electroless Under Bump Metallization for Singulated Semiconductor Die**, *Matthew Jordan, E Baca, J Pillars, C Michael, A Hollowell*, Sandia National Laboratories

Multi project-wafers (MPWs) allow multiple customers to share the cost of a manufacturing run from an advanced semiconductor foundry. This offers a cost-effective solution for low volume the fabrication or prototyping of application specific integrated circuits (ASICs). This practice is especially appealing for those in academia or government that often only require small quantities of devices for research or niche applications. With many products on a wafer, all the products must adhere to the same strict design rules. In practice this means that the final metallization is made using AlCu. This presents challenges for advanced packaging of MPW die as AlCu is not compatible with conventional flip chip solder because of oxidation of the AlCu metal. Further complicating the integration of MPW die is the fact that they are singulated prior to delivery, preventing the use of lithography, and thus ruling out the deposition and patterning of solder-compatible metals over the AlCu. This leaves the use of electroless plating schemes to prepare MPW die for 2.5D/3D die stacking.

We propose a batch process to facilitate MPW die processing through the electroless under bump metallization (UBM) process. This process includes passivation of the Si die sidewalls post dicing, MPW die mounting, batch Zn or Sn immersion followed by electroless Ni, electroless Pd, immersion Au (ENEPIG) or electroless Ni, immersion Au (ENIG) UBM deposition for reliable, UBM deposition. We have demonstrated 2.5D integration of batch processed, AlCu finished die that have UBM deposited using this process to an interposer using electroplated Cu pillars bumps and Au bumps.

Supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

11:00am **MN+NS+PS-WeM-10 MEMS-based Atomic Force Microscopy Probes: From Electromechanical to Optomechanical Vibrating Sensors**, *Bernard Legrand*, LAAS-CNRS, France; *L Schwab*, LAAS-CNRS, Univ Toulouse, France; *P Allain, I Favero*, MPQ, CNRS, Univ Paris Diderot, France; *M Faucher, D Théron*, IEMN, CNRS, Univ Lille, France; *B Walter*, Vmicro SAS, France; *J Salvetat*, CRPP, CNRS, Univ Bordeaux, France; *S Hentz, G Jourdan*, CEA-LETI, France

**INVITED**

Scanning probe microscopy has been one of the most important instrumental discoveries during the last quarter of the last century. In particular, atomic force microscopy (AFM) is a cross-disciplinary technique able to provide sample morphology down to the atomic scale. It offers invaluable tools to support the development of nano-sciences, information technologies, micro-nanotechnologies and nano-biology. For more than 20 years, boosting the scan rate of AFM has been an increasingly important challenge of the community. However still today, performing routine and user-friendly AFM experiments at video rate remains unreachable in most cases. The conventional AFM probe based on a micro-sized vibrating cantilever is the major obstacle in terms of bandwidth and resonance frequency.

Following a brief description of the context of the work, the talk will first describe the development of AFM probes based on MEMS devices that make use of ring-shaped microresonators vibrating above 10 MHz. A focus will be dedicated to the electrical detection scheme. Based on capacitive transduction and microwave reflectometry, it achieves a displacement resolution of  $10^{-15}$ m/VHz, allowing the measurement of the thermomechanical vibration of the MEMS AFM probes in air. Imaging capability obtained on DNA origamis samples at a frame rate greater than 1 image/s will be shown as well as investigation of block copolymer surfaces to elucidate the tip-surface interaction when vibration amplitudes are lower than 100 pm.

In the following, our recent research direction at the convergence of the fields of micro/nanosystems and VLSI optomechanics on silicon chips will be presented. Optomechanical resonators allow indeed overcoming the resolution limitation imposed by usual electromechanical transduction schemes. Here, we will introduce fully optically driven and sensed optomechanical AFM probes which resonance frequency is above 100 MHz and Brownian motion below  $10^{-16}$ m/VHz, paving the way for high-Speed

AFM operation with exquisite resolutions at sub-angstrom vibration amplitudes.

11:40am **MN+NS+PS-WeM-12 Suppressing Secondary Grain Growth in  $\text{Sc}_{0.125}\text{Al}_{0.875}\text{N}$  Using a CMOS Compatible Electrode**, *Giovanni Esteves, M Berg, M Henry, B Griffin, E Douglas*, Sandia National Laboratories

The electromechanical response of AlN can be enhanced by doping Sc into AlN up to ~43%. Challenges arise in processing high Sc doped AlN films due to the presence of secondary grain growth. Templating  $\text{ScAl}_{1-x}\text{N}$  (ScAlN) from a platinum bottom electrode has shown immense success in yielding highly textured *c*-axis ScAlN without the presence of secondary grain growth. However, platinum is not complementary metal-oxide-semiconductor (CMOS) compatible which makes it unattractive to those in industry. There is a need for a new bottom electrode that suppresses secondary grain growth while maintaining CMOS compatibility. In this work,  $\text{Sc}_{0.125}\text{Al}_{0.875}\text{N}$  and AlN films were grown on various underlying CMOS compatible metal stacks. Optimal film microstructure and texture was obtained for films deposited on highly textured {111} AlCu<sub>0.05</sub> bottom metal. AlN and ScAlN thicknesses were 750 nm and 850 nm and showed rocking curves of 0.81° and 1.09°, respectively. Atomic force microscopy was used to determine the presence of secondary grain growth and film roughness. The success of this bottom metal stack is attributed to lattice matching and low surface roughness which allows for highly oriented *c*-axis textured AlN and ScAlN. This work presents a metal stack that allows for the creation of higher Sc-doped AlN films while maintaining a high-quality microstructure and texture. Therefore, allowing for commercialization of Sc-doped AlN technologies which are capable of higher electromechanical coupling coefficients than AlN devices.

*This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.*

12:00pm **MN+NS+PS-WeM-13 A Low Voltage NEMS Relay. Design, Fabrication and Challenges**, *A Solot, A Dinescu*, National Institute for R&D in Microtechnologies (IMT), Bucharest, Romania; *M Fernandez-Bolaños, A Ionescu*, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland; *Gina Adam*, National Institute for R&D in Microtechnologies (IMT Bucharest), Romania

Microelectromechanical switches (MEMS) have a wide variety of applications, such as in radio frequency switching, sensing, etc. thanks to their high non-linearity, sensitivity and integrability. Unfortunately, traditional MEMS typically need tens of volts for actuation, which prevents their use in applications that require low voltage CMOS circuitry. The typical size for MEMS switches is ~100µm, but recent work [1] has shown a scalable two-terminal nanoelectromechanical (NEMS) switch with low actuation voltage (<1V). The pipe clip structure is based on side edge actuation and is prone to reliability issues due to stiction since the electrode width is quite large (~300nm). We propose a structure based on a protrusion (dimple) small contact area and tunable dimensions during the fabrication process.

This paper presents a nanoelectromechanical switch with <3V actuation voltage. The proposed design is based on a fixed bottom electrode line (Pt) and two pillars that support a metallic nanowire (~100nm wide) beam line.

Since stiction is a significant issue for this device, the design includes protrusions (dimples) positioned in the center of the beam line with the scope of creating a small contact point with the bottom electrode. The structure is electrostatically actuated through a voltage applied on the beam while the fixed electrode is grounded. A small air gap between the beam and the bottom electrode line is crucial for reducing the actuation voltage, but can cause problems during the release. Finite element simulations in Comsol Multiphysics 5.2 were used to investigate the constraint space needed for the design of a NEMS relay with such a low actuation voltage, as needed for compatibility with a typical 3.3V CMOS technology. These simulations informed the geometries explored in the fabrication of a low power NEMS device with a double-clamped metallic beam. The surface micromachining process was developed to have a low-thermal budget (< 200 °C) and be multilayer CMOS compatible. The fabrication flow was based on SiO<sub>2</sub> as an inorganic sacrificial layer for

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obtaining a clean release. A mix of photolithography and e-beam lithography, lift-off and dry etching steps utilized are described, and challenges during the electrical characterization are discussed. Future design iterations focused on different beam designs are also presented.

J.O. Lee, Y.H. Song, M.W. Kim, M.H. Kang, J.S. Oh, H.H. Yang, and J.B. Yoon, "A sub-1-volt nanoelectromechanical switching device", *Nature nanotechnology*, 8(1), 36-40, 2013.

## Nanometer-scale Science and Technology Division Room 203A - Session NS+2D+AN+MN+MP+SE-WeM

### Micro, Nano and Opto Mechanics

**Moderators:** Robert Ilic, National Institute of Standards and Technology (NIST), Alokik Kanwal, NIST Center for Nanoscale Science and Technology

8:20am **NS+2D+AN+MN+MP+SE-WeM-2 The Collective Behavior of Large Ensembles of Coupled MEMS Cantilevers with Varying Natural Frequencies**, *Christopher Wallin*, National Institute of Standards and Technology, Center for Nanoscale Science and Technology; *N Dick*, Tel Aviv University, Israel; *R De Alba*, *D Westly*, National Institute of Standards and Technology, Center for Nanoscale Science and Technology; *S Grutzik*, Sandia National Laboratories; *A Zehnder*, *R Rand*, Cornell University; *V Aksyuk*, National Institute of Standards and Technology, Center for Nanoscale Science and Technology; *S Krylov*, Tel Aviv University, Israel; *R Ilic*, National Institute of Standards and Technology, Center for Nanoscale Science and Technology

The collective behavior of nonlinear, coupled micro- and nano-electromechanical (M/NEMS) resonators has been shown to exhibit a host of nontrivial dynamics including abrupt pattern switching, multistability, hysteresis, intrinsically localized modes, and synchronization. Additionally, M/NEMS resonator arrays are extremely responsive to environmental perturbations making them excellent candidates for sensing applications when operated linearly. With our work, we investigate the collective dynamics of coplanar interdigitated arrays of prismatic microcantilevers operating in both the nonlinear and linear regimes.

Two opposing, partially interdigitated cantilever arrays with 100 cantilevers apiece were fabricated using a silicon-on-insulator wafer. The device consists of a unique geometry in which each array has cantilever lengths expanding linearly across the device in opposite directions giving a distribution of natural frequencies. The arrays were engineered to allow for large scale, nonlinear out-of-plane beam deflections through the removal of the entire silicon handle layer beneath the active array area.

For sufficiently large drive amplitudes, the resonators begin oscillating via combination parametric resonance (CPR) across the entire array. The CPR driven oscillations occur across a broad frequency band. The tunable coupling between nearest-neighbor cantilevers through fringing electrostatic fields provides a mechanism to vary the CPR response. Due to the sizable deflections, the device's nonlinearities are apparent including hysteresis effects. Our experimental results are supported and expanded by the development of a reduced order model based on the Galerkin decomposition which generates the leading features of our data including the CPR band.

When operating in the linear regime, the natural modes of the array have localized characteristics whereby a limited number of beams oscillate at each of the natural mode frequencies. Operating the device at higher harmonics increases mode separation as the propagation bands stretch. The distinct resonant peak separation coupled with the spatially confined modal response make higher harmonic operation of tailored, variable length cantilever arrays well suited for a variety of resonant based sensing applications.

8:40am **NS+2D+AN+MN+MP+SE-WeM-3 Piezoelectric Optomechanical Systems**, *Krishna Coimbatore Balram*, University of Bristol, UK **INVITED** Nanoscale optomechanical systems, which rely on the strong interactions between co-localised optical and mechanical modes in nanoscale cavities, have been explored for a wide variety of applications ranging from sensing to signal transduction [Aspelmeyer et al., *Rev. Mod. Phys.* (2014)]. In this talk, I will discuss piezoelectric optomechanical platforms for efficient signal transduction between the radio frequency (RF) and optical domain. We use GaAs as our model platform (Balram et al., *Optica* (2014), *Nature Photonics* (2016), *Phys. Rev. Applied* (2017)) and discuss some of the

research opportunities and challenges in this field, especially as we move towards higher mechanical frequencies ( $> 10$  GHz).

9:20am **NS+2D+AN+MN+MP+SE-WeM-5 Absolute Deflection Measurements in a MEMS/NEMS Fabry-Perot Interferometry System**, *Roberto De Alba*, *C Wallin*, *G Holland*, National Institute of Standards and Technology; *S Krylov*, Tel Aviv University, Israel; *R Ilic*, National Institute of Standards and Technology

Micro- and nano-electromechanical systems (MEMS/NEMS) are among the most sensitive devices for detection of ultra-weak forces, masses, and displacements. The small scale of these structures affords them very high frequencies (MHz to GHz), high quality factors, rich nonlinear phenomena, and many other beneficial traits that make them ideal as sensors and testbeds of fundamental physics. Fabry-Perot laser interferometry is a widespread and robust technique for probing MEMS/NEMS devices because it is non-invasive and provides exceptional motion sensitivity ( $\approx 1$  pm/Hz<sup>1/2</sup>) from DC to roughly 100 MHz. This technique utilizes the silicon substrate beneath the MEMS/NEMS device as a static reference mirror; doing so provides common-mode noise rejection in contrast to interferometers that use an external reference mirror. Furthermore, this technique is compatible with a wide range of MEMS/NEMS materials, from common insulators and conductors to graphene and other atomically-thin membranes.

Despite the many strengths of this experimental technique, it suffers from two main drawbacks. Firstly, the measured signal becomes highly nonlinear for device displacements larger than  $\lambda/4$ , where  $\lambda$  is the laser wavelength. Secondly, because the silicon backplane is immovable, there is no simple or established technique for calibrating device motion. As such, published results utilizing this setup typically report deflection in "arbitrary units." In this work, we focus on fully characterizing the nonlinear aspects of a MEMS/NEMS Fabry-Perot interferometer and developing a generalized approach to calibrate device motion based the wavelength of light. We will demonstrate how to quickly and accurately determine both static and dynamic MEMS/NEMS deflection by measuring reflected laser power in the time domain. We will further show how a single calibration (made in the large-amplitude regime) can be applied to subsequent measurements taken at lower amplitudes as well as to measurements taken in the frequency domain (e.g. by a lock-in amplifier). Lastly, we will demonstrate the capability of imaging the first three vibrational modes of a MEMS cantilever by using a scanning laser.

9:40am **NS+2D+AN+MN+MP+SE-WeM-6 Silicon on Insulator Electrostatically Actuated Bistable Cantilevers for Resonant Displacement/Acceleration Sensing**, *O HaLevy*, *E Benjamin*, *N Krakover*, *Y Kessler*, *Slava Krylov*, Tel Aviv University, Israel

Resonant accelerometers incorporating vibrating beams demonstrate higher sensitivity and better robustness when compared to their statically operated counterparts. Electrostatic softening of the beams electrostatically coupled to the proof mass allows to enhance sensitivity of the resonant accelerometers. The displacement of the proof mass affects the gap between the mass and the beam and results in the beam's frequency change, which is maximal in the vicinity of the critical limit points of the voltage-deflection curve. The use of the snap-through buckling for this purpose is attractive since it is fully reversible and does not involve contact. While double-clamped curved bistable beams designed to demonstrate snap-through behavior can serve as resonant acceleration sensors [1], they suffer from high sensitivity to temperature and residual stress.

In this work we report on a design and fabrication of an electrostatically actuated bistable resonant cantilever [2], which demonstrates low sensitivity to the temperature and to the residual stress. The concept is based on the tailoring of the actuating force in such a way that the beam in its initial "as fabricated" configuration is positioned in the vicinity of the critical point. This is achieved by designing the actuating electrodes to be significantly thicker than the beam. Our reduced order (RO) Galerkin and coupled finite elements (FE) models results show that the frequency to deflection sensitivity of the  $L = 150 \mu\text{m}$  long,  $h = 16 \mu\text{m}$  wide and  $d = 1 \mu\text{m}$  thick cantilever can reach 20 Hz/nm. This is equivalent to the frequency to acceleration sensitivity of 388 Hz/g, obtained for the case of a  $4 \text{ mm} \times 4 \text{ mm} \times 20 \mu\text{m}$  proof mass.

While the model results are promising, fabrication of the device incorporating the beams and the electrodes of the different thicknesses is challenging. We demonstrate fabrication of the 50  $\mu\text{m}$  thick electrodes and  $\approx 6 \mu\text{m}$  thick cantilevers from the same device layer of a Silicon on Insulator (SOI) wafer. Two-stage deep reactive ion etching (DRIE) process was used

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for an initial patterning of the electrodes and of the cantilever and for the thinning of the beams. We discuss the details of the fabrication process and preliminary experimental results.

[1] N. Krakover, B. R. Ilic and S. Krylov, "Displacement Sensing Based on Resonant Frequency Monitoring of Electrostatically Actuated Curved Micro Beams," *J. Micromech. Microeng.*, **26**, pap. 115006, 2016.

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11:00am **NS+2D+AN+MN+MP+SE-WeM-10 Electron-Photon-Phonon Hybrid Systems Based on Compound Semiconductor Mechanical Resonators, Hiroshi Yamaguchi**, NTT Basic Research Laboratories, Nippon Telegraph and Telephone Corporation, Japan **INVITED**

The use of compound semiconductor heterostructures as the elastic materials in the fabrication of micro/nanomechanical resonators has advantages, such like the improvement of mechanical properties through strain engineering, optomechanical transduction through carrier-mediated coupling, and piezoelectrically controllable nonlinearity [1]. The hybrid properties play the essential role in the operation where the different excitations of phonons, photons, and electrons are mutually interacted. In this invited talk, I will review our recent activities studying the electronic [2], photonic [3], and phononic [4] functions in GaAs-based mechanical resonators.

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11:40am **NS+2D+AN+MN+MP+SE-WeM-12 Size Dependent Mechanics of Elastomers, Le Li, N Alsharif, K Brown**, Boston University

Elastomers are fascinating materials owing to the fact that their mechanical properties are dictated by entropy. Due to their low modulus, chemical compatibility, and ease of processing, they are widely applied in fields from soft lithography to medical devices. While it is well accepted that they exhibit fascinating size-dependent mechanical properties when confined to thin films, the structure-property relationships that govern confined elastomers are difficult to unambiguously determine due to the mechanical influence of rigid support structures and unavoidable contributions from adhesion. As a result, a consensus regarding the moduli of elastomeric thin films has not emerged. Here, we present a combined computational and experimental approach to measure the true mechanical properties of thin elastomer films. First, we utilize extensive finite element simulations to determine a correction to the Hertzian contact model that depends upon a dimensionless film thickness and the polymer Poisson's ratio. In order to verify this correction, films composed of three different thermoplastics were studied using an atomic force microscopy (AFM) nanoindenting. Interestingly, all three were observed to soften when confined to films thinner than 100 nm, in agreement with literature reports of buckling experiments. To explore softer elastomeric materials that exhibit categorically different behavior, we extended this correction to the Johnson-Kendall-Roberts (JKR) model that considers adhesion in contact mechanics. Elastomer thin films with different crosslink densities were studied using AFM nanoindentation and finite element simulation to determine their moduli. We observed a drastic stiffening on all elastomeric films when they were confined to sub-micrometer thicknesses. More importantly, modulus of all sub-100 nm elastomer films converges to the same trend regardless of bulk crosslink density. We present a hypothesized molecular model explaining this behavior. These results shed new light on the nanomechanics of elastomers and provide a general process for exploring size-dependent mechanics in polymers.

## 2D Materials Focus Topic

### Room 201B - Session 2D+MN+NS+SS-WeA

#### IoT Session: Surface Chemistry, Functionalization, Bio and Sensor Applications

**Moderator:** Daniel Walkup, National Institute of Standards and Technology (NIST)/ University of Maryland, College Park

2:20pm **2D+MN+NS+SS-WeA-1 Impact of Hydrogen on Graphene-based Materials: Atomistic Modeling and Simulation of HRSTEM Images**, *C Guedj*, Univ. Grenoble Alpes, CEA, LETI, France; *L Jaillet, F Rousse, Stéphane Redon*, Univ. Grenoble Alpes, CNRS, INRIA, Grenoble INP\*, LJK, France, France

The hydrogen energy transition is highly probable, because hydrogen is the most abundant element in the universe and represents an ideal “green” source of energy. Meanwhile, the safe hydrogen production and storage remains a major challenge still in progress. Potential production and storage materials include graphene. In terms of electronic and optoelectronic applications, hydrogen can tune the bandgap of graphene [1]. Hydrogen also plays a major role during the Chemical Vapour Decomposition (CVD) growth of graphene [2]. Hence, hydrogenated graphene-based materials are potentially relevant for various technological applications.

To understand and optimize the device efficiency and the interface engineering, it is advantageous to perform advanced nanocharacterizations, linked to numerical modelling and simulations. This task is particularly difficult, because hydrogen is labile and prone to rapid reorganization. This structural evolution may be monitored with transmission electron microscopy (TEM) techniques [3,4,5], but in spite of significant progresses, the direct detection of hydrogen with High Resolution Scanning Transmission Electron Microscopy (HRSTEM) or energy-loss spectroscopy still remains a serious challenge.

We investigate here the interaction of hydrogen with graphene using the Brenner module of the SAMSON software platform <https://www.samson-connect.net> and we propose an original methodology to characterize its structural arrangement at the atomic scale by simulating HRSTEM images to interpret experimental results. In particular, we compare the effect of hydrogen on dark field (DF), bright field (BF), high-angle annular dark field (HAADF) and annular bright field (ABF) images, to estimate the best technique suited to hydrogen detection.

In addition, we present the effect of carbon vacancies and adatoms on the stability of hydrogen coverage, associated to the HRSTEM signatures of the most stable configurations. These results provide the necessary building blocks to analyze the structure and energetics of hydrogenated graphene-based materials at the atomic scale.

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2:40pm **2D+MN+NS+SS-WeA-2 High Density H<sub>2</sub> and He Plasmas: Can They be used to Treat Graphene?**, *Hasan-Al Mehedi*, Laboratoire des Technologies de la Microélectronique, CNRS-UJF, France; *D Ferrah*, Cea, Leti, Minatec, France; *J Dubois*, Laboratoire des Technologies de la Microélectronique, CNRS-UJF; *C Petit-Etienne*, Laboratoire des Technologies de la Microélectronique, CNRS-UJF, France; *H Okuno*, Cea, Inac/sp2m/lemma; *V Bouchiat*, Institut Néel, CNRS-UJF-INP; *O Renault*, CEA/LETI-University Grenoble Alpes, France; *G Cunge*, Laboratoire des Technologies de la Microélectronique, CNRS-UJF, France

Since graphene and other 2D materials have no bulk, a major issue is their sensitivity to surface contaminations, and the development of cleaning processes is mandatory. High density plasmas are attractive to treat (clean, dope, pattern) 2D materials because they are a mature industrial technology adapted to large area wafer. However, in these plasmas the substrate is bombarded by a high flux of both thermal radicals and reactive ions with typical energy above 10 eV, which can easily damage atomic layer thin materials. We have investigated systematically the interaction of H<sub>2</sub> and He inductively coupled plasmas (ICP) with graphene in industrial reactors. We report a specific issue associated with the use of H<sub>2</sub> plasma: they etch the inner part of plasma reactor walls, thus releasing impurities in the plasma, most notably O atoms that etch graphene and Si atoms

which stick on it. The presence of parasitic oxygen presumably explains the discrepancies found in the literature regarding the impact of reactive plasmas on graphene damages. To get rid of this issue we propose to use a fluorinated aluminum chamber. In this case, fluorine atoms which are shown to be harmless to graphene are the only impurity in the plasma. Under such conditions H<sub>2</sub> ICP plasma is shown to clean graphene without damages if the ion energy is kept below about 15 eV.

3:00pm **2D+MN+NS+SS-WeA-3 Novel Binder-free Ag@Ni(OH)<sub>2</sub> over Graphene/Ni Foam and Glucose Sensing**, *Tong-Hyun Kang, J Yu*, DGIST, Republic of Korea

Graphene combining with metal nanoparticles or other compounds is widely recognized to be a viable strategy to assemble high-activity catalysts. Unique properties of high conductivity and transparency, 2D morphology, and high stability in acid and alkaline solutions make graphene an excellent electron transfer medium on the interface of graphene/active materials as catalysts. Among them, graphene/metal nanoparticle (G/MNP) composites have been attracting more interest because of remarkably enhanced catalytic property, which is ascribed to a synergic effect from the interface of graphene and active sites. In general, reducing agents and electrodeposition methods have been employed to *in-situ* reduce metal ions such as Au<sup>3+</sup>, Pt<sup>4+</sup>, Ag<sup>+</sup>, and Cu<sup>2+</sup> (M<sup>n+</sup>) to MNPs on the graphene to form G/MNP composites. In this study, graphene is grown on nickel foam (NF) by chemical vapor deposition (CVD), which is directly used for MNP deposition. Different from bare NF, special phenomenon is observed that the graphene-coated nickel foam (GNF) composite can greatly speed up the electrodeless reduction of M<sup>n+</sup> ions on the surface of the graphene. Interestingly, the MNP deposition and Ni(OH)<sub>2</sub> nanosheet assembly simultaneously occur on the GNF. Binder-free Ni(OH)<sub>2</sub>-wrapped Ag hybrid developed on the GNF (Ag@Ni(OH)<sub>2</sub>-GNF) is found to serve as an efficient electrochemical sensor because of its unique structure. A low detection limit of 0.3 μM and high sensitivity are achieved for the glucose detection, which confirms that the hierarchical electrode structure of Ag@Ni(OH)<sub>2</sub>-GNF composite is highly effective to have extensive applications.

3:20pm **2D+MN+NS+SS-WeA-4 Surface Modification and Magnetization of Carbon Based Nanostructures**, *Rina Tannenbaum*, University of Stony Brook; *I Kim*, Gachon University, Korea; *S Sharma*, University of Stony Brook

We describe here a novel synthesis for the facile decoration of carbon nanomaterials (CNM) with monodisperse γ-Fe<sub>2</sub>O<sub>3</sub> magnetic nanoparticles.

These procedures were developed for multi-walled carbon nanotubes (MWNTs), reduce graphene (rGO) and reduced graphene nanoroses (rGO-roses). The decoration of these carbon nanomaterials with γ-Fe<sub>2</sub>O<sub>3</sub> induces the magnetization of these structures and opens up the potential for their use in novel applications.

CNM/γ-Fe<sub>2</sub>O<sub>3</sub> magnetic nanostructures were fabricated through a modified sol-gel process using ferric nitrate nonahydrate, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O as a starting material. Nucleation sites for the iron oxide were generated at the CNM surface due to the electrostatic interaction between Fe (III) ions and the carboxylate surface groups of acid-treated CNMs. The occurrence of gelation was inhibited by the addition of the NaDDBS surfactant, before the addition of propylene oxide, which is a gel promoter. The surfactant interfered in the growth stage of the iron oxide nanoparticles (gel phase) through to the coordination of the NaDDBS molecules to the iron (III) centers due to the attraction between the negatively-charged hydrophilic head of the surfactant and the positively-charged iron. The rGO-roses were further fabricated from decorated rGO via a novel emulsion process.

Various characterization methods were used to confirm the formation of well-defined maghemite nanoparticles, and show that they were tethered to the walls of the CNMs. The tethered γ-Fe<sub>2</sub>O<sub>3</sub> nanoparticles imparted magnetic characteristics to the CNMs, which in turn, became superparamagnetic. The magnetic carbon nanotubes and magnetic rGO were introduced into a polymer matrix [P] and were oriented parallel to the direction of an externally-applied magnetic field. The anisotropic nanocomposites were then used as anodes in lithium ion batteries. The magnetic rGO-roses were used as nuclear magnetic resonance contrast material.



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4:20pm **2D+MN+NS+SS-WeA-7 Chemical Modification of Graphene and Carbon Nano Tubes as viewed by XPS and NEXAFS Spectroscopies underpinned by DFT Spectra Simulation**, *C Ehlert, E Donskyi*, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany; *P Girard-Laurialt*, McGill University, Canada; *R Illgen*, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany; *A Lippitz*, Bundesanstalt für Materialforschung und -prüfung (BAM); *R Haag, M Adeli*, Freie Universität Berlin, Germany; **Wolfgang Unger**, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany

Graphene is a two-dimensional carbon network with unique properties. However, its low solubility, poor reactivity and the limited accessibility of a well-defined basal plane are major challenges for applications. An ideal method to overcome these problems is the covalent attachment of functional molecules to its surface which enable further reactive modifications for specific applications. There are several technologies for surface functionalization of graphene and related CNT materials. To get control on the functionalization process and to optimize the performance of the modified surfaces analytical tools for surface chemical characterization are required. X-ray absorption (NEXAFS) and photoelectron spectroscopy (XPS) have been identified to be rather powerful here [1-3]. Specifically, NEXAFS spectroscopy underpinned by quantum chemical spectrum simulations [4] is unique in a way to address changes of aromaticity and defect formation at the graphene surface during functionalization.

For relevant surface modification technologies, we present examples on how NEXAFS and XPS are fit for purpose. All presented modifications aim on the production of platforms for defined functional 2D nanomaterials, as for example multi-functional hybrid architectures. In detail we investigated:

- A wet chemical method for covalent functionalization of graphene sheets by a one-pot nitrene [2+1] cycloaddition reaction under mild conditions. Here a reaction between 2,4,6-trichloro-1,3,5-triazine and sodium azide with thermally reduced graphene oxide (TRGO) results in defined dichlorotriazine-functionalized graphene sheets.
- Graphene and carbon nanotube functionalized by Vacuum-Ultraviolet (VUV) induced photochemical or r.f. cw low pressure plasma processes to introduce amino, hydroxy or brominated functionalities.

To underpin finger-print information delivered by C K-edge NEXAFS we studied the effects of selected point and line defects as well as chemical modifications for a single graphene layer model by density functional theory based spectrum simulations.

## Acknowledgement

We acknowledge support by the team at the BESSY II synchrotron radiation facility in Berlin, Germany, as well as Dr. A. Nefedov (Karlsruhe Institute of Technology, KIT) from the HE-SGM Collaborate Research Group.

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4:40pm **2D+MN+NS+SS-WeA-8 Elastic Spongy Graphene-Functionalized Silicon Anode with Excellent Cycle Stability in Li battery**, *Byong-June Lee, J Yu*, DGIST, Republic of Korea

Graphite plays a prominent role as a typical anode material in the lithium ion batteries (LIBs) because of its high lithiation-dilithiation reversibility and low voltage window. Unfortunately, the capacity is limited to 372 mAh g<sup>-1</sup>[1,2]. To search for materials with higher lithium storage capacity, a great number of investigations on metal oxides (or sulfides), Sn, P, and Si have been carried out in recent decades. Among these materials, silicon can make alloy with lithium in the form of Li<sub>22</sub>Si<sub>5</sub> to deliver a highest theoretical gravimetric capacity of ~4200 mAh g<sup>-1</sup>, and thus is considered to be one of the most promising anode materials for next generation LIB. It is worth mentioning that its quite low delithiation potential and high lithium storage capacity can provide a wide working voltage window and energy density, which enable promising potential application in electric vehicles. However, those advantages are seriously offset by a great challenge of large volume expansion during lithiation process and the resultant breakage of bulk silicon particles and solid electrolyte interface (SEI), which causes a serious

damage to the electrode structure and thus gives rise to a fast decay of the specific capacity [3].

In this work, novel 3D spongy grapheme (SG)-functionalized silicon is for the first time demonstrated by chemical vapor deposition for a LIB anode, which can overcome the common silicon anode issues such as poor conductivity and volume expansion of Si as well as transfer of Li ion towards the Si. The elastic feature of graphene has excellent function to self-adaptively buffer the volume variation during charge-discharge process. In particular, different from traditional graphene or carbon shells (core-shell and yolk-shell), the spongy 3D graphene networks provide much improved unique functions with excellent long-cycle stability and rate capability. The Si@SG electrode exhibits excellent cycling performance with high reversible specific capacity [4]. A superior 95% capacity retention is achieved after 510 cycles. All the electrochemical performances get benefits from the well-designed functional SG shells, where interconnected nano-graphene structure not only guarantees a high conductive network but also provides more free paths for excellent mass transfer in addition to self-adaptive buffering capability.

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5:00pm **2D+MN+NS+SS-WeA-9 Electrical and Structural Changes of Multilayer WSe<sub>2</sub> Transistors: Atmospheric Gas Adsorption and Long Term Aging**, *Anna Hoffman*, University of Tennessee Knoxville, usa; *M Stanford, C Zhng*, University of Tennessee Knoxville; *I Ivanon*, Oak Ridge National Laboratory; *A Oyedele, D Mandrus*, University of Tennessee Knoxville; *L Liang, B Sumpter, K Xiao*, Oak Ridge National Laboratory; *P Rack*, University of Tennessee Knoxville

Interest in transition metal dichalcogenides (TMDs) for opto-electronic applications has been growing recently due to their unique properties and layered structure. Surface science and DFT simulations have corroborated p-type doping and n-type suppression of O<sub>2</sub> and H<sub>2</sub>O adsorption in TMDs however, electrical characterization has not been fully investigated. This presentation will demonstrate the reversible suppression of n-type conduction in ambi-polar WSe<sub>2</sub> via water adsorption, which logically has a larger impact as the WSe<sub>2</sub> thickness decreases. Additionally, we observe a reversible and irreversible n-type suppression and p-type doping which we attribute to H<sub>2</sub>O adsorption and isoelectronic oxygen chemisorption, respectively, at chalcogen vacancies during long term aging in atmosphere over 6 weeks. Finally, controlled oxygen plasma exposure is utilized to oxidize and p-type dope WSe<sub>2</sub>. We will overview our device fabrication and electrical testing procedure, and transfer characteristics for our as-fabricated devices for various WSe<sub>2</sub> thicknesses in air and in vacuum will be illustrated. Long-term (6 week) electrical measurements in both air and vacuum are compared to the as-fabricated devices. Finally, complementary atomic force microscopy and Raman Spectroscopy are used to characterize the devices

5:20pm **2D+MN+NS+SS-WeA-10 Ion Migration Studies in Exfoliated 2D Molybdenum Oxide via Ionic Liquid Gating for Neuromorphic Device Applications**, *Cheng Zhang, P Pudasaini, A Oyedele*, University of Tennessee Knoxville; *A Ivelev, K Xiao, T Ward*, Oak Ridge National Laboratory; *D Mandrus*, University of Tennessee Knoxville; *O Ovchinnikova*, Oak Ridge National Laboratory; *P Rack*, University of Tennessee Knoxville

The formation of an electric double layer in ionic liquid (IL) can electrostatically induce charge carriers and/or intercalate ions in and out of the lattice which can trigger a large change of the electronic, optical and magnetic properties of materials and even modify the crystal structure. We present a systematic study of ionic liquid gating of exfoliated 2D molybdenum trioxide (MoO<sub>3</sub>) devices and correlate the resultant electrical properties to the electrochemical doping via ion migration during the IL biasing process. A nearly nine orders of magnitude modulation of the MoO<sub>3</sub> conductivity is obtained for the two types of ionic liquids that are investigated. In addition, notably rapid on/off switching was realized through a lithium-containing ionic liquid whereas much slower modulation was induced via oxygen extraction/intercalation. Time-of-Flight Secondary Ion Mass Spectrometry confirms the Li intercalation. Results of short-pulse tests show the potential of these MoO<sub>3</sub> devices as neuromorphic computing elements due to their synaptic plasticity.

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5:40pm **2D+MN+NS+SS-WeA-11 Infrared Absorption of Nanometer-scale Thermally Reduced Graphene Oxide**, *Erin Cleveland, J Nolde, G Jernigan, E Aifer*, U.S. Naval Research Laboratory

Strong optical absorption is of fundamental importance to infrared (IR) sensors, and it has been well established that graphene is one of the strongest IR absorbing materials, with approximately 2.3% absorption in the IR and visible regions for a single layer. While reduced graphene oxide (RGO) may not have quite the same absorption strength as graphene on a layer-by layer basis, we believe that by controllably reducing the oxygen concentration within the GO films we can increase the absorption of the RGO film to approach that of graphene. RGO films, unlike graphene, however, can be made arbitrarily thick, allowing for much higher absorbance in a single pass. Here we explore the use of GO films of varying thickness and UHV annealing temperature to achieve near 100% midwave IR absorbance in a quarter-wave reflection filter structure consisting of an RGO film on top of a  $\lambda/4$ -thick SiO<sub>2</sub> layer deposited over a Ti/Pd mirror.

Graphene oxide (GO) is a two-dimensional network consisting of a graphene basal plane decorated with oxygen moieties in the forms of carbonyls, epoxies and hydroxyl groups resulting in variable number of  $sp^2$  and  $sp^3$  bonding geometries. Theory indicates that GO bandstructure and transport are strongly dependent on the ratio of the  $sp^2$  and  $sp^3$  bonding fractions, and therefore, by controllably removing specific oxygen groups, one can tune its electronic, optical, and chemical properties. While it is difficult to modify the oxygen concentration using wet chemical processing, e.g. using hydrazine, GO can be thermally reduced in H<sub>2</sub>-N<sub>2</sub> forming gas with more precise control. However, this procedure, like chemical reduction promotes the occurrence of N and H impurities, as well as carbon vacancies within the graphene basal plane, significantly degrading the electronic quality of the film. Here, we use ultrahigh vacuum ( $<10^{-9}$  Torr) annealing to controllably reduce the oxygen concentration in GO films while introducing fewer defects. Not only does UHV annealing prevent the introduction of impurities, but after oxygen removal, dangling bonds tend to reform in hexagonal structure. UHV annealing also enables in-vacuo measurement by x-ray photoelectron spectroscopy (XPS) to precisely characterize the overall oxygen concentration and its distribution within alcohol, epoxy and carbonyl species. Following an 800°C UHV anneal for example, we find that the oxygen concentration is reduced to ~5%, and the layer spacing is equivalent to epitaxial graphene grown on the C-face of SiC.

6:00pm **2D+MN+NS+SS-WeA-12 Dielectric Properties of Carbon Nanomembranes prepared from aromatic Self-Assembled Monolayers and their application in All-Carbon Capacitors**, *Xianghui Zhang, P Penner, E Marschewski*, Bielefeld University, Germany; *T Weimann, P Hinze*, Physikalisch-Technische Bundesanstalt, Braunschweig, Germany; *A Götzhäuser*, Bielefeld University, Germany

Carbon nanomembranes (CNMs) are two-dimensional materials that are made by cross-linking self-assembled monolayers (SAMs) of aromatic molecules via low energy electron irradiation. Previous studies of the charge transport in molecular junction incorporating SAMs and CNMs of oligophenyl thiols has been carried out by using conical eutectic Gallium-Indium (EGaln) top-electrodes<sup>1</sup> and conductive probe atomic force microscopy (CP-AFM)<sup>2</sup>. Additional investigations of the dielectric properties of pristine SAMs and CNMs were performed by impedance spectroscopy on EGaln tunneling junctions. Here we demonstrate the fabrication and characterization of all-carbon capacitors (ACCs) composed of multilayer stacks of dielectric CNMs that are sandwiched between two types of carbon-based conducting electrodes: (1) trilayer graphene made by chemical vapor deposition and mechanical stacking; (2) pyrolyzed graphitic carbon (PGC) made by pyrolysis of cross-linked aromatic molecules. The junction area is defined by the width of electrode ribbons, ranging from 1 to 2500  $\mu\text{m}^2$ , and the separation between two electrodes is tuned by the number of CNM layers. The frequency response of nanocapacitors was measured with an LCR meter. A dielectric constant of 3.5 and a capacitance density of up to 0.5  $\mu\text{F}/\text{cm}^2$  were derived from the junction capacitance. A dielectric strength of 6.2 MV/cm was determined. These results show the potential of carbon nanomembranes to be used as dielectric components in next-generation environment-friendly carbon-based molecular electronic devices.

<sup>1</sup> P. Penner, X. Zhang, E. Marschewski, F. Behler, P. Angelova, A. Beyer, J. Christoffers, A. Götzhäuser, *Journal of Physical Chemistry C*, 2014, 118, 21687.

<sup>2</sup> X. Zhang, E. Marschewski, P. Penner, A. Beyer and A. Götzhäuser, *Journal of Applied Physics*, 2017, 122, 055103.

**Extending Additive Manufacturing to the Atomic Scale**  
**Focus Topic**

**Room 102B - Session AM+MP+NS-WeA**

**Atomic Scale Manipulation with SPM**

**Moderator:** Sven Rogge, University of New South Wales, Australia

2:20pm **AM+MP+NS-WeA-1 Advanced Scanning Probe Lithography: Processes, Nanopatterning and Nanoelectronics**, *Ricardo Garcia*, Inst Ciencia Materiales Madrid, CSIC, Spain  
**INVITED**

The nanoscale control afforded by scanning probe microscopes has prompted the development of a wide variety of scanning probe-based patterning methods. Some of these methods have demonstrated a high degree of robustness and patterning capabilities that are unmatched by other lithographic techniques. However, the limited throughput of scanning probe lithography has prevented their exploitation in technological applications. Here, we review the fundamentals of scanning probe lithography and its use in materials science and nanotechnology. We introduce several methods, interactions and/or processes such as chemical, mechanical or thermal that enable the tip to modify surfaces. In particular, the presentation is focused on describing the fundamentals and applications of oxidation SPL for nanopatterning and device fabrication of nanoscale field-effect transistors, quantum dots, biosensors and molecular architectures involving a variety of systems from 2D materials to biomolecules; from self-assembled monolayers to silicon.

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3:00pm **AM+MP+NS-WeA-3 Integrated Devices made Using Atomically Precise Advanced Manufacturing**, *D Ward, D Campbell, M Marshall, T Lu, L Tracy, L Maurer, A Baczweski, Shashank Misra*, Sandia National Laboratories

Atomically precise advanced manufacturing (APAM) has enjoyed considerable success in demonstrating high profile physics demonstrations, such as the single atom transistor. However, a considerably broader application space would open up if other transistor elements could be integrated with APAM devices, opening the door to high gain and room temperature operation. However, integration is generally limited by the high temperatures required to prepare pristine silicon substrates for APAM, and by the low temperatures at which phosphorus donors diffuse away once placed into silicon once APAM is complete. Here, we describe progress in integrating metal-dielectric surface gates to achieve high gain, and compensation doping to achieve room temperature operation. The Digital Electronics at the Atomic Limit (DEAL) project is supported by Sandia's Lab Directed Research and Development Program, and was performed in part at the Center for Integrated Nanotechnologies, a U.S. DOE Office of Basic Energy Sciences user facility. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

4:20pm **AM+MP+NS-WeA-7 Electrical Transport Properties of Si:P  $\delta$ -layer Devices**, *Ranjit Kashid, X Wang, P Nambodiri, J Hagmann*, National Institute of Standards and Technology (NIST); *S Schmucker*, University of Maryland College Park; *J Wyrick, C Richter, R Silver*, National Institute of Standards and Technology (NIST)

Si:P has been realized as one of the ideal systems for donor-based quantum computation. Site-selective doping of phosphorous atoms at the atomic scale using Scanning Tunneling Microscopy (STM) lithography on the Si(100) 2x1:H surface enables the fabrication of these devices. In the past, our group has demonstrated that degenerately doped & well confined Si:P monolayers can be fabricated using phosphine dosing and low-temperature Molecular Beam Epitaxy (MBE). In addition, a wide range of 1D and 2D nanoscale devices can be fabricated by combining STM lithography and low-temperature MBE. Here, we present magnetotransport and low-frequency 1/f noise measurements on degenerately doped 1D nanowires, 2D Hall Bars, and van der Pauw structures defined using STM lithography. Specifically, we investigate the

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dephasing mechanism and present a comparative analysis of transport between STM patterned and mesa etched Si:P  $\delta$ -layer van der Pauw structures to further elucidate the effects of STM patterning on transport properties.

4:40pm **AM+MP+NS-WeA-8 Atomically Precise Tip Positioning for Automated Writing of Atomic-scale Devices**, James Owen, E Fuchs, J Randall, J Von Ehr, Zyvex Labs

Hydrogen depassivation lithography has enabled unprecedented sub-nanometer precision in the positioning of dopant atoms in silicon,[1] advancing the field of silicon quantum electronics. It has also been used for localised atomic layer deposition of Si [2] and TiO<sub>2</sub>[3].

In pursuit of our overall vision of Atomically Precise Manufacturing, we are pursuing a number of tactics towards automated fabrication of atomically precise structures. STM lithography vectors are automatically aligned to the surface atomic lattice, and patterns can be input as geometric shapes or arbitrary bitmaps. To improve tip position precision, we have developed real-time creep and hysteresis error correction. Using this, we have previously demonstrated open-loop atomic precision patterning over length scales up to 100 nm. Above this scale, where hysteresis errors are more significant, we are able to reduce the position errors by ~90%.

In parallel with real-time position corrections, we have developed automatic fiducial alignment routines. The tip position can either be aligned to previously-drawn patterns or to deliberate fiducial marks. A large pattern can therefore be stitched together from write fields within which atomic precision can be obtained. Thus, precise patterning can be scaled to large areas.

In the burgeoning field of Quantum Metamaterials[4], large arrays of single dopant atoms are required, with extreme position precision and very high yield. However, the yield of the current thermal process for P limits the yield to 70%[5].

Based on recent work on removal of H from surface PH<sub>2</sub> species[6], we are developing a tip-assisted incorporation process, which prevents the recombination and desorption process. For this application, we need to write single-dimer patterns to adsorb only one PH<sub>3</sub> molecule. For these small patterns, Automated Feedback Controlled Lithography is used, so as to remove exactly the required H atoms from the surface. We are working to improve the detection of the H atom removal, using not only the spike in tunnel current but also the change in the local barrier height [7].

1. M. Fuechsle, et al. *Nat Nano* **7** 242-246 (2012) DOI:: 10.1038/nnano.2012.21

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3. J. B. Ballard, J. H. G. Owen, et al. *J. Vac. Sci. Technol. B*, **32**, 41804 (2014).

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5. J. G. Keizer, S. Koelling, P. M. Koenraad, and M. Y. Simmons *ACS Nano* **9** 12537-12541 (2015)

6. Q. Liu, Y. Lei, X. Shao, F. Ming, H. Xu, K. Wang, and X. Xiao, *Nanotechnology*, **27**(13), 135704, (2016).

7. F. Tajaddodianfar, S. O. R. Moheimani, J. Owen, and J. N. Randall, *Rev. Sci. Instrum.*, **89**(1), 13701, (2018)

5:00pm **AM+MP+NS-WeA-9 Kilobyte Scale Data Storage through Autonomous Atom Assembly**, S Otte, David Coffey, Delft University of Technology, Netherlands **INVITED**

The ability to manipulate individual atoms by means of scanning tunneling microscopy (STM) opens up opportunities for storage of digital data on the atomic scale. Recent achievements in this direction include data storage based on bits encoded in the charge state, the magnetic state, or the local presence of single atoms or atomic assemblies. However, a key challenge at this stage is the extension of such technologies into large-scale rewritable bit arrays. We demonstrate a digital atomic scale memory of up to 1 kilobyte (8,000 bits) using an array of individual surface vacancies in a chlorine terminated Cu(100) surface. The chlorine vacancies are found to be stable at temperatures up to 77 K. The memory, crafted using scanning tunneling microscopy at low temperature, can be read and re-written automatically by means of atomic scale markers, and offers an areal density of 502 Terabits per square inch, outperforming state-of-the-art hard disk drives by three orders of magnitude.

5:40pm **AM+MP+NS-WeA-11 Extending the Capabilities of STM-based Dopant Device Fabrication**, T Skeren, N Pascher, S Köster, Andreas Fuhrer, IBM Research - Zurich, Switzerland **INVITED**

Since the invention of the first bipolar transistor, integrated circuits have evolved to incredibly complex, ultra-scaled devices with on the order of 10<sup>9</sup> transistors per chip. Even if these devices no longer rely on bipolar technology, excellent control of highly doped regions is still a critical factor for device performance. Moreover, single dopant atoms in a silicon crystal or nanoscale silicon transistors are thought to be candidates for spin qubits with a long spin lifetime.

The hydrogen resist lithography technique is capable of preparing atomic scale planar dopant devices. This is enabled by a large difference in chemical reactivity of the bare and hydrogen passivated Si (001): 2x1 surface. Using a scanning tunneling microscope (STM), the hydrogen layer of the H:Si (001) surface is locally desorbed with nanometer precision, exposing areas of reactive Si. When a gaseous dopant precursor such as phosphine or diborane is introduced, the hydrogen layer acts as a resist and the dopants stick only to the desorbed areas. Compared to conventional fabrication methods, hydrogen resist lithography enables degenerate d-doping with sub-nanometer lateral resolution and abrupt doping profiles.

We have extended the hydrogen-resist technique to p-type doping with diborane and present electrical transport measurements on p-type dopant wires and a simple planar pn-junction fabricated by STM patterning.

In addition, we have developed a CMOS compatible device platform for STM-based atomic-scale device fabrication. The scheme uses pre-fabricated samples with electrical contacts and alignment markers and a hydrogen terminated, reconstructed Si:H(001) surface that is protected from the ambient environment by a capping chip.

The sample surface can be used directly for STM-patterning and atomic device fabrication after in-situ removal of this capping chip. After STM device-fabrication the samples are reintegrated into the CMOS workflow by hydrophobic bonding for wafer scale contacting.

Full functionality of this approach is demonstrated with magnetotransport measurements on degenerately doped STM patterned Si:P nanowires up to room temperature, made possible by the use of silicon on insulator substrates.

## Biomaterial Interfaces Division

### Room 104B - Session BI+AC+AS+HC+NS+SS+TF-WeA

#### Current and Future Stars of the AVS Symposium II

Moderator: David Boris, U.S. Naval Research Laboratory

2:20pm **BI+AC+AS+HC+NS+SS+TF-WeA-1 Medard W. Welch Award Lecture: A Surface Scientist's Journey from Small Molecules to Biomolecules and Biomaterials**, David G. Castner<sup>1</sup>, University of Washington **INVITED**

Surface science plays an important role in a wide range of research and development areas such catalysis, biomaterials, microelectronics, clean energy and corrosion. The toolbox of surface scientist allows us to easily move across research topics and make significant impacts in both industrial and academic settings. The typical surface scientist is an expert in multiple techniques, surface modification, sample preparation/handling and instrumentation. We have all benefited from the significant and numerous advances that have occurred in the past 40 years in terms of improved instrumentation, introduction of new techniques and development of sophisticated data analysis methods, which has allowed us to perform detailed analysis of increasing complex samples. For example, comprehensive analysis of surfaces and surface immobilized molecules with modern surface science instrumentation provides an unprecedented level of detail about the immobilization process and the structure of the immobilized molecules. Results from x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), near edge x-ray absorption fine structure (NEXAFS), surface plasmon resonance (SPR) and quartz-crystal microbalance with dissipation (QCM-D) biosensing, atomic force microscopy, and sum frequency generation (SFG) vibrational spectroscopy combined with computation methods such as molecular dynamic (MD) and Monte Carlo (MC) simulations provide important information about surface chemistry and structure. However, even with the advances that have been achieved with these powerful surface science

<sup>1</sup> Medard W. Welch Award Winner

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techniques, there still remain many significant challenges for surface scientist. These include characterizing the surface chemistry and structure of nanoparticles, determining the atomic level structure of complex molecules bound to surfaces, 3D imaging of samples, and improved sample preparation methods that maintain materials in a relevant state when using ultra-high vacuum based analysis techniques.

This talk will discuss my adventures as a surface scientist starting from chemisorption and reactivity studies of small molecules on single crystal surfaces followed by industrial catalysis research and eventually moving to biomedical surface analysis with side ventures into areas such as clean energy. It has been an exciting journey and I will use it to provide some examples of the multidisciplinary nature of surface science as well as discuss opportunities for addressing future challenges.

**3:00pm BI+AC+AS+HC+NS+SS+TF-WeA-3 Invited Talk-Future Stars of AVS Session: Making, Studying, and Designing Hierarchically Structured Soft Materials, Keith A. Brown<sup>1</sup>, Boston University**

Nature realizes extraordinary materials by structuring them precisely from the molecular scale to the macroscopic scale. While nature may have perfected this process over evolutionary time scales, synthetically recapitulating this level of control is tremendously difficult due to the large number of length scales involved and our limited knowledge of interactions between these scales. Faced with the daunting challenge of synthetically realizing soft hierarchical materials, we have adopted a three pronged strategy to: (1) make structures with control from the molecular scale to the macroscopic scale by directing bottom-up growth processes with top-down control, (2) learn how the properties of such materials emerge from their hierarchical structure, and (3) design the best performing structures using novel approaches borrowed from machine learning and autonomous research. In this talk, we will on report recent progress in this complementary areas of making, studying, and designing hierarchical materials. In particular, we will focus on two major classes of materials, nanoparticle-based structures where the assembly and organization of particles leads to emergent mechanical properties at the bulk scale and polymer-based materials where we are connecting the synthesis, patterning, and properties of polymer structures across scales. In addition to lessons about the fundamental properties of hierarchically organized soft matter, we will highlight the synergies possible when combining, synthesis, detailed characterization, and advances in materials design.

**3:20pm BI+AC+AS+HC+NS+SS+TF-WeA-4 Invited Talk-Future Stars of AVS Session: Vapor Phase Infiltration for Transforming Polymers into Hybrid Materials: Processing Kinetics and Applications, Mark Losego<sup>2</sup>, Georgia Institute of Technology**

Vapor phase infiltration (VPI) is an emerging processing technology for infusing polymers with inorganic constituents to create new organic-inorganic hybrid materials with novel chemical, electrical, optical, and/or physical properties. These new hybrid materials have demonstrated applications including chemical separations, photovoltaics, and microelectronics patterning. This talk will focus on our development of a fundamental VPI processing kinetics phenomenology to create a pathway for rational design of material composition and structure. By measuring VPI compositional profiles as a function of space or time and temperature, we can extract fundamental energy barriers for the sorption, diffusion, and reaction processes and delineate amongst different rate limiting steps. In our materials development, we often find that partial infiltration of a polymer film, fiber, or foam is sufficient to impart desired properties; so rational design of the infiltration kinetics can enable desired performance without waste in processing time or materials. Here, we will demonstrate several examples including our work to create chemically insoluble polymers and membranes. We find, for example, that infiltration depths of about 0.75 microns are sufficient to yield PMMA chemically insoluble in organic solvents regardless of whether it is in a thin film geometry or a macroscopic plexiglass object of centimeters in dimension. In PIM-1 membranes used for chemical separations, we find that we can achieve > 30 wt% inorganic loading with a single infiltration exposure. After infiltration, these membranes become stable in new separations solvents that previously swelled and/or dissolved the polymer.

(Submitted for the Future Stars of the AVS Symposium.)

**4:20pm BI+AC+AS+HC+NS+SS+TF-WeA-7 Invited Talk-Future Stars of AVS Session: Surface Preparation Methods for the Selective Oxidation of Ethanol to Acetaldehyde over TiO<sub>2</sub>/Au(111), Ashleigh Baber<sup>3</sup>, D Boyle, J Wilke, V Lam, D Schlosser, James Madison University**

Obtaining a molecular-level understanding of the reaction of alcohols with heterogeneous model catalysts is critical for improving industrial catalytic processes, such as the production of hydrogen from alcohols. The use of reducible oxides provides a source of oxygen on Au(111) for the reaction of ethanol, which is easily regenerated in the presence of an oxygen background. The redox chemistry of small alcohols, including methanol and propanol, has been studied on Au(111) supported TiO<sub>2</sub> nanoparticles, yet the active site for the chemistry has not yet been elucidated. Depending on the surface preparation conditions, Au(111) supported TiO<sub>2</sub> nanoparticles react with small alcohols to form either reduced and oxidized products. The desire to selectivity form oxidized or reduced products merits an investigation of alcohol reactivity over differently prepared TiO<sub>2</sub>/Au(111) surfaces. In this work, a systematic study of ethanol reactivity over several TiO<sub>2</sub>/Au(111) surfaces elucidates the effect of surface conditions on the selectivity of the reaction between ethanol and TiO<sub>2</sub>/Au(111). The reactivity of the surface for ethanol oxidation was altered by controlling the oxidation state of TiO<sub>x</sub> (x<2). Atomic force microscopy (AFM) provides information regarding the structure of the Au(111) supported TiO<sub>2</sub> nanoparticles and ultrahigh vacuum temperature programmed desorption (TPD) monitors the selectivity of the reaction between ethanol and TiO<sub>2</sub>/Au(111). The presence of TiO<sub>2</sub> nanoparticles on Au(111), ~25 nm in diameter, led to the catalytic conversion of ethanol to acetaldehyde at temperatures greater than 400 K. Low coverages of fully oxidized TiO<sub>2</sub> nanoparticles on Au(111) are active for the selective oxidation of ethanol to form acetaldehyde.

**4:40pm BI+AC+AS+HC+NS+SS+TF-WeA-8 Invited Talk-Future Stars of AVS Session: Single Atom Catalysis: An Atomic-Scale View, Gareth Parkinson<sup>4</sup>, TU Wien, Austria**

Single-atom catalysis is a rapidly emerging area of research that aims to maximize the efficient usage of precious metals through "single atom" active sites. Although catalytic activity has been demonstrated for several single-atom catalyst systems, an inability to accurately characterize the catalyst based on single atom active sites ensures that that the field remains controversial, and little is really known about how a single atom adsorbed on a metal oxide support catalyzes a chemical reaction. In this lecture, I will describe how we are addressing the crucial issues of stability and reaction mechanism using a surface science approach. The work is based on the magnetite (001) surface, which exhibits an unusual reconstruction based on subsurface cation vacancies.

The surface stabilizes ordered arrays of metal adatoms (of almost any variety) with a nearest neighbor distance of 0.84 nm to unprecedented temperatures as high as 700 K. Crucially, because the geometry of the adatoms is uniform and precisely known, reactivity experiments are performed on a well-defined model system, and theoretical calculations can be performed to shed light on the mechanisms at work. Several examples of our recent work will be used to illustrate the trends discovered to date, including how strong CO adsorption destabilizes Pd and Pt adatoms leading to rapid sintering, and how extraction of lattice oxygen from the metal-oxide is central to catalytic activity in the CO oxidation reaction.

**5:00pm BI+AC+AS+HC+NS+SS+TF-WeA-9 Invited Talk-Future Stars of AVS Session: Multimodal Chemical and Functional Imaging of Nanoscale Transformations Away from Equilibrium, Olga Ovchinnikova<sup>5</sup>, Oak Ridge National Laboratory**

The key to advancing energy materials is to understand and control the structure and chemistry at interfaces. While much of the dynamic chemistry can be studied on macro-scale systems, there is a lack of means to localize chemical measurements and correlate them to nanoscale structure of the material. Through a unique merger of advanced scanning probe microscopy and mass spectrometry techniques rooted in innovative data processing and control algorithms, we are now able to understand the interplay between chemical and physical functionality at the fundamental length using multimodal chemical imaging. This multimodal imaging transcends existing techniques by providing nanoscale structural imaging with simultaneous quantitative nanomechanical properties and

<sup>1</sup> Future Stars of the AVS

<sup>2</sup> Future Stars of the AVS

<sup>3</sup> Future Stars of the AVS

<sup>4</sup> Future Stars of the AVS

<sup>5</sup> Future Stars of the AVS

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quantitative chemical analysis. In this talk I will discuss how we have developed and used this capability to visualize dynamic material transformations at interfaces, to correlate these changes with chemical composition, and to distill key performance-centric material parameters. One exciting capability is that the AFM can be used to drive materials away from equilibrium at the nanoscale with highly localized electric fields. This allows field confinement effects on localized chemistry in materials to be locally probed, especially at interfaces. This in turn yields direct information on key energy related questions such as electron and ion motion distribution and transport at and between interfaces. We have applied this approach to the study of systems and processes that underlie energy capture, conversion and storage, including photovoltaics and oxide ferroelectrics, which have historically eluded comprehensive understanding of the mechanisms behind the spatially heterogeneous interfacial chemistry and its link to material performance. Overall, I will focus on ways to unlock the mystery of active interface formation through intertwining data analytics, nanoscale elemental and molecular characterization, with imaging; to better grasp the physical properties of materials and the mechanistic physics-chemistry interplay behind their properties.

**5:20pm BI+AC+AS+HC+NS+SS+TF-WeA-10 Invited Talk-Future Stars of AVS Session: Expanding the Structural Toolkit to Characterize Heavy Actinide Complexes, Rebecca Abergel<sup>1</sup>, Lawrence Berkeley Lab, University of California, Berkeley; G Deblonde, A Mueller, P Ercius, Lawrence Berkeley National Laboratory; A Minor, Lawrence Berkeley Lab, University of California, Berkeley; C Booth, W de Jong, Lawrence Berkeley National Laboratory; R Strong, Fred Hutchinson Cancer Research Center**

Structural characterization of actinide elements from actinium to einsteinium can be a challenging task due to the high radioactivity and limited availability of some of the isotopes of interest. However, significant work is needed to address a certain lack of understanding of the fundamental bonding interactions between those metal centers and selective ligands. Such understanding presents a rich set of scientific challenges and is critical to a number of applied problems including the development of new separation strategies for the nuclear fuel cycle, the need for decontamination after a nuclear accident or the use of radioisotopes for new cancer treatments. Our studies utilize luminescence sensitization, UV-Visible, X-ray absorption, and X-ray diffraction spectroscopic techniques as well as transmission electron microscopy and electron energy loss spectroscopy to investigate specific heavy actinide coordination features. Using simple inorganic complexes but also strong hard oxygen-donor ligands as well as more elaborate higher molecular weight protein assemblies allows the differentiation of heavy actinide species even when limited to minute amounts of materials. Innovative structural characterization approaches based on X-ray absorption, X-ray diffraction and electron microscopy that were applied to series of isostructural systems and used to derive coordination trends in the later 5f-element sequence will be discussed.

**5:40pm BI+AC+AS+HC+NS+SS+TF-WeA-11 Invited Talk-Future Stars of AVS Session: Trends in Adsorbate Interactions with Bimetal Surfaces, Liney Arnadottir<sup>2</sup>, L Sprowl, Oregon State University**

Surface chemistry plays an important role in a large range of applications and technologies, such as catalysis and electrocatalysis, device fabrication through film growth, and degradations through oxide formation, carbonization, and corrosion. Bimetal surfaces are of increasing interest for single atom catalysis and corrosion resistance of alloys. Previous studies have shown correlations between adsorbate interactions and d-band shifts for different metals as well as for alloying effects of metal sandwich structures, but for mixed metal surfaces the nature of the adsorption site can change (ensemble effect) as well as the number of electrons in the surface layer which effects the d-band center. Here we explore correlations of adsorbate interactions with mixed metal surfaces through density functional theory calculations of adsorbate interactions with different facets, (100) and (111), of pure Ni and eleven Ni-based surface alloys as well as Ni in different host metal. We find that the addition of surface alloying atom has little effect on the binding of CO and C but C binding varies for different facets. On the other hand, O binding is highly dependent on the alloying element due to ensemble effect. This has an interesting effect on the predicted reaction energies of CO dissociation which is endothermic on the (111) facet and exothermic on the (100) facet governed by C interactions but the changes in the reaction energy within each facet are mostly governed by the ensemble effect on O adsorption.

The relationship between the formation energy of the mixed metal surface and adsorbate interactions will also be discussed.

## **MEMS and NEMS Group Room 202B - Session MN+2D+AN+NS-WeA**

### **IoT Session: MEMS for IoT: Chemical and Biological Sensing**

**Moderators:** Robert Davis, Brigham Young University, Sushma Kotru, University of Alabama

**2:20pm MN+2D+AN+NS-WeA-1 BioMEMS for Eye Applications, Yu-Chong Tai, California Institute of Technology**

**INVITED**

The field of Micro-Electro-Mechanical Systems (MEMS) has advanced tremendously for the last 20 years. Most noticeably, however, the field has mostly advanced in microsensors such as pressure sensors, accelerometers, gyros, microphones for cell phone and smart instrumentation applications. Looking forward though, in my opinion, one future direction of MEMS/NEMS is for micro biomedical devices. Among many possible biomedical applications, one challenging but promising branch is micro implants. Why micro implants? Body tissues (especially neurons), once severely damaged, do not repair or regenerate easily and often leave behind permanent debilitating deficits. Engineering implant technologies to interface intact tissues and/or to replace defective functions have continued to be the main solutions for many diseases. As our world is facing more severe aging population problems, significant growth in implant applications is foreseeable. As a matter of fact, there are already many existing commercially available implants such as pacemakers and cochlear implants, but they all have a lot to improve. For examples, cardiovascular implants like defibrillator and pacemakers are still bulky, mechanically rigid, power hungry, and functionally limited. The future implants should be even smaller, flexible, power efficient and more versatile so that they can be used at places not possible before. This talk will review the research of implants done at the Caltech MEMS lab. More specifically, this talk will focus on bioMEMS implant devices to treat eye diseases. Examples of devices will cover the four major ophthalmic diseases, i.e., cataract, glaucoma, age-related macular disease and diabetic retinopathy that make of close to 80% of world blindness. It is believed that BioMEMS can also have many other opportunities for other organs in our body too.

**3:00pm MN+2D+AN+NS-WeA-3 Real-Time, Single Cell, Size Measurements using a Facile, Multimode Microwave Resonator, Selim Hanay, H Aydogmus, A Secme, H Pishch, M Kelleci, Bilkent University, Turkey**

In this study, a facile microwave sensor is designed and fabricated to detect transient cells one by one and extract their morphological and electrical properties in real time, without labeling. Multiple modes can be measured by multiplexing the electronic frequencies to obtain multiple analytic parameters at the same time. Our simple fabrication technique obviates the need to complex fabrication process.

A microwave sensor, in the form of a microstrip line resonator, is constructed by fixing copper tape at the back and the front side of a 1-mm thick glass slide. The backside is covered entirely with the tape to form a ground plane; on the front side, a copper tape was thinned within a few mm, extended across the slide and terminated with SMA feed through. On the front side, just below the copper tape, five capillary tubes are placed to transport the cells into the active sensing region. Microwave signals are transmitted through the two SMA ports at the end of the glass slide, perpendicular to the flow. The resonator is formed by electrically shorting the input/output ports. An initial characterization of the device is done by using spectrum analyzer so that its first and second order mode frequencies are obtained.

A digital phase-locked loops (PLL) measurement system with PI controller was constructed to track the resonance frequencies of the first two modes simultaneously in real-time. The PLL system tracks the two modes of the microstrip line resonator to sense the frequency shifts originating from the passage of the cells in the capillary.

As a proof of concept, initial PLL measurements were done with DI water. As water flows through the tube, frequency shifts around 100 kHz were observed in both modes. Later on, wildtype *Skbr3* breast cancer cells were flown through the same capillary. Frequency shifts in both modes were the responses of the resonator to the passage of the *Skbr3* cells beneath microstrip-line. The ratio between the first and second mode frequency shifts can be used to determine the location of each cell by two-mode theory. The analyzed data indicates almost a constant slope, verifying the

<sup>1</sup> Future Stars of the AVS

<sup>2</sup> Future Stars of the AVS

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positional response of the sensors. Moreover, the size distribution of the cells is cumulated around a contour line for constant size as expected.

Earlier, we had detected single cells and distinguished different oncogenic cell lines using a PDMS based device. With this work, single-cell detection and sizing are accomplished with a device paradigm that does not require any lithography, metal deposition under vacuum or precise alignment of electrodes.

We acknowledge funding from European Research Council (ERC) Starting Grant (REM, 758769).

4:20pm **MN+2D+AN+NS-WeA-7 Magnetic Microsystems for Communications, Rob Candler**, University of California at Los Angeles  
**INVITED**

We are witnessing a rapid expansion of embedded devices (IoT) that have a variety of functions but a common requirement, to communicate with one another. These devices will be connected on a scale previously unseen, and they will therefore require an approach to efficiently generate and receive electromagnetic waves in a small form factor. One such approach is to rethink the way electrically small antennas operate, shifting from a current-based antenna to a voltage-coupled multiferroic antenna. Multiferroics are material systems with coupled magnetic and electrical properties, and they offer a new route for the miniaturization of magnetic field-coupled devices. Multiferroic systems allow for the conversion of magnetic flux to a voltage (and vice versa) without the need of a wire loop, avoiding inefficiencies due to Ohmic loss. *In particular, strain-coupled heterostructures* of magnetostrictive and piezoelectric materials have received much attention, as they can offer magneto-electric coupling many orders of magnitude higher than found in single-phase materials. A rapidly emerging research space in multiferroics is the development of miniature wireless devices, such as antennas and energy harvesters, taking advantage of the efficient flux-to-voltage conversion of multiferroics. In this talk, I will present work showing the impact of multiferroic coupling on the ferromagnetic resonance in GHz Bulk Acoustic Wave resonators, as well as investigations in frequency mixing from non-linear multiferroic effects. These results are all in support of our goal to create a microscale multiferroic antenna that is orders of magnitude more efficient than its classical antenna counterpart.

Furthermore, continued miniaturization of existing and emerging components that use magnets (atomic clocks, quantum computing, magnetic memory) will increase their sensitivity to external magnetic fields as well as the crosstalk between components. To address this need, we are developing techniques for on-chip magnetic shielding using multiple layers of permalloy. We will present recent results showing microscale magnetic shields fabricated by electroplating multiple permalloy layers into molds, as well as milliscale shields that were conformally electroplated on 3D printed sheaths.

5:00pm **MN+2D+AN+NS-WeA-9 MEMS-Based Resonant Sensors for IoT Applications, Oliver Brand, M Kim, P Getz**, Georgia Institute of Technology  
**INVITED**

The presentation discusses resonant microsensors, in which the measurand affects a characteristic of the resonance behavior of a resonant microstructure or a resonant circuit, such as its resonance frequency or quality factor. Resonant sensing is a very versatile sensing approach and can be adapted to a large variety of physical, chemical and biological measurands. Especially when using the resonance frequency as the sensing signal, high resolution is achievable since frequencies can be measured accurately. The presentation will highlight two possible implementations of resonant chemical sensors for Internet of Things (IoT) applications, a cantilever-based electromechanical resonator and a purely electrical L-C resonance circuit.

The first example is an electro-mechanical resonant chemical sensor based on a silicon hammerhead structure coated with a polymeric sensing film for the detection of volatile organic compounds. The presentation will highlight how proper selection of the resonance mode, in this case an in-plane vibration mode, and device geometry can improve device performance and how fast temperature modulations of the resonant sensors enable the observation of signal transients that contain additional analyte information. The sensors are fabricated using a CMOS-compatible bulk-micromachining process, have resonance frequencies between 400-800kHz and achieve sub-ppm limits of detection for select analytes.

The second example is a purely electrical resonant chemical sensor in form of a flexible and stretchable L-C (inductor-capacitor) sensor, which is battery free and can be wirelessly interrogated. To achieve stretchable

sensor characteristics, the spiral inductor and interdigitated capacitor structures are formed by a liquid metal, eutectic gallium-indium (EGaln). A subtractive reverse stamping technique is used to form the conducting liquid metal lines with dimensions as small as 2µm inside PDMS microchannels and a 3D heterogeneous integration technique is applied to vertically stack and electrically interconnect the capacitor and inductor structure. Liquid and gaseous analytes change the capacitance and are detected by wirelessly measuring the resonance frequency of the L-C circuit around 143MHz.

5:40pm **MN+2D+AN+NS-WeA-11 Etched Silicon Microcolumn For Tunable Thermal Gradient Gas Chromatography, Aaron Davis, P Schnepf, P Ng, R Vanfleet, R Davis, B Jensen**, Brigham Young University

The connection of the digital and physical world will be strengthened by chemical sensors that can measure complex mixtures of molecules. Gas chromatography is the gold standard for identification of volatiles and gases. Conventional gas chromatography systems have unparalleled resolution, but are large and power intensive. Microcolumn gas chromatographs are more portable but have dramatically reduced resolution. Combining the resolution of conventional systems with the size factor of micro systems is important for improving the affordability and portability of high performance gas analysis. Recent work has demonstrated feasibility of high resolution separation of gases in a benchtop-scale short-column system by controlling thermal gradients through the column. In order to further decrease the size of a gas chromatography system, microfabrication techniques were used to demonstrate the fabrication of a thermally controllable micro-scale gas chromatographic column with a small footprint (3 cm square). To fabricate microcolumns we are using deep-reactive-ion-etching, nickel evaporation, and wafer bonding. The design of the 20 cm column utilizes 21 individually controllable thin film heaters and solid conduction cooling to produce the desired thermal profile.

## Nanometer-scale Science and Technology Division Room 203A - Session NS+MN+PC+SS-WeA

### IoT Session: Bio at the Nanoscale

**Moderators:** Juraj Topolancik, Roche Sequencing Solutions, Liya Yu, NIST Center for Nanoscale Science and Technology

3:00pm **NS+MN+PC+SS-WeA-3 Nanoscale Label-free Imaging of Protein Molecules via Photo-induced Force Microscopy, D Nowak, Sung Park**, Molecular Vista

Nanoscale real space imaging of biological and biomaterial surface is not straightforward even with advances in microscopy techniques. Photo-induced Force Microscopy (PiFM) [1] combines infrared (IR) absorption spectroscopy and atomic force microscopy (AFM) via illumination of the tip-sample junction with tunable IR laser light and mechanical detection of forces acting on the tip in response to absorption of light by the sample. By mapping the IR absorption of the sample as a function of IR wavelength and position, nm-scale resolution is achieved in displaying the locations of heterogeneous materials on the surface of a sample. For protein molecules, amide I and II bands are readily accessible via tunable quantum cascade laser and provide ways to interrogate the molecule's local chemical environment. PiFM can provide both high resolution spectral imaging at a fixed wavenumber and full PiFM spectrum (analogue to FTIR spectrum) with a spectral resolution of 1 cm<sup>-1</sup> and spatial resolution of sub-10 nm. Results on collagen molecules, individual icosahedral protein cages, and nanoparticle/protein systems will be presented.

[1] D. Nowak et al., *Sci. Adv.* **2**, e150157 (2016).

3:20pm **NS+MN+PC+SS-WeA-4 Evaluating Reaction-diffusion Immunoassays via High-resolution Imaging Techniques, Imanda Jayawardena**, University of Queensland, Australia; *S Carrie*, Monash University, Australia; *L Grondahl*, University of Queensland, Australia

Immunodiffusion is a simple assay used for the determination of a target protein concentration in a biological sample using a distance-based measurement. The assay allows the sample containing the antigen of interest to combine with an antiserum in a gel-based substrate leading to the formation of a ring-shaped precipitate ('precipitin ring'), the size of which is proportional to target protein concentration.<sup>1</sup> Using the malarial antigen HRP2 and antisera from immunized rabbits as the model system, for the first time, we are investigating transforming the current immunodiffusion assays into a more rapid and sensitive format.

# Wednesday Afternoon, October 24, 2018

The traditional assay substrate, agarose, is a severely diffusion limited system. The porosity of the gel is a key determinant of diffusion properties and is an essential parameter required for the study and modification of the assay. However, the scientific data on agarose pore size determination is based on artefact laden microscopy images of agarose hydrogels. Thus, we have performed an in-depth investigation on best imaging techniques for accurate pore size determination. The precipitin ring structure is a band of antigen-antibody precipitate, in significant contrast with the surrounding gel substrate. A brief preliminary investigation has been reported by Fedorov et al. on precipitin ring structure<sup>2</sup>, and we have extended this work by applying microscopic imaging techniques.

For imaging hydrogels, high pressure frozen gels were subjected to cryo-SEM<sup>3</sup>, and was established as the most accurate technique to study the native structure of the gel. Atomic force microscopy was found to complement cryo-SEM data while CLSM due to its limited resolution was found to be inadequate for the imaging of hydrogels. For imaging the protein-rich precipitin ring structure, high pressure frozen ring sections were subjected to cryo-SEM, however, more meaningful insight on the ring structure was obtained in this instance through CLSM studies.

Herein, we aim to present our work described above on imaging agarose hydrogels for accurate pore size determination and imaging precipitin ring structures associated with immunodiffusion assays.

1. Mancini, G.; Carbonara, A. t.; Heremans, J. *Immunochemistry* **1965**

2. Fedorov, A. A.; Kurochkin, V. E.; Martynov, A. I.; Petrov, R. V. *Journal of Theoretical Biology* **2010**

3. Aston, R.; Sewell, K.; Klein, T.; Lawrie, G.; Grøndahl, L. *European Polymer Journal* **2016**

4:20pm **NS+MN+PC+SS-WeA-7 The Last Nanometer – Hydration Structure of DNA and Solid Surfaces Probed by Ultra-High Resolution AFM, Uri Sivan, K Kuchuk, I Schlesinger, Technion - Israel Institute of Technology, Israel** **INVITED**

Recent advancements in atomic force microscopy facilitate atomic-resolution three-dimensional mapping of hydration layers next to macromolecules and solid surfaces. These maps provide unprecedented information on the way water molecules organize and bind these objects. Since the hydration structure governs the energetics of solvation and interactions between objects immersed in solution, the new data are invaluable when trying to resolve fundamental questions such as identification of molecular binding sites and interaction mechanisms.

After a short presentation of our home-built microscope, characterized by sub 0.1 Å noise level, the talk will focus on two representative studies. The first one will disclose our recent finding that in solutions in contact with atmosphere, hydrophobic surfaces are generically coated with a dense layer of adsorbed gas molecules. This layer renders the hydrophobic interaction a certain universality, regardless of the underlying surface. The second study will present our recent success in obtaining ultra-high resolution images of DNA and 3d maps of its hydration structure. This study shows that labile water molecules concentrate along the DNA grooves, in agreement with known position of DNA binding sites.

5:00pm **NS+MN+PC+SS-WeA-9 Open-hardware, High-speed Atomic Force Microscopy using Photothermal Off-resonance Tapping, Georg Fantner, École Polytechnique Fédéral de Lausanne, Switzerland** **INVITED**

Self-assembly of protein complexes is at the core of many fundamental biological processes. To reach a comprehensive understanding of the underlying protein self-assembly reactions, high spatial and temporal resolution must be attained. This is complicated by the need to not interfere with the reaction during the measurement. Since self-assemblies are often governed by weak interactions, they are especially difficult to monitor with high-speed atomic force microscopy due to the non-negligible tip-sample interaction forces involved in current methods. Here we develop a high-speed atomic force microscopy technique, photothermal off-resonance tapping (PORT), which is gentle enough to monitor self-assembly reactions driven by weak interactions. Using photothermal actuation on ultra-small HS-AFM cantilevers we perform force-distance curves at two orders of magnitude higher rates than in conventional off-resonance methods. From the time-domain tip sample interaction we extract tip-sample force curves to quantify the “static” forces due to the cantilever deflection, and the “impact” forces due to the rapid deceleration of the cantilever tip upon impact. Experimental characterization of the tip-

sample forces in HS-tapping mode-AFM and PORT revealed that imaging forces in PORT are less than 1/5<sup>th</sup> of those exerted in conventional HS-AFM.

One of the key enabling factors for PORT is the real time control of the cantilever position using photothermal excitation. This requires low level, control of the feedback architecture and optimized AFM instrumentation. I will discuss the relevant components developed in my laboratory and explain how we share them with the broader scientific community using an open-hardware scheme.

We apply PORT to dissect the self-assembly reaction of SAS-6 proteins, which form a nine-fold radially symmetric ring-containing structure that seeds formation of the centriole organelle present in all eukaryotic cells. Using machine learning algorithms we traced hundreds of molecules over time to extract reaction kinetics from single molecule interactions. These measurements show that 9-fold closed SAS-6 rings are under pre-tension in their natural state. Due to the high temporal and force resolution provided by PORT, we found that, contrary to the current belief, more than one assembly route exists to reach the nine fold symmetry. These observation resets our current thinking about the assembly kinetics of this crucial step in cell replication.

5:40pm **NS+MN+PC+SS-WeA-11 Development of Multimodal Chemical Nano-Imaging for *in situ* Investigations of Microbial Systems, A Bhattarai, B O'Callahan, P El Khoury, Scott Lea, Pacific Northwest National Laboratory; K Park, E Muller, M Raschke, University of Colorado Boulder**

Existing genomic and biochemical methods cannot directly probe the physical connections involved in microbial metabolic processes over relevant length scales, spanning the nano-meso-micrometer spatial regimes. Determining the location and function of such biomolecules would aid in identifying the mechanisms governing microbial interactions. We are addressing these technical and conceptual gaps by developing a single multimodal chemical imaging platform that can interrogate biomolecules in living systems using three complementary label-free, nanoscale, ultrasensitive chemical imaging techniques:

Infrared scattering scanning near-field optical microscopy (IR s-SNOM)

Tip-enhanced Raman nano-spectroscopy (TERS)

Multimodal hyperspectral optical nano-spectroscopy.

We have built and developed these imaging modalities independently prior to integration into a single, multimodal chemical nanoscope. As part of our benchmarking experiments, we performed TERS measurements targeting prototypical systems and constructs and demonstrated <1 nanometer precision in ambient TERS chemical imaging measurements.<sup>[1]</sup> We also established an overall broader scope of TERS<sup>[2]</sup> and illustrated that TERS is not restricted to nanoscale chemical imaging, but can also be used to probe different aspects of local fields confined to a few nanometers. Our new setup, equipped with a hyperspectral imager, enables hyperspectral fluorescence, optical absorption, dark-field scattering, Raman scattering, and topographic imaging. Recently, we used this capability to visualize pigments in lipid monolayers and within a single live *T. lutea* cell in solution.<sup>[3]</sup> For IR s-SNOM, we are working on developing an AFM capable of bottom illumination and collection of IR light to support measurements in aqueous environments. The approach would use a piezoelectric scanner mounted ZnSe prism to enable evanescent wave illumination and collection of scattered IR light. We are also benchmarking the IR s-SNOM with the TERS and hyperspectral imaging modalities on a number of model biological systems including bacteria, collagen, and cytochromes.

This unique AFM-based instrument could be used to investigate a wide range of biomolecules through their characteristic electronic and vibrational signatures, over the nano-meso-micrometer scales. This platform will not only enable recording chemical images of single microbial cells at the subcellular level, but it will also enable mapping entire microbial communities with chemical selectivity.

1. Bhattarai A and El-Khoury PZ (2017) *Chem Commun***53**(53): 7310-7313.
2. Bhattarai A et al. (2017) *Nano Lett***17**(11): 7131-7137.
3. Novikova IV et al. (2017) *Chem Phys***498-499**: 25-32.

## 2D Materials Focus Topic

Room 201B - Session 2D+EM+MI+MN+NS+SS-ThM

### Novel 2D Materials

Moderator: Han Wang, University of Southern California

8:20am **2D+EM+MI+MN+NS+SS-ThM-2 Controlled Growth of 2D Ni-Silicate and Silica Films on Ni<sub>x</sub>Pd<sub>1-x</sub>(111) Substrates**, *Chao Zhou, X Liang, G Hutchings, Z Fishman, J Jhang, S Hu, S Ismail-Beigi, U Schwarz, E Altman*, Yale University

The discrete lattice constants and distinct chemical properties of different transition metal substrates hamper the systematic study of how the substrates can influence two-dimensional (2D) materials growth. The recent report of single-crystal epitaxial Ni-Pd alloy films with continuously tunable lattice constants open the possibilities to tackle this issue. Two-dimensional silica and transition-metal-doped silicate films prepared on metal substrates can be 2D analogues of porous bulk zeolites. In this research, 2D silica and Ni-silicate films were prepared on Ni<sub>x</sub>Pd<sub>1-x</sub> (111) substrates under different growth conditions. After annealing in 2×10<sup>-6</sup> Torr oxygen, Ni from the alloy substrates incorporates into the silica structure to form a crystalline 2D Ni-silicate structure, while an amorphous 2D silica bilayer can be observed after being annealed in 4×10<sup>-8</sup> Torr oxygen. Density functional theory (DFT) was employed to model various silica and silicate phases on Ni<sub>x</sub>Pd<sub>1-x</sub> (111) substrates. The results show that the 2D Ni-silicate films are thermodynamically stable on the substrates when the oxygen chemical potential is in the oxygen-rich range. In oxygen-deficient environments, 2D silica tends to form a stable Ni-free phase. With continuous control over the composition of NiPd alloy films, the surface strain applied on the Ni-silicate films through the lattice mismatch between the substrate and overlayer could also be continuously tuned. Only single-domain commensurate crystalline 2D Ni-silicate can be observed in zero or low-strain systems, while a second incommensurate crystalline domain which is rotated by 30° with respect to the commensurate domain can be observed when the lattice mismatch is over 1.85%.

8:40am **2D+EM+MI+MN+NS+SS-ThM-3 Topological Materials**, *Hsin Lin*, Institute of Physics, Academia Sinica **INVITED**

Topological materials host various novel quantum phases of electrons which are characterized by band topology and topologically protected surface/edge states. Despite recent progress, intense world-wide research activity in search of new classes of topological materials is continuing unabated. This interest is driven by the need for materials with greater structural flexibility and tunability to enable viable applications in spintronics and quantum computing. We have used first-principles band theory computations to successfully predict many new classes of topologically interesting materials, including Bi<sub>2</sub>Se<sub>3</sub> series, the ternary half-Heusler compounds, TlBiSe<sub>2</sub> family, Li<sub>2</sub>AgSb-class, and GeBi<sub>2</sub>Te<sub>4</sub> family as well as topological crystalline insulator (TCI) SnTe family and Weyl semimetals TaAs, SrSi<sub>2</sub>, (Mo,W)Te<sub>2</sub>, Ta<sub>2</sub>S<sub>2</sub>, and LaAlGe family. I will also highlight our recent work on unconventional chiral fermions in RhSi and several material candidates for new TCI.

9:20am **2D+EM+MI+MN+NS+SS-ThM-5 Few-Layer Rhenium Disulfide Synthesized Via Chemical Vapor Deposition**, *Michael Valentin*, Army Research Laboratory; *A Guan, A Nguyen, I Lu, C Merida, M Gomez*, University of California, Riverside; *R Burke, M Dubey*, Army Research Laboratory; *L Bartels*, University of California, Riverside

Transition metal dichalcogenides (TMDs) are exciting new materials that have received much attention due to their semiconducting properties in the direct bandgap. Well-studied TMDs, such as molybdenum disulfide (MoS<sub>2</sub>) and tungsten diselenide (WSe<sub>2</sub>), exhibit a direct bandgap in the monolayer form, but an indirect bandgap in the bulk form. Rhenium disulfide (ReS<sub>2</sub>), on the other hand, is a new TMD that is unique in its ability to retain a direct bandgap independent of thickness. By using chemical vapor deposition (CVD), few-layer ReS<sub>2</sub> is synthesized and characterized by optical methods such as Raman spectroscopy and photoluminescence. We also show characterization results for atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), transmission electron microscope (TEM), and electrical transport to determine thickness, crystallinity, homogeneity, and electrical characteristics for use in future flexible electronics.

9:40am **2D+EM+MI+MN+NS+SS-ThM-6 Dipolar Disorder of a van-der-Waals Surface Revealed by Direct Atomic Imaging**, *M Susner*, Air Force Research Laboratory; *M McGuire, Petro Maksymovych*, Oak Ridge National Laboratory

Recently, the family of transition metal thiophosphates –exhibiting ferroelectric, antiferromagnetic and correlated electron ground states – have gained attention as possible control dielectrics for the rapidly growing family of 2D and quasi-2D electronic materials [1]. Being van-der-Waals crystals, the surfaces of these materials can be created without dangling bonds, unlike those of complex oxides. Yet, because of robust insulating properties, the structure of their surfaces, the role of disorder, the structure of the topological defects in the order parameter and many other properties directly relevant to their prospective interfaces is almost entirely unknown.

Here we present the first atomically resolved imaging of CuScP<sub>2</sub>S<sub>6</sub> s carried out using cryogenic non-contact atomic force microscopy. The surface exhibits good crystalline ordering at the atomic scale, revealing contrast on sub-unit cell level. The most remarkable property is long-range commensurate modulation of the surface morphology, with a topographic amplitude of only 2-3 pm. Combined with XRD analysis of the bulk and Monte-Carlo simulation of the Ising model on triangular lattice, we propose that the modulation arises from antiferroelectric polarization domains, albeit with frustrated long-range order. The key structural ingredient for this state is centrosymmetric position of Sc<sup>3+</sup> within the layer, which forces the surrounding displacing Cu+1 ions to adopt a frustrated antiferroelectric state - in direct analogy frustrated magnetic systems. We will further discuss the peculiarities of nc-AFM imaging of this materials from the statistical analysis of the variation of images between scan, as well as the force-distance curve arrays. The possibility to directly visualize polar order opens broad opportunities to understand the atomistic aspect of ferroelectric, glassy and incommensurate phases in this material class, beginning with CuInP<sub>2</sub>S<sub>6</sub> – which exhibits Curie temperature ~315K and giant negative electrostriction [2]. Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy. Microscopy experiments were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

[1] Susner Michael A., Chyasnovichyus Marius, McGuire Michael A., Ganesh Panchapakesan, and Maksymovych Petro, *Advanced Materials* **29**, 1602852 (2017).

[2] S. M. Neumayer, E. A. Eliseev, M. A. Susner, A. Tselev, B. J. Rodriguez, S. Jesse, S. V. Kalinin, M. A. McGuire, A. N. Morozovska, P. Maksymovych, and N. Balke, *ArXiv:1803.08142 [Cond-Mat]* (2018).

11:00am **2D+EM+MI+MN+NS+SS-ThM-10 Advanced ARPES Analyzer and Momentum Microscope KREIOS 150 – Concepts and first results on layered materials and topological insulators**, *Paul Dietrich, M Wietstruck, T Kampen, A Thissen*, SPECS Surface Nano Analysis GmbH, Germany

Modern ARPES analyzers provide a high degree of parallelization in data acquisition, recording hundreds of energy and angle channels simultaneously. Additionally, integrated deflectors enable users to perform angle scanning perpendicular to the analyzer's entrance slit to record (k<sub>x</sub>, k<sub>y</sub>, E) data sets without sample rotation. However, the design of conventional analyzers implies a limited acceptance angle and corresponding accessible momentum space volume. Due to the trade-off between acceptance angle and angle resolution multiple changes in sample position and lens modes are necessary during a typical high resolution ARPES experiment. The new KREIOS 150 Energy Analyzer uses an extractor zoom lens design to overcome these limitations.

This new lens provides a full solid acceptance angle with highest angular resolution. In contrast to standard ARPES measurements with conventional hemispherical analyzers, electronic structure data from and beyond the 1<sup>st</sup> Brillouin zone is recorded without any sample movement. In addition the lens of such an instrument can work in a lateral imaging mode for microscopy as well. This enables navigation on the sample and reduces the size of the area under investigation in ARPES down to a few micrometers in diameter. This combination of large acceptance angle, high angular resolution and small acceptance area, makes this instrument the ideal tool for electronic structure studies on small samples or sample areas. The design is compact with a straight optical axis.

The capabilities of this instrument were tested at the UE 56/2 at the Bessy II synchrotron in Berlin. Specification tests show excellent angle and lateral resolution as well as small spot capability down to 2µm FOV. Subsequently



# Thursday Morning, October 25, 2018

real live samples like Graphene on Germanium were measured. Even on macroscopically rough surfaces like Graphene on NbSe<sub>2</sub> excellent ARPES and X-PEEM results could be obtained. By taking advantage of the small spot capability of the KREIOS 150 meaningful band structure data has been recorded on such patchy samples.

Acknowledgements: We thank Yu. Dedkov (University of Shanghai, China) and M. Foinin (University Konstanz) for providing beamtime and samples for the measurements with KREIOS 150 at BESSY II.

11:20am **2D+EM+MI+MN+NS+SS-ThM-11 Carbon Nanomembranes with Sub-nanometer Channels: 2D Materials for Water Purification with High Selectivity and Highest Permeance**, Y Yang, P Demytyev, N Biere, D Emmrich, P Stohmann, R Korzetz, X Zhang, A Beyer, S Koch, D Anselmetti, **Armin Götzhäuser**, Bielefeld University, Germany

Clean water is a global challenge, and membrane filtration is a key technology to achieve it. Here, we report on carbon nanomembranes (CNMs) with sub-nanometer channels that prove to be excellent water filters, combining a high selectivity with an exceptionally high water permeance. The CNMs are fabricated via the cross-linking of terphenyl self-assembled monolayers [1], resulting in a ~1.2 nm thick membrane perforated by channels with diameters below ~0.7 nm and areal densities of ~10<sup>18</sup>m<sup>-2</sup>. When tested as filter membranes, it was found that the CNMs efficiently block the passage of most gases and liquids [2]. However, water passes through, and it does this with a record-breaking permeance of ~1.1×10<sup>-4</sup> mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>. This suggests that water molecules translocate fast and cooperatively through the sub-nanometer channels. Assuming all channels in a TPT-CNMs are active in mass transport, we find a single-channel permeation of ~66 water molecules·s<sup>-1</sup>·Pa<sup>-1</sup>. We compare this with molecular transport through other carbon nanoconduits, such as carbon nanotubes or membrane proteins (aquaporins). As the fabrication of CNMs is scalable, their utilization opens a path towards the application of 2D-materials in energy-efficient water purification.

[1] A. Turchanin and A. Götzhäuser: Carbon Nanomembranes, *Adv. Mater.* **2016**,28, 6075.

[2] Y. Yang, P. Demytyev, N. Biere, D. Emmrich, P. Stohmann, R. Korzetz, X. Zhang, A. Beyer, S. Koch, D. Anselmetti, A. Götzhäuser, *ACS Nano*, in press.

11:40am **2D+EM+MI+MN+NS+SS-ThM-12 Discovery of Dirac Monolayers and Elucidation of Functonalites by Advanced Soft X-ray Spectroscopy**, **Iwao Matsuda**, University of Tokyo, Japan **INVITED**

Vapor deposition of three-dimensional (3-D) crystal on a substrate often results in formation of the novel 2-D materials with intriguing electronic states. The approach has been well-known in the field of "Surface Science", which has attracted our attentions over the past decades. Triggered by fabrication of the graphene layers, researches on such monatomic sheets have extended to various kinds such as silicene, germanene and so on. Soft X-ray spectroscopies, such as photoemission spectroscopy, have been used to directly probe electronic states of monatomic layers and also to examine carrier dynamics under the *operando* condition. We recently observed Dirac Fermions in a 2-D boron sheet, borophene, that forms spontaneously on the Ag(111) surface. Furthermore, we found pairing of the Dirac cones due to Moire-periodic perturbations of the overlayer-substrate interactions. In the Cu<sub>2</sub>Si monolayer, we also discovered the 2-D Dirac nodal line fermions that are protected by the mirror reflection symmetry. In the presentation, I will describe details of our research on the novel 2-D Dirac materials and introduce the advanced soft X-ray techniques that reveal their functionalities for developing devices.

[1] B. Feng, *IM et al.*, *Phys. Rev. Lett.*, **118**, 096401 (2017).

[2] B. Feng, *IM et al.*, *Adv. Mater.* **30**, 1704025 (2018).

[3] B. Feng, *IM et al.*, *Nature Comm.*, **8**, 1007 (2017).

## Electronic Materials and Photonics Division Room 101A - Session EM+MI+MN+NS-ThM

### Nanostructures for Electronic and Photonic Devices

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

8:00am **EM+MI+MN+NS-ThM-1 Extreme Nanophotonics from Ultrathin Metallic Junctions**, **Maiken Mikkelsen**, Duke University **INVITED**  
New optical nanomaterials hold the potential for breakthroughs in a wide range of areas from ultrafast optoelectronics such as modulators, light sources and hyperspectral detectors, to efficient upconversion for energy

applications, bio-sensing and on-chip components for quantum information science; they also serve as inspiration for entirely new devices and technologies. An exciting opportunity to realize such new nanomaterials lies in controlling the local electromagnetic environment on the atomic- and molecular-scale, (~1-10 nm) which enables extreme field enhancements, but represents a largely unexplored length scale. We use creative nanofabrication techniques at the interface between chemistry and physics to realize this new regime, together with advanced, ultrafast optical techniques to probe the emerging phenomena. Here, I will provide an overview of our recent research demonstrating tailored light-matter interactions by leveraging ultra-small plasmonic cavities fabricated using bottom-up techniques. Examples of our demonstrations include perfect absorbers and combinational colors [*Adv. Mat.* **27**, 7897 (2015), *Adv. Mat.* **29**, 1602971 (2017)], actively tunable nanostructures [*Nano Lett.*, **18**, 853 (2018)], tailored emission from two-dimensional semiconductor materials [*Nano Lett.* **15**, 3578 (2015), *ACS Phot.* **5**, 552 (2018)] and strong coupling.

8:40am **EM+MI+MN+NS-ThM-3 The Geode Process: A Route to the Large-Scale Manufacturing of Functionally-Encoded Semiconductor Nanostructures**, M Mujica, G Tutunçoglu, V Breedveld, S Behrens, **Michael Filler**, Georgia Institute of Technology

Future large-area electronic and photonic technologies will require the manufacturing of materials and devices at very high rates without sacrificing nanoscale control of structure and composition. Semiconductor nanowires, for example, can be produced with exquisite spatial control of composition and morphology using the vapor-liquid-solid (VLS) mechanism that, however, remains limited to very small manufacturing rates. Here, we introduce the Geode process to synthesize functionally-encoded semiconductor nanowires at throughputs orders of magnitude beyond the state-of-the-art. Central to the Geode process are sacrificial, porous-walled, seed particle-lined silica microcapsules, whose interior surface serves as a high-surface area growth substrate. Microcapsules protect the growing nanostructures, are produced with a scalable emulsion templating technique, and are compatible with large-scale chemical reactors. We will show how microcapsule structure and drying is influenced by silica nanoparticle type and concentration, emulsification parameters, and nanoparticle cross-linking agent. We will also demonstrate the synthesis of Si nanowires with programmable dopant profiles on the microcapsule interior, which not only shows the versatility of the process, but also allows the impact of precursor gas transport limitations to be characterized.

9:00am **EM+MI+MN+NS-ThM-4 Disordered Microsphere-Based Coatings for Effective Radiative Cooling under Direct Sunlight**, S Atiganyanun, J Plumley, K Hsu, University of New Mexico; T Peng, Air Force Research Laboratory; **Sang M. Han**, S Han, University of New Mexico

Radiative cooling is a process where a material loses heat due to strong emission of photons in the mid-infrared spectrum and enhanced light scattering in the solar region. This process would allow cooling of materials below the ambient temperature under the sun without the use of electricity and therefore would significantly reduce energy consumption. In this work, we have demonstrated a passive radiative cooling of disordered silica microsphere coatings below the ambient temperature while exposed to direct sunlight. To fabricate the coatings, silica microspheres are deposited by colloidal sedimentation method and spray coating method. In the first method, silica colloidal stability is disrupted by addition of KCl solution. The instability causes the colloids to agglomerate and sediment, creating a disordered uniform coating. In the second method, much like commercial painting, the colloidal solution is forced through a spray nozzle and deposited onto a substrate. Scanning electron microscopy show that the resulting structures are disordered without short- or long-range order. Optical measurements also indicate that the coatings produced under optimal conditions have a short transport photon mean free path of approximately 4-8 μm in the solar spectral region. These coatings also exhibit high emissivity above 95% in the atmospheric transparency window. These results suggest strong photon scattering properties in the visible region, while providing a strong thermal emission. Such films would enable effective radiative cooling. To test the cooling performance, we apply this film on top of a black substrate and expose the material to a direct sunlight during the summer in New Mexico. Temperature measurement of the samples shows that our coating reduces the substrate temperature below that of the ambient air by as much as 12 °C during daytime. Similar testing with a commercial solar-rejection paint indicates that the silica coating performs better than the commercial paint by 4.7 °C on average. Additionally the similar technique is used to fabricate disordered coatings made of polystyrene-polymethyl methacrylate microspheres. Outdoor experiments have shown that the polymer coatings

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perform better than the commercial paint by 5.5 °C on average. Disordered coatings made of microspheres in a paint format will also be discussed.

9:20am **EM+MI+MN+NS-ThM-5 Assessing Strain Relaxation in Nanostructured InGaN Multiple Quantum Wells Using X-Ray Diffraction Reciprocal Space Mapping and Photoluminescence Spectroscopy**, *Ryan Ley, C Pynn, M Wang, S DenBaars, M Gordon*, University of California at Santa Barbara

The III-Nitrides are excellent materials for LEDs, lasers and power electronics due to their tunable bandgap and high defect tolerance. These materials are increasingly important for displays in mobile and portable electronic devices, which currently suffer from short battery lives because displays based on liquid crystals or organic LEDs are inefficient. Producing high quality III-Nitride material with the indium compositions needed for efficient green and red emission is presently very challenging, due in large part to strain effects resulting from the large lattice mismatch between InGaN and GaN. However, there are some indications that nanostructuring can reduce or eliminate some of these strain issues.

This talk will highlight our recent work using colloidal and templated lithography and Cl<sub>2</sub>/N<sub>2</sub> plasma etching to fabricate nanoscale InGaN/GaN LED structures (diameter = 150-600nm), and how sub micron scale patterning affects the strain state and optical behavior of MQW emitters. InGaN/GaN LED structures were grown by MOCVD on c-plane sapphire substrates and characterized before and after nanopatterning using on-axis (0002) and off-axis (10-15 and 11-24) XRD reciprocal space maps (RSM), rocking curves and photoluminescence (PL) spectroscopy at 14K. RSM analysis found degrees of relaxation of 30% and 20% for the smallest and largest structures, respectively, and rocking curves revealed a 0.7nm decrease in the InGaN quantum well thickness. These relaxation effects also correlate well with spectral blue shifts (~10-15nm) in the PL, which are supported by 1D quantum mechanical and electrostatic simulations. Overall, this work shows that nanopatterning of InGaN/GaN active emitters at sub-micron length scales can reduce strain related issues in the III-Nitrides and potentially allow higher incorporation of indium for green and red emission.

9:40am **EM+MI+MN+NS-ThM-6 Scalable, Tunable, and Polarization-Independent High Contrast Grating Reflectors for Integration into Resonant-Cavity micro-LEDs**, *Pavel Shapturenka, S DenBaars, M Gordon*, University of California at Santa Barbara

III-nitride blue and green micro-LEDs have exhibited quantum efficiencies of over 40%, which is a nearly fivefold efficiency boost over current OLED and LCD digital display technologies. In order to realistically continue LED miniaturization below 10 microns for high-resolution and near-eye pixel displays, it is necessary to maintain emission directionality and output power. One method to accomplish this is to make a resonant-cavity micro-LED device with a high-reflectance mirror and an output coupler.

We demonstrate a low-cost, tunable, and scalable colloidal lithography method to fabricate suspended TiO<sub>2</sub> high-contrast grating (HCG) reflectors across the visible wavelength range for eventual integration as an output coupler in a resonant-cavity LED. Silica spheres (310-960 nm diameter), deposited via Langmuir-Blodgett dip-coating, were used as a mask to define a quasi-ordered, hexagonal pattern on a 200 nm thick TiO<sub>2</sub> film.

Subsequent pattern transfer with SF<sub>6</sub> reactive ion and XeF<sub>2</sub> chemical etching of sacrificial Si layers beneath the TiO<sub>2</sub> layer yielded a periodic, high index contrast between the suspended array structure and the surrounding air medium. Near-normal-incidence reflectance measurements on structures of increasing hole pitch (310-960 nm) showed an increase in maximum reflected wavelength from 370 to >1000 nm, while maintaining a high-%R bandwidth of 40-100 nm. The reflectance was also observed to be polarization-independent. Finite-difference time domain (FDTD) simulations of structural imperfection stemming from the colloidal lithography process, e.g., deviations in hole diameter, pitch, and hexagonal symmetry, indicate that absolute reflectance is most affected by hole offset from hexagonal lattice positions. The talk will highlight processing methods, optical characterization of HCGs, and underlying trends in the effect of HCG geometry on optical response as predicted by FDTD simulations. This work suggests that scalable fabrication of visible-wavelength HCGs is feasible and holds promise for integration into resonant-cavity LEDs.

11:00am **EM+MI+MN+NS-ThM-10 Nano-optical Activation of Defect-bound Excitons in Monolayer WSe<sub>2</sub>: Towards Room-temperature 2D Single-photon Optoelectronics**, *Jim Schuck*, Columbia University **INVITED**

The emergence of two-dimensional (2D) monolayer transition metal dichalcogenides (1L-TMDC) as direct bandgap semiconductors has rapidly accelerated the advancement of room temperature, 2D optoelectronic devices. Optical excitations on the TMDCs manifest from a hierarchy of electrically tunable, Coulombic free-carrier and excitonic many-body phenomena. In our most recent nano-optical investigations of these materials, we have demonstrated that a model hybrid architecture, a nano-optical antenna and a 1L-WSe<sub>2</sub> nanobubble, activates the optical activity of BX states at room temperature and under ambient conditions. These results show that engineered bound-exciton functionality as, in this case, localized nanoscale light sources, can be enabled by an architectural motif that combines localized strain and a nano-optical antenna, laying out a possible path for realizing room-temperature single-photon sources in high-quality 2D semiconductors.

11:40am **EM+MI+MN+NS-ThM-12 Light Scattering Properties of Silver Nanoprisms in Different Environments**, *Yuri Strzhemechny*, Texas Christian University; *S Requena*, Harris Night Vision; *H Doan*, Texas Christian University; *S Raut*, University of North Texas Health Science Center; *Z Gryczynski*, Texas Christian University; *I Gryczynski*, University of North Texas Health Science Center

Embedding nanostructures into different environments, such as polymer matrices, organic and biological solutions oftentimes produces unique optoelectronic properties of the resulting compound system that are distinct from those of the host and nano-filler. Such strong modifications can be caused by the interface phenomena, the change in the spatial distribution and orientation of the nanostructures or a combination thereof. In this work, we report on optical properties of silver triangular prism nanoparticles embedded in water, lipid solutions, and polyvinyl alcohol (PVA) polymer thin films. For our studies, using a common chemical reduction routine, we synthesized, batches of silver nanoparticles with different size distributions and distinct size-dependent dipole resonance spectra. Silver nanoprisms suspended in water yielded a noticeable wavelength-dependent depolarization of scattered light associated with different surface plasmon modes. Consequently, the same nanostructures were placed into lipid environments to estimate the rejection of a polarized background scattering during depolarization measurements. After that, the composite thin films were fabricated via incorporation of silver nanoparticles into PVA. We studied linear dichroism in those Ag/PVA films, as-prepared and subjected to controllable stretching. Re-orientation of the nanoprisms upon stretching leads to a significant increase of the linear dichroism for the plasmonic modes associated with the in-plane dipole oscillations and a decrease of the linear dichroism corresponding to the out-of-plane plasmonic modes. These observations are in good agreement with the assumption that stretching of the nanocomposite films leads to an anisotropic realignment of the nanoprisms.

12:00pm **EM+MI+MN+NS-ThM-13 Core-Shell Processing of BTO Nanocomposites for Optimal Dielectric Properties**, *Kimberly Cook-Chennault*, Rutgers University

High permittivity polymer-ceramic nanocomposite dielectric films leverage the ease of flexibility and processing of polymers and functional properties of ceramic fillers. Physical characteristics of these materials can be tuned for application to a variety of applications, such as, advanced embedded energy storage devices for printed wired electrical boards and battery separators. In some cases, the incompatibility of the two constituent materials; hydrophilic ceramic filler and hydrophobic epoxy can limit the filler concentration and therefore, dielectric properties of these materials. Use of surfactants and core-shell processing of composite fillers is traditionally used to achieve electrostatic and steric stabilization for adequate ceramic particle distribution. This work aims to understand the role of surfactant concentration in establishing meaningful interfacial layers between the epoxy and ceramic filler particles by observing particle surface morphology, dielectric permittivity and device dissipation factors. A comprehensive study of nanocomposites that were comprised of non-treated and surface treated barium titanate (BT) embedded within an epoxy matrix was performed. The surface treatments were performed with ethanol and 3-glycidyloxypropyltrimethoxysilan, where the best distribution, highest value of permittivity (~ 48.03) and the lowest value of loss (~0.136) were observed for the samples that were fabricated using 0.5 volume fraction of BaTiO<sub>3</sub> and 0.02 volume fraction of silane coupling agent.

## MEMS and NEMS Group

Room 202B - Session MN+2D+AN+MP+NS-ThM

### Optomechanics and 2D NEMS

**Moderator:** Max Zenghui Wang, University of Electronic Science and Technology of China

8:00am **MN+2D+AN+MP+NS-ThM-1 Towards Microwave to Telecom Wavelength Quantum Information Transfer using Cavity Optomechanics, John Davis**, University of Alberta, Canada **INVITED**

The past few years have seen the rapid maturation of quantum information processors, particularly in the category of superconducting microwave circuits. With claims from leading companies that they will commercialize quantum processors in the next five years, we must wonder what quantum technologies should be developed in tandem to fully utilize these processors. For example, we are all acutely aware that while our personal computers are powerful, they are considerably more useful and interesting when networked together. So how can we likewise network quantum processors? Especially since the microwave signals of superconducting processors cannot be transmitted at room temperature without thermal decoherence. What if instead, one could link superconducting processors together through existing fiber-optic networks, which are already capable of long distance quantum information transfer? Hence the development of a transducer of quantum information from the microwave to telecom domain has become highly desirable. I will describe the current state of microwave to optical transducers, and how our lab is working towards this goal. Specifically, I will discuss the progress and challenges associated with the development of fiber-coupled telecom-wavelength cavity optomechanical resonators, and 3D superconducting microwave cavities, operating at millikelvin temperatures. I will also discuss ongoing collaborations that could enable implementation of quantum information transducers in a large-scale fiber network in Alberta.

8:40am **MN+2D+AN+MP+NS-ThM-3 1D/2D NEMS Quantum Information Processing, Guangwei Deng**, Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China 610054, Chengdu, Sichuan, China.0 **INVITED**

In this talk, I will introduce our recent works on 1D and 2D NEMS, including carbon nanotube and graphene resonators. First, I will show our efforts on scaling 2D quantum dot chips with a microwave resonator [1, 2], where the resonator served as the quantum bus. Then we tried to explore nano-electromechanical resonators as phonon buses. I will introduce some works about strongly coupled nano-mechanical resonators based on carbon materials, such as carbon nanotube and graphene. These resonators have very high resonant frequencies and are highly tunable. We have experimentally realized the strong coupling between charge transport and mechanical motions [3, 4, 5], and also observed strong coupling between different modes of one mechanical resonator. Moreover, we realized the coherent phonon Rabi operation using the strong coupling [6] and we further implement a tunable distant strong coupling between two mechanical resonators [7]. These results have shown that the strongly coupled nano-mechanical resonators can provide a platform for the coherent electron-phonon interactions, the long distance phonon (electron) interactions and entanglement state generation, and we can exploit them as future quantum buses for solid state qubits, such as quantum dot based qubits [8].

#### References:

- [1] Deng, G. W. et al., Charge number dependence of the dephasing rates of a graphene double quantum dot in a circuit QED architecture. *Phys. Rev. Lett.* **115**, 126804 (2015).
- [2] Deng, G. W. et al., Coupling two distant double quantum dots with a microwave resonator. *Nano Lett.* **15**, 6620 (2015).
- [3] Deng, G. W. et al., Strongly coupled nanotube electromechanical resonators. *Nano Lett.* **16**, 5456 (2016).
- [4] Li, S. X. et al., Parametric strong mode-coupling in carbon nanotube mechanical resonators. *Nanoscale* **8**, 14809-14813 (2016).
- [5] Luo, G. et al., Coupling graphene nanomechanical motion to a single-electron transistor. *Nanoscale* **9**, 5608-5614 (2017).
- [6] Zhu, D. et al., Coherent phonon Rabi oscillations with a high-frequency carbon nanotube phonon cavity. *Nano Lett.* **17**, 915-921 (2017).
- [7] Luo, G. et al., Strong indirect coupling between graphene-based mechanical resonators via a phonon cavity. *Nature Commun.* **9**, 383 (2018).

- [8] Zhang, Z. Z., et al., Electro-tunable artificial molecules based on van der Waals heterostructures. *Sci. Adv.* **3**, e1701699 (2017).

9:20am **MN+2D+AN+MP+NS-ThM-5 Characterization and Modeling of Radio Frequency Graphene Resonant Channel Transistor, Yuehang Xu**, University of Electronic Science and Technology of China, China; *T Mei*, University of Electronic Science and Technology of China **INVITED**

Graphene's unique properties, including low mass and high stiffness, ultrahigh strength, and high electronic mobility, enable graphene nanoelectromechanical systems (NEMS) very suitable for low power high frequency circuits. Local gate graphene resonant channel transistors (G-RCTs) can reduce parasitic electromagnetic (EM) coupling and thus has good potential in high frequency integrated circuits. To develop the G-RCTs high frequency circuits, a compact model that can predict a G-RCT's performance and implement into standard circuit simulators is essential.

This paper presents a high-frequency nonlinear equivalent circuit model of G-RCTs including a nonlinear electromechanical model of doubled clamped graphene mechanical resonators. To describe the temperature-dependent modal dispersion, both bias- and temperature-dependent effects are considered. The temperature-dependent built-in strain, the bias-based electrostatic force and the spring restoring force including the nonlinear term upon deformation are used to describe the mechanical motion of the suspended beam. Good agreement between simulated and measured results can be achieved as shown in Fig.1. Moreover, the nonlinear effects including harmonic distortion, third-order intermodulation distortion (IMD), and the hysteresis and nonlinear behavior of G-RCTs are also studied. Fig.2 and Fig.3 are results of mechanical nonlinear characteristics and duffing nonlinear behavior of G-RCTs, respectively. The results in show that the mechanical nonlinearity has strong effects on nonlinear distortion for G-RCTs. The proposed nonlinear equivalent circuit model could be useful for Graphene NEMS in the applications of high frequency integrated circuits.

11:20am **MN+2D+AN+MP+NS-ThM-11 Reconfigurable Resonant Responses in Atomic Layer 2D Nanoelectromechanical Systems (NEMS), Zenghui Wang**, University of Electronic Science and Technology of China, China; *R Yang, P Feng*, Case Western Reserve University

Atomic layer semiconducting crystals have emerged as a new class of two-dimensional (2D) materials, exhibiting great promises for both fundamental research and technological applications. Their outstanding electromechanical properties make these materials ideal for constructing novel 2D NEMS, providing opportunities for leveraging their unique device properties across multiple information-transduction domains, at scales down to individual atomic layers. One particularly interesting category of 2D NEMS is 2D nanoelectromechanical resonators, which hold potentials for making the next generation RF signal transduction and processing components, with miniaturized size, ultra-low power consumption, and compatibility with transparent and flexible circuits.

Towards future applications in the 5G era, multi-band RF signal handling capability is desired, as the number of bands each mobile device need to have access to significantly increases, and it would be impractical to simply increase the number of RF components that can only function under one RF frequency, as the space required for mounting such components scales with the number of bands. Therefore, ultralow-power tunable and reconfigurable RF devices that can adapt to different frequencies would be one solution to this challenge.

Here we present experimental demonstration of nanomechanical resonators based on layered MoS<sub>2</sub> atomic crystals that have reconfigurable resonant responses. By carefully studying the temperature-dependent frequency response in such MoS<sub>2</sub> resonators[1], we discover clear, repeatable hysteretic behavior as the device temperature is changed[2]. Leveraging this phenomenon, we achieve switchable resonance frequency  $f_{res}$  in such devices by using heating and cooling pulses. Specifically, for an example MoS<sub>2</sub> resonator, during heating pulses, the  $f_{res}$  decreases to ~20MHz. Once the device recovers to room temperature,  $f_{res}$  stabilizes at ~26MHz. During cooling pulses,  $f_{res}$  increases to ~29MHz, and upon reverting to room temperature  $f_{res}$  stays at ~24.5MHz, which is clearly different than the other room temperature state. Our findings suggest that such atomic-layer MoS<sub>2</sub> NEMS resonators could be used towards developing reconfigurable RF components whose frequency response can be switched between different states.

- [1] R. Yang, et al., *IEEE UFFC*, pp 198-201, 2015. [2] Z. Wang, et al., *IEEE UFFC*, pp 783-786, 2015.

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11:40am **MN+2D+AN+MP+NS-ThM-12 Cavity Optomechanics: Dynamics and Applications**, *Eyal Buks*, Israel Institute of Technology, Israel **INVITED**  
The field of cavity optomechanics deals with a family of systems, each composed of two coupled elements. The first one is a mechanical resonator, commonly having a low damping rate, and the second one is an electromagnetic cavity, which typically is externally driven. Both radiation pressure and bolometric force can give rise to the coupling between the mechanical resonator and the cavity. In recent years a variety of cavity optomechanical systems have been constructed and studied, and phenomena such as mode cooling, self-excited oscillation, and optically induced transparency have been investigated. The first part of the talk will be devoted to some dynamical effects including synchronization and intermittency. In the second part some applications of optomechanical cavities for sensitive sensing will be discussed.

## Nanometer-scale Science and Technology Division

**Room 102B - Session NS+AN+EM+MI+MN+MP+PS+RM-ThM**

### Nanopatterning and Nanofabrication

**Moderators:** Brian Hoskins, National Institute of Standards and Technology (NIST), Meredith Metzler, University of Pennsylvania, Leonidas Ocola, IBM Research Division, T.J. Watson Research Center

8:00am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-1 Femtosecond Laser Processing of Ceria-Based Micro Actuators**, *Jenny Shklovsky*, Tel Aviv University, Israel; *E Mishuk*, Weizmann Institute of Science, Israel; *Y Berg*, Orbotech Ltd, Israel; *N Vengerovsky*, *Y Sverdlov*, Tel Aviv University, Israel; *I Lubomirsky*, Weizmann Institute of Science, Israel; *Z Kotler*, Orbotech Ltd; *S Krylov*, *Y Shacham-Diamond*, Tel Aviv University, Israel

The integration of piezoelectric and electrostrictive materials into micromachined Si devices is viewed as an important technological milestone for further development of Microelectromechanical Systems (MEMS). Recently, it was demonstrated that gadolinium-doped ceria (CGO) exhibits very large electrostriction effect, which results in large electrostrictive strains and high energy densities under very low frequencies (0.01 – 1 Hz). Lead-free CGO is chemically inert with respect to Si, making it an attractive candidate for implementation in MEMS actuators. However, the integration of CGO into MEMS devices is challenging due problems associated with using conventional patterning techniques involving lithography and etching.

In this work, we have successfully created functional double-clamped beam micro-actuators made of CGO films confined between the top and bottom Al/Ti electrodes. The stack containing the electrodes and the  $\approx 2 \mu\text{m}$ -thick CGO film was first blanket-deposited on top of the Si wafer. Cavities were then deep reactive ion etched (DRIE) in the wafer leading to forming of the free-standing rectangular membranes, 1.5 mm  $\times$  0.5 mm in size. Finally,  $\approx 1.2$  mm long and  $\approx 100 \mu\text{m}$  wide the double-clamped beams were cut from the membranes using a femtosecond (fs) laser, demonstrating an unharmed technique for CGO patterning. Laser pulse energies, overlaps and number of line passes were varied during the experiments, to achieve successful cuts through the suspended layer by a clean ablation process. The optimized process conditions were found at a fluence of  $\sim 0.3 \text{ J/cm}^2$  for a pulse width of 270 fs, where minimal damage and accurate processing was achieved with minimized heat-affected zones.

Resistivity measurements between the top and the bottom electrodes before and after fs laser cutting revealed that the cutting has no influence on the electric parameters of the device and no electrical shorts are introduced by the laser processing. Vertical displacement measurements under bipolar AC voltage (up to 10 V), at the frequency range of 0.03 – 2 Hz, demonstrated the functionality of the micro-actuator. A displacement of  $\approx 45 \text{ nm}$  at the voltage of 10 V at 50 MHz was achieved. The actuator didn't show any mechanical or electrical degradation after continuous operation. Our data confirm that fs laser cutting is a useful technique for processing CGO films. The developed techniques may be expanded to other materials used for fabrication of MEMS devices, enabling fast, high yield and high-quality patterning of materials that are challenging to pattern using conventional etching-based methods.

\*Three first authors contributed equally to this abstract.

8:20am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-2 Synthesis of Functional Particles by Condensation and Polymerization of Monomer Droplets in Silicone Oils**, *Prathamesh Karandikar*, *M Gupta*, University of Southern California

The initiated chemical vapor deposition (iCVD) process is an all-dry, vacuum process used to deposit a wide variety of functional polymers. Typically, the monomer and initiator radicals are introduced simultaneously at process conditions leading to undersaturation of monomer vapors. In this work we report a sequential vapor phase polymerization method in which monomer droplets were first condensed onto a layer of silicone oil and subsequently polymerized via a free radical mechanism to fabricate polymer particles.

The viscosity of the silicone oil was systematically varied from 100 cSt through 100,000 cSt. A heterogeneous particle size distribution was produced at low viscosities of silicone oil where the smaller particles were formed by the cloaking and engulfment of monomer droplets nucleated at the vapor-liquid interface and the larger particles were formed by coalescence inside the liquid. Coalescence could be inhibited by increasing the viscosity of the silicone oil leading to a decreased average radius and a narrower size distribution of the polymer particles. A transition to polymer film formation was observed for the 100,000 cSt silicone oil substrates. We studied the polymerization of two different monomers, 4-vinyl pyridine and 2-hydroxyethyl methacrylate, since these polymers have a variety of useful properties such as pH-responsiveness and biocompatibility. Our process enables fabrication of functional particles with average diameters ranging from 100 nm – 500 nm with fast reaction times ( $\approx 15$  min). The advantages of our method for the fabrication of polymer particles are that it does not require surfactants or organic solvents and features short reaction times compared to conventional polymer particle synthesis methods such as emulsion polymerization.

8:40am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-3 Competition Between Scale and Perfection in Self-assembling Structures**, *James Liddle*, NIST Center for Nanoscale Science and Technology **INVITED**

Biology relies on self-assembly to form complex, highly-functional structures, inspiring the search for synthetic systems capable of forming similarly complex structures. Such systems typically operate under diffusion-limited, near-equilibrium conditions, making the problem even more challenging. Multi-functional, molecularly-addressable nanostructures of arbitrary shape can be built using DNA-mediated self-assembly. While this is a powerful method, and recent developments in DNA nanostructure fabrication have expanded the available design space, fabrication based on DNA alone can suffer from low yields and is hampered by the need to trade off size and mechanical rigidity.[1,2]

We have been working to both understand the factors that limit the yield of self-assembled structures, and to devise approaches to overcome them. As the number of discrete components used to assemble a structure increases, yield decreases exponentially. We circumvent this limit, by using a two-stage, hierarchical self-assembly process, which allows us to create large structures with high yield.[3] Our process employs a small number of discrete, sequence-specific elements to shape the structure at the nanoscale and define the large-scale geometry. A generic building block – a DNA binding protein, *RecA* – rigidifies the structure without requiring any unnecessary information to be added to the system.

Blending sequence-specific and structure-specific elements enables us to expand the self-assembly toolbox and make micrometer-scale, rigid, molecularly-addressable structures. More generally, our results indicate that the scale of finite-size self-assembling systems can be increased by minimizing the number of unique components and instead relying on generic components to construct a framework that supports the functional units.

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[2] Schiffels, D., Liedl, T. & Fygenson, D. K. Nanoscale structure and microscale stiffness of DNA nanotubes. *ACS Nano* **7**, 6700-6710, doi:10.1021/nn401362p (2013).

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[3] Schifffels, D, Szalai, V. A., Liddle, J. A., Molecular Precision at Micrometer Length Scales: Hierarchical Assembly of DNA-Protein Nanostructures, *ACS Nano*, **11**, 6623, (2017)

9:20am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-5 Polymer Templated Annealing of DNA Patterned Gold Nanowires**, Tyler Westover, B Aryal, R Davis, A Woolley, J Harb, Brigham Young University

Using DNA origami as a bottom up nanofabrication technique, gold nanowires are formed via directed assembly of gold nanorod seeds and connected by electroless plating. This metal deposition process results in wires with low conductivities compared to bulk gold. Junctions between plated seeds are likely the cause of this low conductivity. Annealing of the nanowires could potentially improve the conductance, however, nanowire annealing at low temperatures (200° C) results in wires coalescing into beads. A polymer encapsulation layer was deposited to maintain overall nanowire shape during annealing. The polymer templated anneal resulted in a resistance reduction, in some cases, to below 1000 ohms. Resistance measurements were performed using a four point resistance configuration. Electrical contacts to the randomly oriented 400 nm long wires were made by electron beam induced deposition. Nanowire morphology was measured before and after annealing by scanning electron and high resolution transmission electron microscopy.

11:00am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-10 Directed Self-assembly of Block Copolymers for Applications in Nanolithography**, Paul Nealey, University of Chicago **INVITED**

DSA of block copolymer films on chemically nanopatterned surfaces is an emerging technology that is well-positioned for commercialization in nanolithography and nanomanufacturing. DSA of (PS-*b*-PMMA) films on lithographically defined chemically nanopatterned surfaces is one focus of our activities in which the main research objectives revolve around understanding the fundamental thermodynamics and kinetics that governs assembly, and therefore patterning properties such as 3D structure, perfection, and processing latitude. A second focus is to use the physical and chemical principles that we have elucidated for DSA of PS-*b*-PMMA towards the development of block copolymer systems capable of self-assembling into the sub 10 nm regime and continuing to meet the stringent constraints of manufacturing. The research is enabled by the recent development of techniques to combine metrology tools (TEM tomography, GISAXS, RSoXS, high-speed APF), theoretically informed coarse grained models, and evolutionary algorithms to quantitatively determine and predict the independent process and material parameters that result in different 3D structures of assembled domains.

11:40am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-12 Three Dimensional Mesoporous Silicon Nanowire Network Fabricated by Metal-Assisted Chemical Etching**, Deepak Ganta, C Guzman, R Villanueva, TAMIU

Mesoporous nanowires have gained huge attention due to their applications in energy and sensing. The high surface area along with the quantum confinement effect lead to improved performance of the electrochemical devices during energy conversion and storage. 3D structure or nanowire network improves the reaction site surface area even further along all the three dimensions, enhancing both light and heat absorption. There is also a huge demand for inexpensive, non-lithographic methods to fabricate 3D network of nanowires, which are also mesoporous, with better control of both dimensions and porosity, over a large surface area. They can be very useful in some broad range applications such as solar energy conversion, energy storage, water harvesting, environmental control, bio-sensing, and thermoelectrics.

To address the problem, we report a simple and inexpensive method of fabricating 3D mesoporous Si nanowire network by metal-assisted chemical etching (MacEtch). Degenerately doped p-type silicon or p+ silicon wafer (0.001 ~0.005 Ω·cm) was coated with about 22 nm silver film at 350 °C for 5~6 hours in a vacuum furnace (pressure < 3×10<sup>-7</sup> Torr). Scattered silver particles with different sizes were formed as a result of the dewetting process. Then we deposited 10~11 nm of noble metal (Au) at 0.5 Å/s rate, followed by silver lift-off to obtain an Au mesh as an etching mask. The mixture of a chemical solution of HF: H<sub>2</sub>O<sub>2</sub>: Ethanol = 30:1:1 is used as a chemical etchant under room temperature. The time of immersion of the silicon wafer in the etchant effects the aspect ratio of the silicon nanowire array. After MachEtch, the Au is removed by immersing the sample in the aqua regia solution. The ratio of the chemicals in the etchant will affect the

por size. The aspect ratio of the silicon nanowire network can be controlled by the etching rate. The etching rate was roughly one μm/min. The 3D network is formed as the result of the 1D silicon nanowires (50 nm -100 nm) was varied, followed by critical point drying to carefully control the uniformity of 3D silicon nanowire network on the entire surface area of the 6-inch silicon wafer.

Analysis of the 3D mesoporous silicon nanowire network was conducted using Scanning Electron microscopy (SEM), and the top view image confirmed the 3D network of silicon nanowires. The pore sizing (2-50 nm) along with the crystallinity confirmed from the high-resolution transmission electron microscopy (TEM) images with the diffraction patterns.

12:00pm **NS+AN+EM+MI+MN+MP+PS+RM-ThM-13 Enhancing Light Extraction from Free-standing InGaN/GaN light Emitters Using Bio-inspired Backside Surface Structuring**, L Chan, C Pynn, S DenBaars, Michael Gordon, University of California at Santa Barbara

A simple, scalable, and reproducible nanopatterning method to create close-packed (moth-eye like) patterns of conical nano- and microscale features on InGaN/GaN LED surfaces, and on the backside outcoupling surface of LED devices, is presented. Colloidal lithography via Langmuir-Blodgett dip-coating using silica masks (d = 170–2530 nm) and Cl<sub>2</sub>/N<sub>2</sub>-based plasma etching produced features with aspect ratios of 3:1 on devices grown on semipolar (20-21) GaN substrates. The resulting InGaN/GaN multi-quantum well (MQW) structures were optically pumped at 266/405 nm, and light extraction enhancement was quantified using angle-resolved photoluminescence (PL). A 4.8-fold overall enhancement in light extraction (9-fold at normal incidence) relative to a flat outcoupling surface was achieved using a feature pitch of 2530 nm. Extraction enhancement occurs due to the graded-index (GRIN) effect and breaking of the TIR condition via increased diffuse scattering and diffractive effects, the importance of which evolves with moth-eye feature size. PL results also demonstrate that colloidal roughening, which has greater geometric tunability and works on any GaN orientation, is equivalent to current, c-plane only photoelectrochemical (PEC) roughening methods. Patterning the outcoupling backside of a semipolar device, rather than the topside, is also a technologically feasible approach to fabricate electrically pumped devices because it avoids issues associated with making large area (topside) p-contacts, etching close to or into the active emitter region (destroying the MQWs), or disrupting guided modes in thin-film LEDs layers on sapphire. Because of its simplicity, range of optical control, and wide substrate compatibility, the colloidal lithography technique is a promising alternative to existing commercial processes and a future pathway for enhanced extraction engineering in free-standing polar, nonpolar, and semipolar III-nitride LEDs.

## Surface Science Division

### Room 203C - Session SS+EM+NS-ThM

#### Defects in and Functionalization of 2D Materials

**Moderators:** Lars Grabow, University of Houston, Greg Kimmel, Pacific Northwest National Laboratory

8:00am **SS+EM+NS-ThM-1 Holes, Pinning Sites and Metallic Wires in Monolayers of 2D Materials**, Thomas Michely, University of Cologne, Germany **INVITED**

The moiré formed by a monolayer of hexagonal boron nitride with Ir(111) provides through a chemisorbed valley region within a physisorbed mesa a unique site for its functionalization. Through gentle ion irradiation and mild annealing a regular array of vacancy clusters is created with the clusters positioned at the valleys where their edges bind to the substrates. Such a nanomesh with a regular array of holes with sizes below 1 nm holds promise for filter applications. Through vapor phase deposition of a variety of materials (e.g. Au or C) arrays of clusters with of tunable size and high thermal stability are formed at valley regions. Compared to the graphene moiré the templating effect of the hexagonal boron nitride moiré is superior due to the uniqueness of the valley pinning site in the unit cell.

Monolayers of hexagonal boron nitride or graphene are also excellent substrates for the on-surface synthesis of new compounds ranging from metal-organic nanowires to transition metal disulfides created by reactive molecular beam epitaxy with elemental sulfur. This synthesis method provides clean, well-decoupled layers with only well-defined defects.

The most exciting defects we observed so far are two types of mirror twin boundaries in MoS<sub>2</sub> islands. In these boundaries we observe for the first time spin-charge separation in real space making use of the unique local

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spectroscopic capabilities of low temperature STM and STS to identify the position and energy of quantum mechanical states in a one dimensional box. We critically discuss these results in the light of previous related research.

Contributions to this work by Wouter Jolie, Joshua Hall, Clifford Murray, Moritz Will, Phil Valerius, Charlotte Herbig, Carsten Speckmann, Tobias Wekking, Carsten Busse, Fabian Portner, Philipp Weiß, Achim Rosch, Arkady Krasheninnikov, Hannu-Pekka Komsa, Borna Pielic, Marko Kralj, Vasile Caciuc and Nicolae Atodiresei as well as financial support through CRC1238 within projects A01 and B06 of DFG are gratefully acknowledged.

**8:40am SS+EM+NS-ThM-3 CO Chemisorption at Pristine, Doped and Defect Sites on Graphene/Ni(111), Mario Rocca, G Carraro, University of Genova, Italy; M Smerieri, L Savio, IMEM-CNR, UOS Genova, Italy; E Celasco, L Vattuone, University of Genova, Italy**

Due to its electrical properties graphene (G) has been successfully used as a sensing element for the detection of different gases reaching ppm sensitivities which are ascribed to the doping induced by adsorption. The sensitivity depends indeed critically on the chemical nature of the gas and is lower for CO than for other poisoning species. The nature of the active sites is, however, still unclear. If it were due to physisorption, the values of the adsorption energy cannot explain the need for high temperature regeneration of the sensing element. Chemisorption must thus be involved, either at defects or by doping, determining the magnitude of the heat of adsorption and consequently the sensitivity and the range of temperatures at which the sensor can operate. In order to clarify these issues we investigated experimentally adsorption of CO on G supported on polycrystalline Cu and Ni(111) by HREELS and XPS.

No adsorbed CO was found at RT while at 100 K chemisorbed CO forms on G supported on Ni(111). G on Cu is on the contrary inert. This result indicates that the nature of the substrate plays an essential role in the adsorption process. The heat of adsorption  $q$  is estimated to be about 0.58 eV/molecule at low coverage, so that an equilibrium coverage of 0.1 ML is expected at RT under a CO partial pressure of only 10 mbar. We identify top-bridge graphene as the most reactive configuration.

Doping G/Ni(111) by  $N_2^+$  ion bombardment allows for the formation of a second, more strongly bound moiety, characterized by a CO stretch frequency of 236 meV and by an initial heat of adsorption (0.85 eV/molecule). The presence of N (in pyridinic or substitutional sites) enhances therefore significantly the chemical reactivity of G/Ni(111) towards CO.

Finally in presence of isolated defects, created by low energy  $Ne^+$  ions bombardment on single layer graphene supported on different substrates (polycrystalline Cu and Ni(111)), no CO adsorption occurs for defected G/Cu, while HREELS peaks form promptly for G/Ni(111). Two moieties, desorbing just above 350 K, are present under vacuum conditions after exposure at RT. The CO stretch frequencies and the ratio of their intensities indicate that they are due to chemisorbed CO at the G/Ni(111) interface close to the vacancies rather than at the defected G layer. The red-shift of the C1s binding energy indicates that in such regions detachment of the G layer from the substrate occurs.

Amending of vacancies occurs for subsequent exposures, as demonstrated by the reduction of the adsorbed coverage in subsequent CO doses followed by annealing at 380 K, indicating that a Boudouard-like reaction takes place under the graphene cover.

**9:00am SS+EM+NS-ThM-4 Geometry of Cu Islands Buried Beneath the Surface of Graphite, A Lii-Rosales, Ames Laboratory and Iowa State University; S Julien, Northeastern University; Y Han, J Evans, Ames Laboratory and Iowa State University; K Wan, Northeastern University; Patricia A. Thiel, Ames Laboratory and Iowa State University**

Deposition of Cu on a sputtered graphite surface, in ultrahigh vacuum, can be manipulated to produce buried islands of metallic, multilayer Cu. The Cu islands are covered by a graphitic layer consisting of several graphene sheets. This layer drapes like a tarpaulin over the Cu islands. We have observed flat-topped islands as tall as 40 nm and as wide as 600 nm. One of the most striking features of island geometry is the fact that the slope of the tarpaulin at the sides of the islands is invariant over a wide range of island volumes. The variation of the ratio of island diameter to height as a function of island volume is far less regular in the experimental data, suggesting that kinetic limitations may play a role in determining this parameter. To investigate the physical forces responsible for the island geometries, we develop a model for island shape that incorporates the distortion energy of graphene, adhesion of Cu with graphitic surfaces,

adhesion of graphene with graphite, and other parameters. The energy parameters involving Cu surfaces and Cu-carbon interfaces are derived from DFT calculations. The values and trends predicted by the model are discussed and compared with experiment. In particular, the model indicates that the slope of the island sides should be invariant, consistent with experiment.

**9:20am SS+EM+NS-ThM-5 Intercalation of O<sub>2</sub> and CO between Graphene and Ru(0001) and the Role of Defects, Jory Yarmoff, T Li, University of California, Riverside**

Graphene (Gr) is a fascinating 2D material that is being widely being considered for applications in electronic devices due to its unique electronic and materials properties. Also, because of its high thermal stability and inertness, it is a promising candidate for use as a protection layer for metal substrates. Here, graphene films grown on Ru(0001) are exposed to O<sub>2</sub> and <sup>13</sup>CO and investigated with helium low energy ion scattering (LEIS). LEIS spectra collected at different scattering angles can distinguish between adsorbed and intercalated molecules. It is found that O<sub>2</sub> and CO do not adsorb to the graphene surface but instead intercalate between Gr and the substrate. It is shown that a much lower annealing temperature is needed to remove intercalated oxygen than chemisorbed oxygen on bare Ru. During the thermal desorption, some of the graphene is etched away via chemical reaction forming gaseous CO or CO<sub>2</sub>. In addition, carbon vacancy defects are produced in the Gr films via 50 eV Ar<sup>+</sup> bombardment. Isolated single carbon vacancy defects enable molecular adsorption at the defect sites and ease the overall intercalation of oxygen. The defects also improve the thermal etching efficiency of Gr by intercalated oxygen. When the defects are large enough to consist of open areas of bare substrate, oxygen dissociatively chemisorbs to Ru. Intercalated <sup>13</sup>CO molecules sit upright with the O end on top, as on clean Ru. The CO molecules tilt, however, when the temperature is raised. This is likely due to increased vibrational amplitudes combined with the confining effect of the Gr film.

**9:40am SS+EM+NS-ThM-6 Organic-2D Transition Metal Dichalcogenide van der Waals Heterostructures, Yu Li Huang, Institute of Materials Research & Engineering (IMRE), A\*STAR, Singapore; Z Song, National University of Singapore, Singapore; D Chi, Institute of Materials Research & Engineering (IMRE), A\*STAR, Singapore; A Wee, National University of Singapore, Singapore**

The recent emergence of two-dimensional transition metal dichalcogenides (2D TMDs) has led to a rapid burgeoning of the field due to their novel electronic and optical properties with potential electronics/photronics applications. Organic materials, on the other hand, have exhibited great success in the field of flexible electronics, with an extensive number of available molecules with tunable properties. Marrying the fields of organics and 2D TMDs will bring benefits that are not present in either material alone, enabling even better, multifunctional flexible devices. In parallel, the integration of 2D TMDs with selected organics is also a promising and controllable approach to modulate the properties of the TMDs without structural damage, thereby optimizing or even enhancing their desired properties for specific device applications. Central to the realization of all those applications is a fundamental understanding of the organic-2D TMD interface.<sup>1</sup>

Here, we will present our recent studies on hybrid organic/2D TMD heterostructures.<sup>2-4</sup> With combined experiments and theoretical modeling, the interfacial interactions between the organic layers and the TMDs as well as the energy level alignment at the interface are explored. The comprehensive understanding of the underlying physical mechanisms that govern the properties of organic-2D TMD interfaces at the atomic scale is of fundamental importance for developing this technique further for device applications.

## References:

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11:00am **SS+EM+NS-ThM-10 Influence of Surface Functionalization on Surface Topography and Growth of Metal Oxide Structures on HOPG**, *Kathryn Perrine, M Trought, I Wentworth, C de Alwis, T Leftwich*, Michigan Technological University

Growth of heterogeneous catalysts, plasmonic and other nanostructured materials requires atomic level control and molecular level understanding of the growth of metals and metal oxides on surfaces. Surface functionalization of 2D materials can be used to promote selective nucleation of metal oxides with control over the deposition and growth. However, this requires an understanding of surface functionalization. This surface chemical functionalization can be combined with the atomic-level control of atomic layer deposition (ALD). ALD is a vapor deposition technique that utilizes self-limiting surface reactions to grow metal oxides, where the surface functional group initiates the first step in the deposition process.

2D materials are ideal for selective functionalization that may not require lithography steps due to the fact that their sheets are in a stable configuration making them chemically unreactive. Highly oriented pyrolytic graphite (HOPG) is an ideal model of the graphene surface, a well-known 2D material, which is comprised of  $sp^2$  hybridized aromatic hydrocarbon sheets. HOPG consists of stacked graphene sheets where the terraces of the carbon sheets are chemically unreactive in ambient conditions and their defects are highly reactive. Oxidation methods are used to produce an assortment of different functional groups on HOPG and can lead to different types of functionalities on the surface and its defects.

We investigate how surface oxidative etching and functionalization influences the growth of metal oxide structures at tailored defects and functional sites on HOPG. Two different acids were used to etch the HOPG surface to produce functional groups resulting in different surface topographies. The functionalized HOPG was then exposed to trimethylaluminum and water, a well-known ALD reaction, to produce  $Al_2O_3$  as a proof-of-concept to observe the growth of  $Al_2O_3$  on both functional and defect sites. Vibrational spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were used to measure surface functionalization and  $Al_2O_3$  growth on HOPG. Field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and Raman spectral imaging were used to image the changes in surface topography after etching and ALD deposition. Results indicate that the  $Al_2O_3$  deposition and growth is dictated by the surface functionalization and topography. This suggests that understanding the effects of surface functionalization of 2D materials is necessary for controlling the growth of metal oxide structures.

11:20am **SS+EM+NS-ThM-11 Impurity Induced Chemical Properties of BN on Rh(111) Studied by First Principle Calculations: A New Phase**, *Zahra Hooshmand<sup>1</sup>, D Le, T Rahman*, University of Central Florida

Hexagonal boron nitride (h-BN), an insulating layer of  $sp^2$  hybridized structure between B and N, grown on Rh(111) forms a Moiré pattern with elevated (rim) and depression (valley) areas. The valleys are circular dipole rings which act as trapping centers for the adsorption of nanoparticles and molecules [1]. The presence of the native carbon impurities in Rh potentially gives rise to the formation of hexagonal carbon rings under every other rim area as suggested by recent experiments [2] and could lead to new structures and novel chemistry. Here, on the basis of Density Functional Theory (DFT) simulations with dispersion corrections, we show that these rings tend to grow in a manner in which the center of each ring is placed on top of the Rh atom. These rings grow next to each other and form islands which are separated from each other by an equal distance while the BN monolayer remains untouched, i.e. there is no C-B or C-N bond formed. Our calculations show that while no broken bonds between B and N were observed, the increase in the concentration of carbon impurities will enhance the height modulations among different regions of BN Moiré pattern leaving the former valleys unchanged while decreasing their area. The new higher elevated regions show strong accumulation of charge and the lower elevated regions display depletion of charge. This gives rise to modification of dipole rings and results in altered adsorption of pentacene on BN. Our simulations of Scanning Tunneling Microscope (STM) images from this structure, are in good agreement with experimental data for number of rings from 3 to 5. However spatial density of states analysis shows that in the presence of 5 rings islands the gap in BN on the higher elevated regions vanishes and the band gap on these areas for 3 and 4 rings islands reduces. The calculations of local variations in work function also show that these variations become more pronounced by growth of

islands and reduces the work function of lower elevated regions in new phase. This results show that by control of the concentration of local impurities underneath the rim areas in BN, the chemical properties are modified and the monolayer could be engineered for interesting chemical reactions. [1] H. Dil et al., *Science*, 2008, 319, 1824-1826. [2] Koslowski et al. Private communication.

This work was supported by National Science Foundation, Grant #NSF CHE-1465105"

11:40am **SS+EM+NS-ThM-12 Texture of Atomic-layer Deposited MoS<sub>2</sub>: A polarized Raman Study**, *Vincent Vandalon, A Sharma, E Kessels*, Eindhoven University of Technology, The Netherlands, Netherlands; *A Bol*, Eindhoven University of Technology, Netherlands

Advances in optical characterization techniques for 2D transition metal dichalcogenides (2D-TMDs) such as MoS<sub>2</sub> are essential in the context of tailoring the texture and surface functionalization of these materials. Tailoring of the texture of *synthesized* MoS<sub>2</sub> results in uniquely different material characteristics: out-of-plane fins of MoS<sub>2</sub> have been demonstrated to possess excellent catalytic performance, most likely due to exposed catalytically active edge sites, whereas basal plane oriented MoS<sub>2</sub> shows excellent electronic properties. The large impact of texture on the exhibited properties underlines the need for rapid and facile characterization of the texture and especially the angular grain orientation. So far, cross section high-resolution transmission electron microscopy (HR-TEM) is widely employed to obtain insight into texture but it suffers from a limited throughput. On the other hand, Raman spectroscopy has been established as the *go-to* technique for the determination of e.g. film thickness of these TMDs. Here we will show that the angular grain distribution can also be determined using *polarized* Raman spectroscopy

We have found that plasma-enhanced atomic-layer deposition (PE-ALD) of MoS<sub>2</sub> allows control over the texture and results in out-of-plane fins or basal plane oriented material depending on the processing conditions using HR-TEM. To study the texture of the PE-ALD synthesized films with Raman spectroscopy, we have investigated the so far unknown impact of the angular grain distribution on the Raman response. The Raman response of nanocrystalline MoS<sub>2</sub> was modeled for a range of different textures. This allowed us to determine the angular grain distribution from the peak ratio of the two dominant Raman peaks (i.e. the A<sub>1g</sub> and E<sub>2g</sub> modes). Furthermore, the modeling also showed that performing *polarized* variant of Raman spectroscopy is essential for the accurate determination of the angular grain distribution because of the additional information it provides. A systematic polarized Raman study into the evolution of the fraction of out-of-plane material with film thickness allowed us to gain insight into the growth process. Moreover, the influence of a post-deposition high-temperature anneal in a H<sub>2</sub>S atmosphere on the texture, known to yield improved material properties, was also investigated. To conclude, polarized Raman spectroscopy offers a rapid method to gain insight into the angular grain distribution of synthesized MoS<sub>2</sub> and this approach can be readily extended to other MX<sub>2</sub> materials.

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

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## 2D Materials Focus Topic

### Room 201B - Session 2D+EM+MN+NS-ThA

#### Novel Quantum Phenomena in 2D Materials

**Moderator:** Hsin Lin, Institute of Physics, Academia Sinica

2:20pm **2D+EM+MN+NS-ThA-1 Double Indirect Interlayer Exciton in a MoSe<sub>2</sub>/WSe<sub>2</sub> van der Waals Heterostructure, Aubrey Hanbicki, H Chuang, M Rosenberger, C Hellberg, S Sivaram, K McCreary, I Mazin, B Jonker, Naval Research Laboratory**

Tailoring semiconductor heterostructures for specific functionalities has led to varied opto-electronic devices including solar cells, photodetectors, light-emitting diodes and lasers. 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). vdWHs offer novel functionalities making them promising hosts for future devices. One unique new heterostructure property is an interlayer exciton (ILE), a spatially indirect, bound electron-hole pair with the electron in one TMD layer and the hole in the other. Here, using state-of-the-art preparation techniques, we are able to resolve emission from the ILE in a MoSe<sub>2</sub>/WSe<sub>2</sub> heterostructure into two distinct peaks separated by 24 meV at zero field. These peaks have nearly equal intensity, indicating they are of common character, and have *opposite* circular polarizations when excited with circularly polarized light. *Ab initio* calculations successfully account for these observations – they show that both emission features originate from excitonic transitions that are indirect in momentum space and are split by spin-orbit coupling. Also, the electron is strongly hybridized between both the MoSe<sub>2</sub> and WSe<sub>2</sub> layers, with significant weight in both layers, contrary to the commonly assumed model. Thus, the transitions are not purely interlayer in character. This work represents a significant advance in our understanding of the static and dynamic properties of TMD heterostructures.

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.

2:40pm **2D+EM+MN+NS-ThA-2 Comparison of A- and B-exciton Intensity and Polarization in Transition Metal Dichalcogenide Monolayers and Heterostructures, Kathleen McCreary, A Hanbicki, S Sivaram, B Jonker, U.S. Naval Research Laboratory**

We survey a large number of monolayer TMDs to better understand the conditions responsible for various emission characteristics that have been reported in literature. We find that the intensities for both A- and B- peak emission vary widely as a result of sample-to-sample variations. However, a measurable B-peak intensity is evident in all samples. There is a clear linear relationship between the two peak intensities. The emission from the dominant A-peak is commonly several orders of magnitude higher than B-peak emission, resulting in B/A-intensity ratios well below 1%. Yet, as the A-peak intensity decreases, the ratio of B/A monotonically increases, and we observe a B/A ratio up to 30% in monolayer MoS<sub>2</sub>. The A-excitonic emission is further quenched when MoS<sub>2</sub> is incorporated into an MoS<sub>2</sub>/MoSe<sub>2</sub> heterostructure, where we observe comparable A- and B-peak intensities. We attribute these variations to differences in exciton recombination times, clarifying contradictory reports regarding the accessibility and significance of B-peak emission. Furthermore, we observe a high degree of valley polarization in both B-exciton emission in isolated monolayers and A-exciton emission in heterostructures, consistent with our model detailing the rapid exciton lifetimes in B-emission and van der Waals heterostructures.

Supported by core programs at NRL and the NRL Nanoscience Institute

3:00pm **2D+EM+MN+NS-ThA-3 Optospintronics and Magnetism with 2D Materials and Heterostructures, Roland Kawakami, The Ohio State University**

**INVITED**

I will review our latest developments in spintronics, optospintronics and magnetism in two-dimensional (2D) materials and heterostructures. Graphene continues to exhibit improved properties for spin transport and demonstrates additional functionality through the use of vertically stacked heterostructures. One of the interesting new directions is optospintronics enabled by heterostructures of graphene and transition metal dichalcogenides (TMD) [1]. Due to the valley optical selection rules of TMDs

and the large spin-orbit coupling, the helicity of the photon is coupled to the valley spin polarization of electrons. Thus, circularly polarized optical excitation into a TMD/graphene heterostructure generates spin polarization in the TMD that subsequently transfers to the graphene. This optical spin injection into graphene is an example of new functionality for the expanding field of 2D spintronics. In the area of 2D magnets, we have used molecular beam epitaxy (MBE) to deposit monolayer MnSe<sub>2</sub>, which exhibits ferromagnetism at room temperature [2]. These results open the door for new possibilities for magnetoelectronic applications with low dimensional materials.

[1] Yunqiu Kelly Luo, Jinsong Xu, Tiancong Zhu, Guanzhong Wu, Elizabeth J. McCormick, Wenbo Zhan, Mahesh R. Neupane, and Roland K. Kawakami, *Nano Lett.* **17**, 3877 (2017).

[2] Dante J. O'Hara, Tiancong Zhu, Amanda H. Trout, Adam S. Ahmed, Yunqiu Kelly Luo, Choong Hee Lee, Mark R. Brenner, Siddharth Rajan, Jay A. Gupta, David W. McComb, and Roland K. Kawakami, *Nano Lett.* doi: 10.1021/acs.nanolett.8b00683 (2018).

4:00pm **2D+EM+MN+NS-ThA-6 Giant Electromechanical Response in Van-der-Waals Layered Crystals, Sabine Neumayer, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; E Eliseev, National Academy of Sciences of Ukraine; A Tselev, CICECO and Department of Physics, University of Aveiro, Portugal; A Morozovska, National Academy of Sciences of Ukraine; M Susner, M McGuire, Oak Ridge National Laboratory; J Brehm, S Pantelides, Vanderbilt University; N Balke, P Maksymovych, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory** Obtaining ultrathin electromechanically active materials for memory and energy applications encounters numerous challenges as significant downscaling of classical ferroelectrics such as perovskite oxides is severely constrained by size and screening effects. Moreover, interfacing pseudocubic ferroelectrics with 2D electronic materials faces challenges related to defect and impurities, which limit performance. Van der Waals ferroelectrics, especially transition metal thiophosphates such as copper indium thiophosphate (CIPS) yield promising prospects for applications as ultrathin piezoelectric structures and interface materials due to their stable surfaces, layered structure and transition temperatures near room temperature. Here, we use scanning probe microscopy to explore the remarkable functional properties of CIPS across the transition temperature. At low temperatures, strong electromechanical response is measured despite the small polarization values and the material contracts in electric fields rather than expanding. These findings point to giant negative electrostrictive coefficients, which were quantified using Landau-Ginzburg-Devonshire analysis. Above the transition temperature, CIPS shows dielectric tunability comparable to BST at low frequencies. In addition, electromechanical strain exceeding 10 nm displacement was measured upon fully reversible field induced formation of particles on the surface. Complimentary DFT calculations provide further insight into the role of ionic displacement in electromechanical behavior.

Research conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy.

4:20pm **2D+EM+MN+NS-ThA-7 A Universal Method for Measuring Valleytronic Quality of 2D Materials using Conventional Raman Spectroscopy, Steven Vitale, J Varghese, D Nezhich, M Rothschild, MIT Lincoln Laboratory**

Valleytronics offers a new information processing paradigm based on the momentum index of real or quasi-particles in 2D materials as the fundamental unit of information storage instead of charge. A major challenge to realize valleytronic computing is the development of deterministic material growth processes which yield valleytronic-quality material with the requisite valley relaxation lifetime (T<sub>1</sub>) and valley dephasing time (T<sub>2</sub>). Unfortunately direct measurement of T<sub>1</sub> and T<sub>2</sub> requires complex instrumentation to perform ultrafast spectroscopic measurements and thus is not practical for routine material analysis. In this paper, we demonstrate that an accurate and reproducible measurement of T<sub>1</sub>/T<sub>exc</sub> (where T<sub>exc</sub> is the exciton recombination lifetime) can be performed a simple Raman microscope. By simultaneously measuring the photoluminescence of the 2D material and the Raman transition of the underlying silicon substrate as a function of the incident laser polarization angle, one can remove sources of error and equipment-to-equipment variability. This technique is completely general and can be applied to any valleytronic material which can be grown-on or transferred-to a Raman-



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active crystalline substrate, such as silicon. Using this technique we show that valley relaxation in a sample of CVD-grown MoS<sub>2</sub> is an order of magnitude slower at 4 K than at 100 K. Oxidation of MoS<sub>2</sub> left exposed to the ambient environment severely decreases the valleytronic quality of the material. Two-dimensional mapping of the valley relaxation time of CVD MoS<sub>2</sub> domains at 4 K shows a three-fold spatial symmetry which is suggestive of new valley physics phenomena which arise in 2D crystals of finite size. MoS<sub>2</sub> domain size also affects the valley relaxation time, which has significant material-growth implications for real valleytronic applications. Finally we compare these measurements to our calculated requirements for valley relaxation time in a practical information processing device and quantify the challenges for future valleytronic material growth.

4:40pm **2D+EM+MN+NS-ThA-8 Discovery of Intrinsic Ferromagnetism in 2D van der Waals Crystals**, *Xiang Zhang*, *C Gong*, University of California, Berkeley **INVITED**

In this talk, I will present our discovery of the intrinsic ferromagnetism in 2D van der Waals (vdW) crystals, including the prominent dimensionality effect and unprecedented magnetic field control of the Curie temperature in the nearly-ideal 2D Heisenberg ferromagnet. Significant fundamental physics in 2D magnetism and the corresponding exotic phenomena we observed will be expounded. Updated research on the complex magnon scatterings, material level engineering of 2D magnetism, and the development of novel concept of spintronic devices will be further discussed. Finally, I will envision the possible directions towards advancing 2D magnets for practical spintronic applications.

5:20pm **2D+EM+MN+NS-ThA-10 Spectroscopic Evidence of Pair-mediated Bosonic Modes in Superconductor FeSe/SrTiO<sub>3</sub>(100) Film**, *Minjun Lee*, Seoul National University, Republic of Korea, Republic of Korea; *M Oh*, *H Jeon*, *S Yi*, *I Zoh*, Seoul National University, Republic of Korea; *C Zhang*, Seoul National University, Republic of Korea, Republic of Korea; *J Chae*, *Y Kuk*, Center for Quantum Nanoscience, Institute for Basic Science, Republic of Korea

Single layer FeSe on SrTiO<sub>3</sub>(100) is atypical but noticed system in superconductivity. This has unique properties due to the substrate phonon. Unlike other bulk systems, the presence of the interface allows the substrate phonons to affect the superconducting layer. We have investigated substrate phonon effects on superconducting FeSe layer by using scanning tunneling spectroscopy and Eliashberg theory. We were able to measure acoustic, optical and substrate phonons in  $d^2I/dV^2$  spectroscopy. We found these phonon modes attribute to the pairing of electrons in this superconducting layer. These results are analyzed by Eliashberg model and we will discuss the coupling strength of these bosonic features. We have found that the substrate phonon has major contribution to increase the transition temperature of this system.

## Applied Surface Science Division

### Room 204 - Session AS+NS-ThA

#### Profiling, Imaging and Other Multidimensional Pursuits

**Moderators:** Ashley Ellsworth, Physical Electronics, Jordan Lerach, ImaBiotech Corp.

2:20pm **AS+NS-ThA-1 Surface Science Study of Au/Ni/Cr/n-SiC and Au/Cr/Ni/n-SiC Thin Film Ohmic Contact Material**, *Martyn Kibel*, *A Barlow*, La Trobe University, Australia; *P Leech*, RMIT University, Australia

Silicon carbide (SiC) has become a promising semiconductor material for use in elevated temperature and high power devices. Although ohmic contacts to n-SiC have been widely fabricated using a metallization of Ni/n-SiC annealed at ~1000 °C, the formation of nickel silicides at the interface has resulted in uneven roughening of the metal surface. We have examined for the first time the development of ohmic contact materials containing layers of both Ni and Cr (Au/Ni/Cr/n-SiC and Au/Cr/Ni/n-SiC). A detailed study of these layered structures, both as-deposited and subsequently annealed at 750-1000°C has been undertaken using a range of surface analysis techniques. Auger electron spectroscopy (AES) depth profiling, both static and using Zalar rotation, has been used to etch through the layers into the epitaxial SiC. AES elemental mapping, in conjunction with SEM imaging, has been used to record the nature of the surface before and after profiling. AES line scans have also been employed to characterize the subsequent crater walls. In addition, X-ray photoelectron spectroscopy (XPS) depth profiling has been used to characterise the interfaces with a focus on the chemical states of the constituent elements. The nature of the

interfaces between individual layers is discussed as well as the methodologies for generating depth profiles from the acquired data. The analysis has shown a wide-scale interdiffusion of the layers after annealing of the Au/Ni/Cr/n-SiC structure with the formation of surface globules. In comparison, the Au/Cr/Ni/n-SiC contacts have shown a limited interdiffusion of the layers and relatively smooth surfaces, indicating that the intermediate layer of Cr has acted as a diffusion barrier for the Ni. The electrical characteristics of the as-deposited and annealed contacts have been measured using circular transmission line test patterns and the results correlated with the AES and XPS analyses.

2:40pm **AS+NS-ThA-2 3D Imaging of InGaN/GaN based Nanowires and Nanotubes using Time-of-flight Secondary Ion Mass Spectrometry**, *Jean-Paul Barnes*, Univ. Grenoble Alpes, CEA, LETI, France; *A Kapoor*, Univ. Grenoble Alpes, CEA, France; *C Durand*, Univ. Grenoble Alpes, CEA, France; *C Bougerol*, Univ. Grenoble Alpes, CNRS, France; *J Eymery*, Univ. Grenoble Alpes, CEA, France

GaN based nanowire light-emitting diodes (LEDs) can be grown in ordered arrays on sapphire and large Si substrates. The growth of coaxial InGaN/GaN multiple quantum wells (MQWs) on the nonpolar m-plane sidewalls of the GaN wire increases the active region area, reduces the defect density and can increase efficiency in the case of thick QWs due to the absence of quantum confined Stark effect [1]. Variants on this approach include InAlN/GaN MQW tubes and the integration of such wires in flexible substrates [2].

An important parameter controlling the light emission is the indium concentration in the MQWs and their thickness, which may vary along the length of the wire. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been used to perform 3D mapping of the indium concentration in the coaxial MQWs for both GaN wire geometries and InAlN/GaN MQW tube geometries.

Experiments are performed using a dual beam approach with a finely focused (<200 nm spot size) Bi<sub>3</sub><sup>++</sup> analysis beam at 60 keV and oxygen sputtering at 500 eV. The indium concentration is calibrated from a 2-D MQW structure on which the nanowires are deposited for analysis so that TOF-SIMS analysis can be performed on the sidewall perpendicular to the MQWs. The TOF-SIMS analysis on single nanowires has allowed the composition of InGaN quantum wells to be quantified and the fact that the MQW structure becomes thicker towards the end of the nanowire to be determined. The ability to target specific nanowires allows the composition determined by TOF-SIMS to be compared with photoluminescence and cathodoluminescence measurements to link the emission of the wires to the MQW composition and thickness. Using a similar approach it was possible to characterize the InAlN/GaN MQWs on nanotube structures and confirm that the MQW structure remains after selective etching of the GaN core and annealing. Such high resolution TOF-SIMS 3D imaging can also be used for other semiconductor structures such as those grown by selective epitaxial growth of for visualising doping in microelectromechanical systems (MEMS) systems.

This work was carried out on the nanocharacterisation platform (PFNC) of the CEA Grenoble.

#### References:

R. Koester et al. "M-plane core-shell InGaN/GaN multiple-quantum-wells on GaN wires for electroluminescent devices," *Nano Letters* **11** (11), 4839-4845 (2011).

[2] C. Durand et al. "Thin-Wall GaN/InAlN Multiple Quantum Well Tubes," *Nano Letters* **17** (6), 3347-3355 (2017).

3:00pm **AS+NS-ThA-3 Atom Probe Tomography: Applications and Prospects for Surface and Interface Science**, *Austin Akey*, *D Bell*, Harvard University **INVITED**

Atom Probe Tomography (APT) is a three-dimensional, individual-atom composition mapping technique. Specimens are disintegrated atom-by-atom using a combination of high electric fields and voltage or laser pulses, causing individual ions to be ejected towards a position-sensitive detector with high time resolution. The resulting hit position, combined with the ion's time of flight, allows single-Angstrom, single-atom time-of-flight mass spectroscopy to be performed over volumes containing hundreds of millions to billions of atoms. Recent advances in instrument design and automation have greatly expanded the field of materials systems and scientific questions that the technique can address, and it is particularly well suited to analysis of surface and interface composition.

Datasets can be processed and analyzed as highly-localized 1D composition measurements, 2D surface mapping over an arbitrary surface in three-

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dimensions, or full volumetric composition maps, allowing a wide variety of questions to be asked of a material. We present applications including: bulk composition fluctuation and clustering measurements; full 3D composition mapping of electronic devices; interface composition and roughness determination; composition mapping of nanowire and other quasi-one-dimensional structures; and surface and bulk composition of catalytic materials. We also discuss the importance of correlating other microanalysis techniques with APT and give examples of one-to-one correlative work. The development of correlative electron microscopy and APT specimen geometries have allowed otherwise unresolvable questions to be answered, and new work extends this into the realm of combined in-situ and ex-situ measurement of the structural and compositional evolution of materials. Finally, we will discuss future prospects for the technique and its application to surface science.

**4:00pm AS+NS-ThA-6 TOF-SIMS Analysis with High Lateral and High Mass Resolution in Parallel**, *F Kollmer*, IONTOF GmbH, Germany; *N Havercroft*, IONTOF USA; *A Henß*, Justus-Liebig University Giessen, Germany; *J Zakeł*, *D Rading*, *H Arlinghaus*, **Ewald Niehuis**, IONTOF GmbH, Germany

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a very sensitive surface analytical technique. It provides detailed elemental and molecular information about surfaces, thin layers, interfaces, and full three-dimensional analysis of the sample. A general strength of the applied time-of-flight mass analyzer is the very high transmission that is due to the fact that the entire mass range is analyzed in parallel. Any selection of peaks prior to the analysis is not required.

However, the time-of-flight analyzer suffers from a trade-off between mass resolution, lateral resolution, and signal intensity. Even under low intensity conditions highest mass resolution and highest lateral resolution are not obtained at the same time. In our contribution, we will discuss an improved analyzer setup that allows us to overcome this limitation.

In order to obtain a high mass resolution, a time-of-flight analyzer needs a very short start signal for the analysis cycle. Under static extraction conditions, a wider primary ion pulse broadens the width of any peak in the spectrum and thus reduces the achievable mass resolution. However, the generation of very short pulses by bunching inevitably broadens the spot size of the beam and leads to very low primary ion currents as well as long acquisition times. Even under lowest current conditions this approach remains a compromise since it does not allow one to obtain the maximum performance in terms of lateral resolution.

A promising approach in order to overcome this fundamental trade-off is to pulse the analyzer and to extract the secondary ions just after the primary beam hits the surface (delayed extraction). Under delayed extraction conditions, the width of the primary ion pulse no longer influences the uncertainty of the start signal of the time-of-flight analysis. High lateral resolution and high mass resolution are obtained in parallel with long ion pulses at higher, and thus more useful, ion currents. Moreover, the delayed extraction mode does improve the analysis of topographic surfaces in terms of transmission and mass resolution. Although this approach has been well known for many years and is frequently applied in MALDI, the application in TOF-SIMS is only recently increasing. We have optimized this mode and we will show that the achieved improvements are very useful for the analysis of most kinds of samples and analytical tasks and that this mode has the potential to become a standard mode for TOF-SIMS analyses as well.

In our contribution, we will discuss the pros and cons of the delayed extraction mode. Investigated samples include: pharmaceuticals, biological samples and reference samples.

**4:20pm AS+NS-ThA-7 Industrial Applications of Surface Analysis in Chemical Mechanical Planarization**, *Hong Piao*, *Y Liang*, *J McDonough*, *C Ballesteros*, FUJIFILM Planar Solutions, LLC, FUJIFILM Electronic materials USA., Inc.; *E Turner*, FUJIFILM Planar Solutions, LLC, FUJIFILM Electronic materials USA., Inc; *A Mishra*, *R Wen*, FUJIFILM Planar Solutions, LLC, FUJIFILM Electronic materials USA., Inc.

Chemical mechanical planarization/polishing (CMP) is a chemical reaction assisted mechanical polishing process in the semiconductor manufacturing industry to remove overburden material or specific layers in the film stacking and to planarize the topography at the patterned wafer surface. Although the basic principles of CMP are understood, thorough understanding of surface chemical processes which occur during polishing is still lacking, especially the chemistry at the interface of the wafer/slurry/pad. Investigations aimed at understanding fundamental mechanisms usually employ electrochemical techniques. Surface analysis methods remain rather under-utilized in this field, especially when taking

into account the explosive growth of these surface techniques for the analysis of "nano-structured" films in other research fields.

FUJIFILM Planar Solutions (PLNR) is a market leader for metals and dielectric CMP slurries. Our in-house XPS and ToF-SIMS surface analysis tools have greatly enhanced our capabilities in analyzing and understanding surface reactions, their mechanism, and fundamental science and engineering behind the slurry wafer interaction at the interface during CMP.

The goal of this presentation is to review selected results provided by advanced surface analysis tools combined with other complementary testing methods. Examples describing CMP characterization are given in two technological areas that are growing in importance: (1) Cu and Co CMP and (2) Defectivity in front end of line polishing involving dielectrics. We also pay particular attention to show how the recent improvements in instrumentation could open new opportunities and fundamental understanding of how surface analyses can enable improvements in slurry design for CMP, thus leading to the development of next-generation advanced CMP slurries and processes.

**4:40pm AS+NS-ThA-8 Correlative Images of Microscopy Spectroscopy: Beyond the 3D Characterization in Surface Analysis**, *Tanguy Terlier*, Korea Institute of Science and Technology, Republic of Korea; *R Verduzco*, Shared Equipment Authority, Rice University; *Y Lee*, Korea Institute of Science and Technology, Republic of Korea

Technological progress has spurred the development of increasingly sophisticated analytical devices. The full characterization of structures in terms of sample volume and composition is now highly complex. Traditionally, the surface spectroscopic techniques such as AES or ToF-SIMS provide the chemical distribution of sample surfaces. Nevertheless, an important issue in surface analysis is to perform 3D chemical mapping of structured samples with a complex architecture, conserving as well high spatial resolution (lateral and in-depth) as high mass resolution. During the surface analysis, only a projection into 2D surface mapping is achieved which reverse the topographic render after the in-depth analysis. Moreover, the use of ion beam sputtering induces preferential sputtering and damage accumulation due to the sputter beam. So, the surface roughness generated by the sputtering affects the depth profiling of chemical signals. In consequence, the authentic 3D chemical distribution as a function of the depth is completely distorted or lost.

Alternative approaches to resolve the artifacts of 3D chemical images exist. Among these solutions, the use of Scanning Probe Microscopy (SPM) in combination with a surface spectroscopic analysis permits to correct the depth scale of the data and to reduce the artifacts due to the depth profiling. In addition to the data correction, correlative approach using SPM and surface spectroscopy offers the unique possibility to couple topography with 3D chemical information for having access to the accurate volume render. Merging other measurable signals such as electrostatic force microscopy with 3D chemical analysis can also enhanced the understanding of the surface properties and structure characteristics.

After a brief introduction to the data fusion, different methods of 3D reconstruction used in surface analysis will be discussed. In particular, we will show a recent method, the dynamic-model-based volume correction. This method has been applied on a patterned sample using two combination of techniques, SPM/ToF-SIMS and SPM/AES. Then, we have compared the performances of *ex situ* SPM/ToF-SIMS with a new instrument, an *in situ* SPM/ToF-SIMS. To illustrate the new potentials of the correlative imaging method, we have characterized two different samples, a cryo-freezing prepared cell sample and a self-assembled block copolymer film. Finally, we will explore the applications of the correlative microscopy and spectroscopy analyzing a standard SRAM sample that is composed of patterned structures integrating concentration-controlled doping. This sample has provided multi-signal mappings and a quantitative analysis.

**5:00pm AS+NS-ThA-9 3D Structure of Atomically Dispersed Metal Species on an Oxide Single Crystal Surface Studied by Polarization-dependent Total Reflection Fluorescence (PTRF)-XAFS**, *Satoru Takakusagi*, *K Asakura*, Hokkaido University, Japan

Precise size control of metal species on an oxide surface, especially in the range of <1 nm, is now highly important to develop the next-generation catalysts, sensors, and electronic devices. However this is not easy since metal atoms are easily aggregated to form large particles on an oxide surface. This is due to the small stabilization energy and/or the small activation energy for the metal diffusion. If one can obtain a monatomic metal species on an oxide surface, it can be a building block for synthesis of the metal cluster and helps us to control the cluster size in one-atom

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precision. Our group has developed the “premodified surface method” to obtain a highly dispersed metal species on an oxide single crystal surface. In the premodified surface method, the oxide surface is precovered with a functional organic molecule possessing a substituent atom which can strongly coordinate to a metal atom before metal deposition. We have determined the precise 3D structures of such metal species by polarization-dependent total reflection fluorescence (PTRF)-XAFS technique.

In this study, various metals such as Cu, Au, Ni and Pt were vacuum-deposited on a TiO<sub>2</sub>(110) surface premodified with *o*-mercaptobenzoic acid (*o*-MBA) and their 3D structures were determined by the PTRF-XAFS technique. We have found that Cu, Au and Ni were atomically dispersed by bond formation with sulfur of *o*-MBA and oxygen in the TiO<sub>2</sub> lattice, but Pt was aggregated to form clusters. We will discuss the factors that govern single metal dispersion based on the energy difference between sulfur-metal-oxygen and metal-metal bond formations.

**5:20pm AS+NS-ThA-10 XPS Imaging and Spectromicroscopy Investigation of Extended Release Pharmaceutical Tablets, Jonathan Counsell, S Coultas, C Blomfield, Kratos Analytical Ltd, UK; D Scurr, The University of Nottingham, UK; L Mason, University of Nottingham, UK; V Ciarnelli, J Garfitt, S Rigby-Singleton, Juniper Pharma Services Ltd, UK; M Alexander, The University of Nottingham, UK; M Davies, University of Nottingham, UK; C Moffitt, Kratos Analytical Inc.; S Hutton, Kratos Analytical Ltd, UK, United Kingdom of Great Britain and Northern Ireland**

The effects of formulation methodology on the performance of tablets have been studied for decades. Typically tablets consist of the active drug and excipients which influence stability, release rate and binding. HPMC (Hydroxypropyl Methylcellulose) is a hydrophilic polymer commonly used in extended-release tablets as it shows rapid hydration and uniform gel formation. The microstructure of HPMC particles in matrices influences the ability of HPMC to form gel layers after contact with water, thereby affecting release characteristics. While previous studies described the use of Raman spectroscopy as a benchmark method for chemically imaging solid pharmaceutical formulations<sup>1</sup>, there are relatively few contributions reporting the application of XPS (X-ray Photoelectron Spectroscopy) in this field. New insight into tablet component distribution could be employed in the successful formulation design and development process.

Herein we investigate the novel application of XPS to elucidate the distribution of both drug and excipients species. Parallel XP imaging capabilities will be illustrated and demonstrated for several tablet systems yielding information on particle size, distribution and shape. The use of small-spot XPS provides quantitative and chemical-state information on imaging features. The novel use of argon cluster ion bombardment will be discussed for both cleaning and depth profiling. Peak-fitting, pitfalls and limitations will be explored and compared with other complementary techniques such as ToF-SIMS.

Strachan *et al.* Journal of Pharmacy and Pharmacology. 2007. 179-192.

**5:40pm AS+NS-ThA-11 An experimental Guide to Conversion of ToF-SIMS Spectrum to BIG DATA: Application in Analysis of Ultrathin Coatings, Kevin Abbasi, A Avishai, Swagelok Center for Surface Analysis of Materials, Case school of Engineering, Case Western Reserve University**

Thin films are traditionally being characterized using cross sectional analysis with scanning or transmission electron microscopes. Although accuracy of these technique are very high, it's hard to analyze a large number of samples this way. Surface analysis instruments such as X-ray photoelectron spectroscopy (XPS), Auger Electron Spectroscopy (AES) and Time-of-flight secondary ion mass spectrometry (ToF-SIMS) can be used to analyze the top surface and erode it with focused ions. Alternating the analysis and ion etching cycles, concentration profiles can be achieved.

In specific conditions where the element of interest has very low concentration or the thickness of the coating is less than the analysis volume (ultrathin films), ToF-SIMS becomes a very powerful tool as it provides the best detection limit and smallest analysis depth. Extracting useful and specific information from the mass spectra and reducing the dimensionality of very large datasets, is a challenge, that has not been fully resolved. Multivariate analysis has been widely deployed to assist in the interpretation of the ToF-SIMS data. Principal component analysis is a popular approach that can help ease the task of analyzing spectrums acquired at different locations from the top surface, compare it against different samples and help extract trends.

The purpose of this talk is to provide experimental guide for the characterization of ultrathin coatings (both flat and in form of particles). Two set of samples will be described: Inter-diffusion will be characterized

in a flat coating obtained from Atomic layer deposition (ALD) process and contamination analysis will be then discussed on micron size particles with ultrathin coating. Different strategies will be then discussed to obtain concentration profiles using Time-of-flight secondary ion mass spectrometry. Principal component analysis will then be used to successfully convert mass spectrums into big data and extracting similarities between spectrums and samples.

## Electronic Materials and Photonics Division Room 101A - Session EM+2D+NS+PS+RM+TF-ThA

### IoT Session: Flexible Electronics & Flash Networking Session

**Moderators:** Shalini Gupta, Northrop Grumman ES, Sang M. Han, University of New Mexico

**2:20pm EM+2D+NS+PS+RM+TF-ThA-1 Epitaxial Electrodeposition of Electronic and Photonic Materials onto Wafer-size Single Crystal Gold Foils for Flexible Electronics, Jay Switzer, Missouri University of Science and Technology**

**INVITED**

Single-crystal silicon (Si) is the bedrock of semiconductor devices due to the high crystalline perfection that minimizes electron-hole recombination, and the dense SiO<sub>x</sub> native oxide that minimizes surface states. There is interest in moving beyond the planar structure of conventional Si-based chips to produce flexible electronic devices such as wearable solar cells, sensors, and flexible displays. Most flexible electronic devices are based on polycrystalline materials that can have compromised performance due to electron-hole recombination at grain boundaries. In order to expand the palette of electronic materials beyond planar Si, there is a need for both an inexpensive substrate material for epitaxial growth, and an inexpensive and scalable processing method to produce epitaxial, grain-boundary-free films of metals, semiconductors, and optical materials. Recently, in our laboratory, we have developed a process for producing wafer-size, flexible, and transparent single-crystal Au foils by an electrochemical processing method.<sup>[1]</sup> Au is epitaxially electrodeposited onto Si using a very negative applied potential. An interfacial layer of SiO<sub>x</sub> is then produced photoelectrochemically by lateral undergrowth. The Au foil is then removed by epitaxial lift-off following an HF etch. We will report on the electrodeposition of epitaxial films of metal oxide semiconductors such as Cu<sub>2</sub>O and ZnO onto the highly-ordered and flexible Au foils. We will also present new, unpublished results in which we spin-coat epitaxial films of perovskites, such as CsPbBr<sub>3</sub>, directly onto these Au foils and onto other single crystals.

**Acknowledgement:** This presentation is based on work supported by the U.S. Department of Energy, Office of Basic Sciences, Division of Materials Science and Engineering under grant No. DE-FG02-08ER46518.

[1] Mahenderkar N., Chen Q., Liu Y.-C., Duchild, A., Hofheins, S. Chason E., Switzer J (2017). Epitaxial lift-off of electrodeposited single-crystal gold foils for flexible electronics. *Science*, **355**, 1203-1206.

**3:00pm EM+2D+NS+PS+RM+TF-ThA-3 Flexible Electronic Devices Based on Two Dimensional Materials, R Kim, N Glavin, Air Force Research Laboratory; R Rai, K Gliebe, M Beebe, University of Dayton; Air Force Research Laboratory; J Leem, University of Illinois at Urbana-Champaign, Republic of Korea; S Nam, University of Illinois at Urbana-Champaign; R Rao, Air Force Research Laboratory; Christopher Muratore, University of Dayton**

Low temperature synthesis of high quality 2D materials directly on flexible substrates remains a fundamental limitation towards realization of robust, strainable electronics possessing the unique physical properties of atomically thin structures. Here, we describe room temperature sputtering of uniform, stoichiometric amorphous MoS<sub>2</sub>, WSe<sub>2</sub>, and other transition metal dichalcogenides and subsequent large area (>2 cm<sup>2</sup>) photonic crystallization to enable direct fabrication of two-dimensional material photodetectors on large area flexible PDMS substrates. Fundamentals of crystallization kinetics for different monolithic and heterostructured TMDs are examined to evaluate this new synthesis approach for affordable, wearable devices. The photodetectors demonstrate photocurrent magnitudes and response times comparable to those fabricated via CVD and exfoliated materials on rigid substrates and the performance is unaffected by strains exceeding 5%. Other devices and circuits fabricated from crystallized 2D TMDs deposited on large area flexible substrates are demonstrated.

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3:20pm **EM+2D+NS+PS+RM+TF-ThA-4 Contact Resistances and Schottky Barrier Heights of Metal-SnS Interfaces**, *Jenifer Hajzus, L Porter*, Carnegie Mellon University; *A Biacchi, S Le, C Richter, A Hight Walker*, National Institute of Standards and Technology (NIST)

Tin(II) sulfide (SnS) is a natively p-type, layered semiconductor that is of interest for two-dimensional and optoelectronic applications.

Understanding the behavior of contacts to SnS is essential for its use in devices. In this work, contact metallizations with a range of work function metals were characterized on both solution-synthesized, p-type SnS nanoribbons and electron-beam evaporated, polycrystalline SnS thin films. The structure and properties of electron-beam evaporated SnS films were dependent upon deposition temperature and post-deposition annealing. A deposition temperature of 300 °C followed by vacuum annealing at 300 °C resulted in p-type, orthorhombic SnS films. Specific contact resistances of Ti/Au, Ru/Au, Ni/Au, and Au contacts were measured on SnS films using circular transfer length method (CTLM) patterns prior to and after annealing the contacts at 350 °C in argon. All metallizations on SnS thin films were ohmic prior to annealing. A trend of decreasing average specific contact resistance with increasing metal work function was observed for the as-deposited contacts. Annealed Ru/Au exhibited the lowest average specific contact resistance of  $\sim 1.9 \times 10^{-3} \Omega \cdot \text{cm}^2$ . Contacts were additionally patterned onto individual, solution-synthesized SnS nanoribbons. In contrast to the behavior of contacts on electron-beam evaporated films, low work function metals (Cr/Au and Ti/Au) formed Schottky contacts on SnS nanoribbons, whereas higher work function metals (Ni/Au and Pd/Au) formed ohmic or semi-ohmic contacts. Ni/Au exhibited a lower contact resistance ( $\sim 10^{-4} \Omega \cdot \text{cm}^2$  or lower) than Pd/Au ( $\sim 10^{-3} \Omega \cdot \text{cm}^2$  or lower). Schottky barrier heights and ideality factors of Cr/Au and Ti/Au contacts were extracted by fitting current-voltage measurements to a back-to-back Schottky diode model. The ohmic behavior for Ni/Au and Pd/Au and the calculated Schottky barrier heights (0.39 and 0.50 eV for Cr/Au and Ti/Au, respectively) on SnS nanoribbons agree well with behavior predicted by Schottky–Mott theory and suggest a lack of Fermi level pinning.

## **MEMS and NEMS Group**

### **Room 202B - Session MN+2D+AN+NS-ThA**

#### **Nonlinear and Thermal Resonators**

**Moderators:** Meredith Metzler, University of Pennsylvania, Christian Zorman, Case Western Reserve University

2:20pm **MN+2D+AN+NS-ThA-1 Embracing Nonlinearity and Thermal Fluctuations in Nanomechanics**, *Daniel Lopez, D Czaplewski, C Chen*, Argonne National Laboratory; *D Zanette*, Centro Atomico Bariloche, Argentina; *S Shaw*, Michigan State Univrsity **INVITED**

The field of micro-mechanics is now a well-established engineering domain with demonstrated impact in fundamental science and product development. Unfortunately, as the dimensions of the devices are reduced from the micro- to the nano-scale, the direct scaling of the fundamentals principles and fabrication processes cease to work. When going from micro- to nano-mechanical systems, MEMS to NEMS, the devices linear dynamic range can be reduced to the point where the amplitudes needed for lineal response are below the noise level and, as a consequence, operation in the nonlinear regime is unavoidable. Furthermore, thermal fluctuations and fluctuation-induced forces become relatively stronger causing significant changes in their dynamic response and on the manner in which they interact with the surrounding environment. This combination of nonlinear dynamics and high sensitivity to fluctuations has been seen as a deleterious combination for the advance of nano mechanical devices.

Rather than continuing to struggle to avoid these phenomena, it is of interest to consider how micro/nanosystem might effectively capitalize on this nonlinear fluctuating response. In this talk, I will demonstrate that nonlinearity offers unique possibilities for the controlled response of micro and nano mechanical devices and, thereby, a host of novel application opportunities. Examples of these opportunities include the development of compact frequency sources with low phase noise, the engineering of dissipation reservoirs to manipulate energy decay processes, and the enhancement of synchronization range between microscopic and macroscopic oscillators.

3:00pm **MN+2D+AN+NS-ThA-3 Probing Ion Radiation Effects in Silicon Crystals by 3D Integrated Resonating Thin Diaphragms**, *Hailong Chen, H Jia, V Pashaie*, Case Western Reserve University; *W Liao, C Arutt, M McCurdy*, Vanderbilt University; *P Hung*, The Aerospace Corporation; *R Reed, R Schrimpf, M Alles*, Vanderbilt University; *P Feng*, Case Western Reserve University

Space radiation (e.g., solar, galaxy) and man-made radiation environments (e.g., nuclear plant) can expose devices to radiation at doses that may lead to severe damage [1]. In recent decades, a large body of work has been performed to understand radiation effects on mainstream solid state electronic devices [1-3], in particular on MOS devices [2] and integrated circuits [3]. Lately, microelectromechanical systems (MEMS) have seen widespread adoption in consumer, military and aerospace products due to their small size, low power consumption, and in some cases, monolithic integration with electronics [4]. As such, the reliability of MEMS devices for many applications in relatively benign environments has been well established [5]. However, the study of impact on mechanical properties due to radiation-induced damages is an area where limited research has been conducted.

In this work, we report on experimental investigation of heavy ion radiation effects on mechanical properties of Si crystals, by exploiting a novel 3D scheme of using 5 vertically stacked micromachined vibrating Si diaphragms (2 mm × 2 mm × 2 μm) exposed to oxygen ions. Simulations find the stop range of oxygen ions in Si is 7.3 μm. A Pelletron system is employed to irradiate oxygen ions into the Si diaphragms (10.3MeV, with a dose of  $5.6 \times 10^{13}/\text{cm}^2$ ). Before and after radiation, multimode resonances are characterized in vacuum by using an ultrasensitive optical interferometry system. We have observed that diaphragms D1 and D2, which oxygen ions are expected to pass completely through, present modest multimode redshifts ranging from 0.85 kHz to 1.67 kHz, and 0.85 kHz to 1.19 kHz, corresponding to an average fractional frequency shift of 10.5% and 7.0%, respectively. In contrast, for devices D3 and D4, in which most ions are expected to stop, each resonance peak shifts much more dramatically, with a frequency shift of 27.3% and 20.4%. We attribute these large shifts to the very large capture area of the diaphragms, the very heavy and energetic oxygen ions, and high ion dose. Device D5 shows minimal frequency shifts among the five diaphragms because few oxygen ions reach and interact with this device layer. The diaphragm stack exhibits outstanding capability for probing radiation damages in MEMS, not only able to capture the radiation events obviously, but also help analyze different amount and types of damages induced in each stacking layer.

[1] L. Gregory, *et al.*, Proc. IEEE. **62**, 1974. [2] J. R. Srouf, *et al.*, Proc. IEEE. **76**, 1988. [3] H. L. Hughes, *et al.*, IEEE Trans. Nucl. Sci. **50**, 2003. [4] N. Arutt, *et al.*, Semicond. Sci. Technol. **32**, 2017. [5] H. R. Shea, Proc. SPIE. **7928**, 2011.

3:20pm **MN+2D+AN+NS-ThA-4 An Array of Thermally-actuated Nanoresonators for Real-time Mass Spectrometry**, *Martial Defoort, M Sansa, M Gély, G Jourdan, S Hentz*, CEA/LETI-University Grenoble Alpes, France

Micro/Nano-ElectroMechanical Systems (M/NEMS) have attracted much attention in the last years in the mass spectrometry field. They feature high sensitivity, charge independent and single particle detection capabilities, in a mass range where conventional mass spectrometry struggles, hampering the analysis of large mass objects like protein complexes or viruses [1-4].

In general the size and mass of the device defines the size and mass ranges of the particles to measure for frequency tracking and point mass approximation purposes. However, as many silicon M/NEMS are electrostatically actuated, the gap between the driving electrode and the resonator becomes a critical parameter. While for many applications this gap should be as small as possible for high efficiency actuation and high signal-to-noise ratio, a particle landing within the gap results in a catastrophic failure of the device through electrical short-circuit or mechanical anchoring.

We present a new actuation scheme for doubly-clamped beams which relies on the thermal expansion of nano-actuators in silicon due to Joule heating, located close to the anchor of the resonator (Fig. 1), that we demonstrate to work in an array of 20 NEMS (Fig. 2). Unlike some thermoelastic actuation schemes [5], the technique we propose does not require an additional layer (of, for example, a metal) and is readily CMOS-compatible. Because of their small size and thermal capacity, the thermal time constant of the actuators is small enough to drive the resonator up to several 100's MHz with large efficiency and to actuate the two first flexural modes of the same device simultaneously, which is required for single

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particle mass sensing. The detection scheme uses the piezoresistive gauges located on the other end of the beam, as previously presented [6]. We compare the performance of this actuation technique with a standard electrostatic scheme both on the same array and demonstrate the thermal actuation does not affect the level of frequency fluctuations limiting the device mass resolution (Fig. 3).

1. Hanay *et al*, nature nanotechnology 2012.
2. Sage *et al*, nature communications 2015.
3. Sage *et al*, Arxiv 2017.
4. Dominguez-Medina *et al*, Arxiv 2018.
5. Mo Li *et al*, nature nanotechnology 2007.
6. Mile *et al*, nanotechnology 2010.

4:00pm **MN+2D+AN+NS-ThA-6 Nonlinear and Noise Induced Dynamics of High Q Nanomechanical Resonators**, *Jana Huber, E Weig*, University of Konstanz, Germany **INVITED**

Doubly-clamped pre-stressed silicon nitride string resonators excel as high Q nanomechanical systems enabling room temperature quality factors of several 100,000 in the 10 MHz eigenfrequency range when operated under vacuum conditions. To retain the high mechanical quality factor, dielectric transduction is implemented as an all-electrical control scheme avoiding the metallization of the string. To this end, the string is exposed to an inhomogeneous electric field created between adjacent electrodes. The resulting gradient field provides an ideal platform for actuation, displacement detection, frequency tuning as well as strong mode coupling between the in- and out-of-plane modes of the string.

Here we focus on the nonlinear dynamics of the string subject to a strong drive. As a result of the high quality factor, cubic as well as higher order nonlinearities are observed. In the presence of thermal fluctuations, satellite resonances arise which enable deep insights into fundamental properties of the system.

4:40pm **MN+2D+AN+NS-ThA-8 SNIC Bifurcation Generated Mechanical Frequency Comb**, *David Czaplewski, D Lopez*, Center for Nanoscale Materials, Argonne National Laboratory; *O Shoshani*, Ben-Gurion University -Negev, Israel; *A Eriksson*, Chalmers University of Technology, Gothenburg, Sweden; *S Shaw*, Florida Institute of Technology

Microelectromechanical (MEMS) resonant structures can exhibit unexpected behavior when driven to a nonlinear response. Beyond the normal Duffing behavior observed for non-linear resonators, the behavior of a MEMS resonator can become complex at an internal resonance, when the frequencies of two modes of the structure are in a simple ratio, leading to an exchange of energy between the modes. Recently, operation of MEMS oscillators at internal resonance has led to increased frequency stabilization and the creation of coherence time, where the amplitude and frequency of the oscillator remains constant for thousands of oscillations after the external driving is removed. Here, we demonstrate a bursting behavior in the temporal response of a MEMS resonator that produces a frequency comb in the corresponding spectral response. The bursting behavior is a result of a bifurcation in the response of the resonator that occurs at an internal resonance. The fundamental flexural mode exchanges energy with a torsional mode causing the amplitudes of both modes to vary on a time scale (~1s) that is much larger than the period (10  $\mu$ s) of a single oscillation of the resonator. Through analysis of the equations of motion and understanding the complex dynamics of the MEMS resonator, we show that the bursting behavior is the result of a saddle node on an invariant circle (SNIC) bifurcation. By varying the drive amplitude and drive frequency, we experimentally verify the generic scaling of the period of the bursting dynamics and demonstrate control of the spacing in the measured frequency combs. A possible application of this interesting behavior is in the area of biology. The SNIC bifurcation has been used as a standard mechanism for spiking in neuron models with several different types of neurons exhibit bursting behaviors. This suggests that the MEMS resonator can be used as a possible candidate to mimic and therefore study the dynamics of interacting neurons using a purely mechanical structure.

5:00pm **MN+2D+AN+NS-ThA-9 A Buckling-based, DC Controlled, Non-volatile Nanoelectromechanical Logic Memory**, *S Erbil, U Hatipoğlu*, Bilkent University, Turkey; *C Yanık*, Sabancı University; *M Ghavami, Mehmet Selim Hanay*, Bilkent University, Turkey

Here, we demonstrate a buckling based, nanoelectromechanical logic bit with high controllability and low logic input voltage. The device consists of a slender beam to store information through its buckling direction and a comb-drive structure for initiating buckling electrostatically. When an

actuation voltage is applied to the fingers of the comb-drive structure, an axial compressive force is applied to the suspended slender beam which is connected to an anchor from the opposite end. Applied axial force creates a compressive stress on the slender beam which leads to buckling after a critical load. Buckling direction can be controlled (left/right) by changing the applied side-gate control voltages. The capacitive attraction force generated between the beam and the activated electrode controls the direction of the buckling. Control voltage acts as the logic input for writing information and it is only required just before the application of the axial load, so that the beam can be preloaded to the target direction. Lateral deformations as large as 10% of the beam length can be achieved.

Once the beam is buckled to the desired direction, the removal of the guidance voltage does not affect the buckling state of the beam, which indicates successful non-volatile information storage. Moreover, by altering the voltage difference created in the comb-drive structure, buckling amount can be controlled very precisely. Control voltages as low as 0.5V are demonstrated for storing information. The device is fabricated from an SOI wafer by using electron beam lithography, metal deposition and plasma / HF etching techniques. The dimensions of the slender beam are 150nm x 250nm x 40 $\mu$ m for the width, thickness and length respectively. Several videos demonstrating dynamically controlled electrostatic buckling have been recorded during the experiments. The nanoelectromechanical logic memory demonstrated here is scalable since its operation does not require any high-end electronic instruments such as function generators, and can be accomplished by simply using DC power sources. To readout the state of the beam all-electronically, the device is capacitively coupled to a microwave resonator. The changes in the frequency shows clear transitions between buckled and straight states.

It is possible to build two-bit mechanical logic gates and more involved logic units by using proposed nanoelectromechanical logic bit. As a further matter, precise control of the buckling in nanoscale can be very promising for demonstrating the interconnection between information science and thermodynamics.

## Nanometer-scale Science and Technology Division Room 102B - Session NS+2D+AS+MN+PC-ThA

### SPM – Probing Electronic and Transport Properties

**Moderators:** Ondrej Dyck, Oak Ridge National Laboratory, Sergei Kalinin, Oak Ridge National Laboratory, Indira Seshadri, IBM Research Division, Albany, NY

2:20pm **NS+2D+AS+MN+PC-ThA-1 Imaging Currents in Two-dimensional Quantum Materials**, *Katja Nowack*, Cornell University **INVITED**

Magnetic imaging is uniquely suited to the non-invasive imaging of current densities, particularly in two-dimensional devices. In this talk, I will showcase this approach by discussing measurements on HgTe quantum well devices in the quantum spin Hall (QSH) regime. In a nutshell, we scan a superconducting quantum interference device (SQUID) to obtain maps of the magnetic field produced by the current flowing in a device. From the magnetic image we reconstruct a two-dimensional current distribution with a spatial resolution on the micron scale. This allows us to directly visualize that most of the current is carried by the edges of the quantum well devices when tuned into their insulating gaps - a key feature of the QSH state. I will both discuss routes towards improving the spatial resolution of our measurements to sub-micron length scales through a combination of improved image reconstruction and smaller sensor sizes.

3:00pm **NS+2D+AS+MN+PC-ThA-3 Side-gate Construct for Probing Active Energy Levels in Electron Transport through a Solid-state Surface-bound Protein Monolayer**, *Sidney Cohen, B Kayser, C Gua, M Sheves, I Pecht, D Cahen*, Weizmann Institute of Science, Israel

Electron transport studies provide an excellent platform to deduce electronic structure in molecular electronics studies, enabling control and understanding of the pathways and mechanisms involved. Due to their complexity, proteins are used only infrequently in this context, despite convenient properties such as selective binding, self-assembly, light sensitivity, and the possibility to (bio) chemically tailor properties. Here, we study electron transport in monolayer films of Azurin, using a 3-electrode configuration with a novel side-gate. The source and drain are gold substrate and conductive atomic force microscope (C-AFM) probe, respectively. The measuring devices were prepared in a two-step electron beam lithography process, whereby interdigitated drain and gate electrodes with separation of 80 nanometers are patterned from

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macroscopic electrodes, the latter formed optically on a silicon oxide substrate. The gold electrodes are patterned with the gate elevated by 20 nm for improved coupling with the drain. After deposition of the Azurin monolayer on this structure, the carrier chip was wire-bonded for insertion into the AFM. Azurin was incorporated in the device both as copper-containing holo-Azurin, and as apo-Azurin with the Cu ion removed. Stability of source-drain vs.  $V_{\text{source-drain}}$  curves, as well as gate-drain leakage were monitored for validity.  $I_{\text{source-drain}}$  vs.  $V_{\text{source-drain}}$  curves were acquired at different gate voltages, and  $I_{\text{source-drain}}$  at 0  $V_{\text{source-drain}}$  was measured while sweeping  $V_{\text{gate}}$  in both polarities. Asymmetry of current onset for opposing gate biases points to a low-lying LUMO transport level for holo-Azurin. For apo-Azurin this level is shifted to higher values and hence inaccessible. Semi-quantitative location of the tail of this LUMO, as well as value of gate coupling were estimated by changing the work function of the drain electrode, i.e. C-AFM probe, from Pt ( $\phi = -5.3$  eV) to Au ( $\phi = -4.9$  eV). The observations can be rationalized by considering previous electrochemical and theoretical studies.

**3:20pm NS+2D+AS+MN+PC-ThA-4 Adding Electrons One at a Time to Electrostatically Confined Graphene Quantum Dots, Daniel Walkup, C Gutierrez, F Ghahari, National Institute of Standards and Technology (NIST)/ University of Maryland, College Park; C Lewandowski, MIT; J Rodriguez-Nieva, Harvard University; T Taniguchi, K Watanabe, National Institute for Materials Science (NIMS), Japan; L Levitov, MIT; N Zhitenev, J Stroscio, National Institute of Standards and Technology (NIST)**

The Coulomb blockade of adding charges to isolated metallic systems is one of the most characteristic phenomena of quantum dots (QDs). Here, we created circular graphene QDs in a backgated graphene-hexagonal boron nitride (hBN) device by locally ionizing defects in the hBN layer, using the electric field from the tip of a scanning tunneling microscope (STM). Scanning tunneling spectroscopy (STS) enables us to image the local density of states outside and within these circular graphene resonators. At weak magnetic fields, confinement of graphene electrons is poor and Coulomb blockade is not observed. At higher fields, however, the graphene electrons form quantized Landau levels (LLs) separated by energy gaps. In the area of the QD, the LLs are bent by the electrostatic potential creating metallic (compressible) rings where a LL crosses the Fermi energy, separated by circular insulating barriers (incompressible strips), which isolate the dot from the graphene and enable the onset of Coulomb blockade. Tunneling  $dI/dV$  spectra inside the QD reveal a series of Coulomb blockade peaks, which shift as a function of back gate voltage. In the plane defined by gate voltage and sample bias, these peaks form Coulomb lines, whose slope is governed by the relative capacitances between the dot, tip, gate, and sample bias electrodes, and whose relative offsets reveal the addition spectrum of the quantum dot. A characteristic feature of the Coulomb blockade in these systems is the presence of different families of charging lines, one for each LL, which intersect each other and experience avoided crossings. The avoidance pattern of these anticrossings is novel: at the strongest fields, it somewhat resembles the predictions of simple models of electrostatically-coupled QDs, but at weaker fields it diverges very strikingly, and new modeling is needed to reproduce it. This avoidance pattern reflects the interaction of electrons in different LLs, occupying different parts of the QD, and is tunable via the magnetic field and gate voltage. By moving the STM tip, we can tune the tip-dot capacitance, and tunnel into different parts of the dot, enabling a full characterization of the anticrossings in these novel electronic nanostructures.

**4:00pm NS+2D+AS+MN+PC-ThA-6 Bulk and Surface Contribution to the Charge and Spin Transport in Topological Insulators Observed with a Four-Probe Scanning Tunneling Microscope, Wonhee Ko, G Nguyen, Oak Ridge National Laboratory; H Kim, J Kim, Pohang University of Science and Technology, Republic of Korea; A Li, Oak Ridge National Laboratory**

Topological insulators are fascinating materials for future electronics because of its superior charge and spin transport characteristics stemming from their topological nature. However, topological insulators realized in actual materials have both bulk and surface carriers, where the former significantly hampers the topological transport of the later. In this talk, we utilize four-probe scanning tunneling microscope to investigate bulk and surface contribution to the charge and spin transport in bulk-insulating topological insulator  $\text{Bi}_2\text{Te}_2\text{Se}$ . The relative contribution of bulk and surface was varied by changing temperature and transport area, which was measured by variable probe-spacing spectroscopy. The surface dominant regime was already reached at 82 K, where the sample exhibited superior transport properties such as a large surface mobility and high spin polarization. At this regime, the contact to external probes also transforms from Schottky to Ohmic junction. Our result indicates that controlling bulk

and surface contribution to the transport is crucial for realizing topological devices.

**4:20pm NS+2D+AS+MN+PC-ThA-7 Modulation of Single-Walled Carbon Nanotube Electronic Structure by External Electronic Perturbations: Scanning Tunneling Spectroscopy and Density Functional Theory, Benjamin Taber<sup>1</sup>, G Nazin, University of Oregon**

Understanding the local impact of environmental electronic perturbations on the local density of states (LDOS) of single-walled carbon nanotubes (CNTs) is critical for developing CNT-based devices. We present scanning tunneling microscopy and spectroscopy (STM/STS) investigations of CNTs adsorbed on both a metal, Au(111), and a dielectric, monolayer RbI on Au(111), serving as models for stronger and weaker electrostatic interactions, respectively. In both cases, STS revealed modulations in the CNT LDOS corresponding to features in the underlying material. We then corroborate our STM/STS results with density functional theory calculations of the electronic structure of semiconducting CNTs in the presence and absence of an external dipole (a pair of opposite charges). DFT-calculated CNT LDOS quantitatively matched STM/STS results, providing key insight in to the local impact external charges have on CNT electronic structure.

**4:40pm NS+2D+AS+MN+PC-ThA-8 Single Charge and Exciton Dynamics probed on the Molecular Scale, Anna Rosławska, P Merino, C Grosse, C Leon, O Gunnarsson, M Etzkorn, K Kuhnke, K Kern, Max Planck Institute for Solid State Research, Germany**

The performance of organic optoelectronic devices depends on the dynamics of charges and excitons (electron-hole pairs). The relevant processes have been mostly studied by time-resolved techniques with a spatial resolution limited by optical diffraction. In order to overcome this limit, a nanoscale scanning probe approach that enables addressing individual light emitters is preferred. Here we introduce time-resolved scanning tunneling microscopy-induced luminescence (TR-STML) and use it to explore locally the single charge and single exciton regime. The excitonic light originates from structural defects in  $\text{C}_{60}$  thin films on Au(111) that act as charge and exciton traps. Such a defect is a single photon emitter, whose spectrum has a sharp electron-hole recombination feature [1,2]. By measuring the time-resolved electroluminescence due to individual injected charges, it is possible to analyze the formation and recombination processes of single excitons and determine their characteristic time constants[3].

[1] P. Merino, C. Große, A. Rosławska, K. Kuhnke, K. Kern, , Nat. Commun., 6, 8461, 2015.

[2] C. Große, P. Merino, A. Rosławska, O. Gunnarsson, K. Kuhnke, K. Kern, ACS Nano, 11, 1230-1237, 2017.

[3] A. Rosławska, P. Merino, C. Große, C. C. Leon, O. Gunnarsson, M. Etkorn, K. Kuhnke, K. Kern, arXiv:1803.10088.

**5:00pm NS+2D+AS+MN+PC-ThA-9 Microscopic Understanding of the Temperature-dependent Carrier Transport in Ge Nano - Crystal s Films, Dan Shan, Yangzhou Polytechnic Institute, China; J Xu, Nanjing University, China**

Silica-based semiconductor nano-crystals have attracted much interest in recent years due to their possible applications in many kinds of nano-electronic and optoelectronic devices. Compared with Si, Ge has larger electron and hole mobility. Furthermore, Ge has a narrower band-gap and high phonon responsibility in the near-infrared region, so it is suited to many near-infrared applications. In order to further improve the device performance, detailed knowledge of transport mechanisms across these nano-crystals becomes necessary and is considered indispensable.

In this work, hydrogenated amorphous germanium films were prepared by a plasma enhanced chemical vapor deposition technique. Ge nano-crystals (Ge NCs) films were obtained by thermal annealing the as-deposited samples. P-type behavior in Ge NCs films without any external doping is attributed to the holes accumulation caused by acceptor-like surface states. It can be found that the dark conductivity and Hall mobility reach to as high as 25.4 S/cm and 182  $\text{cm}^2/\text{V}\cdot\text{s}$  in the Ge NCs film, which are much higher than the previously reported data. Carrier transport mechanisms of Ge NCs films were investigated by temperature-dependent Hall measurement. Three kinds of temperature-dependent conductivity behaviors, which exhibit the linear relationships of the  $\ln \sigma$  versus  $T^{-3/4}$ ,  $T^{-1/2}$  and  $T^{-1}$ , respectively, were observed in the temperature regions of 10-500 K. It can be confirmed that the thermal activation conduction in the

<sup>1</sup> NSTD Postdoc Finalist

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extended states dominated the carrier transport process above 300 K (300-500 K). Below room temperature, the carrier transport process was dominated by the percolation-hopping conduction at 90-230 K and turned to Mott-VRH conduction when the temperature falling below 50 K (10-50 K).

Furthermore, the different scattering mechanisms in carrier transport process were found in different temperature regions, which were evaluated via temperature-dependent Hall mobilities. In the low temperature region (10-50 K), the carrier Hall mobility is almost temperature independence ( $\mu \sim T^0$ ), revealing the neutral impurities' scattering mechanism dominated the carrier transport process. When increasing the temperature (50-190 K), the carrier transport properties were controlled by the grain boundary scattering mechanism, where the carrier Hall mobility was increased with temperature and exhibited the thermally activated behavior. However, the relationship of  $\mu \sim T^{-0.9}$  was observed above room temperature (300-500 K). It is suggested that the carrier transport is dominated by a superposition of grain boundary scattering and acoustic phonon scattering within the high temperature region.

## Surface Science Division

### Room 203C - Session SS+AS+BI+MI+NS-ThA

#### Organic/Inorganic Surfaces, Interfaces and Nanostructures

Moderator: Denis Potapenko, Princeton University

2:20pm **SS+AS+BI+MI+NS-ThA-1 Investigation of the Stability of Ag Monolayers on Au(111) as a Function of Metal Adatom Diffusion**, *J Phillips, L Harville, H Morgan, L Jackson, G LeBlanc, Erin Iski*, University of Tulsa

The formation of an atomically thin, Ag layer on a Au(111) surface has been shown to significantly alter the thermal properties of the underlying substrate (1). A further exploration into the chemical mechanisms by which these thin films are deposited reveals two different sources of Ag during the formation of the monolayer. Electrochemical Scanning Tunneling Microscopy (EC-STM) and Cyclic Voltammetry (CV) are used to probe the *in-situ* interfaces of these metal systems as well as the adsorption of molecules on metals. EC-STM is a unique technique that, in addition to providing a local probe of the atomic surface structure, also functions as a 3-electrode cell in which redox chemistry can be performed to understand the chemical reactivity of the surface. Also, cyclic voltammograms (CVs) can be generated to provide specific information regarding the nature of the redox events occurring at the surface. The two sources of silver used for the Underpotential Deposition (UPD) process on Au(111) result in significantly different thermal stabilities of the surface. An important question is whether this stability can extend beyond thermal properties, which will be probed using the assembly of amino acids on Ag/Au(111). Using both EC-STM and UHV-STM (ultra-high vacuum STM), it has been shown that amino acids assist in the immobilization of diffusing adatoms on the surface and in the subsequent formation of metal islands (2). Since the molecular deposition in both cases takes place at room temperature, the current understanding is that the atoms on the surface are a function of the temperature of the surface and are not pulled out of the surface itself. Importantly, these systems provide a unique glimpse into metal surface diffusion and offer the ability to study the mass transport of metal atoms. This study focuses on how an application of the thin Ag film on the Au(111) will disrupt or assist in the metal adatom transport and whether the known thermal stability can extend to other surface properties, thus making the afforded stability more general. The interaction of the amino acids with the Ag films deposited at the two different potentials and the associated mass transport as measured by the size of metal islands on the surface will shed light on the stabilities of the two types of Ag layers. The ability to experimentally choose different surface properties based on electrochemical parameters and solution composition during metal deposition could lead to exciting new directions for thin film technologies.

(1) Iski *et al.* *Electrochimica Acta* (2011), 56, 1652-1661.

(2) Iski *et al.* *submitted to Communication Chemistry*, May 2018.

2:40pm **SS+AS+BI+MI+NS-ThA-2 Chain-Length Dependent Reactivity of Thiolate Self-Assembled Monolayers with Atomic Gas Species**, *Jeffrey Saylor, S Brown, S Sibener*, University of Chicago

Thiolate self-assembled monolayers (SAMs) provide platforms for easily customizable organic interfaces, making them an excellent model system for studying the chemical properties of organic thin films. In particular,

their reactions with atomic gas species such as hydrogen and oxygen yield important information about gas-surface interactions in organic films, how static and dynamic disorder influence passivation, as well as various hydrogenation and oxidation reactions. We are currently investigating the reactions of these SAMs with atomic hydrogen (H), using an angle-directed atomic gas source and *in situ* ultra-high vacuum scanning tunneling microscopy (UHV-STM). First, a series of alkanethiolate SAM samples of varying chain length (8 to 11 carbon atoms long) were reacted with H, resulting in the monolayers' conversion from close-packed standing-up phase to lower density lying-down phase. Regardless of chain length or even-oddness, which were expected to impact the effectiveness of H penetration into the monolayer due to differences in the chains' lateral mobility and terminal structure, all samples exhibited common kinetic mechanistic details. The relative reaction rates of different chain lengths were obtained using simultaneous dosing of multiple samples. Second, a close-packed 1H,1H,2H,2H-perfluorodecanethiol SAM (a fluorinated analog of the 1-decanethiol SAM) was reacted with H. Dosing this sample under the same conditions as the 1-decanethiol sample revealed little to no reactivity. Ongoing studies continue to explore the reactivity of this family of saturated SAM systems including investigation of the kinetics and mechanism of the lying-down phase's reactivity with H. Further investigations involving atomic oxygen and different SAM chemical compositions and structures will follow.

3:00pm **SS+AS+BI+MI+NS-ThA-3 Scan Probe Studies of Lithium Transfer through Solid State Electrochemical Interfaces**, *Janice Reutt-Robey*, University of Maryland College Park

INVITED

*All solid-state electrical energy storage devices are of immense interest as safer alternatives to those based upon flammable liquid electrolytes. Understanding the rates and elementary processes for lithium ion transport through anode-solid electrolyte-cathode interfaces is essential, but obscured by heterogeneous samples and unknown local potentials. I will present new nanoscale studies of lithiation/delithiation across well-defined interfaces created with actuated nanobattery junctions. Conventional STM metallic tips, clad with a thin film of electrode material (LiCoO<sub>2</sub> or Li) and a capping film of solid electrolyte (Li<sub>x</sub>Al<sub>2</sub>O<sub>3</sub> or Li<sub>2</sub>O), function as ½ cells. Probes are positioned and electrochemically cycled at singular surfaces of model electrodes – Si(111), Si(100), C(0001). At the nanoscale, hysteresis in charging/discharging is monitored as a function of interface structure and materials properties. UHV measurements preserve the chemical integrity of the material interfaces and allow traditional (cyclic voltammetry, stepped potential) and nontraditional (stepped stress) electrochemical measurements to separate electron/ion contributions to charge transfer. The data reveal how induced variations in local lithium concentration impact rates for charging/discharging and contribute to hysteretic behavior. Further, stress-induced current transients show non-Cottrellian time behavior, attributed to a lithium ion concentration gradient in the solid electrolyte. Modeling of nanobattery data allows for testable predictions of material properties. Finally we show how "inverted" Scanning Tunneling Spectroscopy provides a useful tool to characterize the electrical band gap of the tip 1/2 cell materials, while imaging reveals the distribution pattern of lithium ions at the cycled electrode surfaces.*

*This work was supported as part of the Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award number DESC0001160.*

4:00pm **SS+AS+BI+MI+NS-ThA-6 Adsorption and Self-assembly of Halogenated Organic Molecules on the Si(111)  $\sqrt{3} \times \sqrt{3}$ -Ag Surface**, *Renjie Liu*, Lakehead University, Canada; *C Fu, A Moiseev, M Rao, Y Chen, D Perepichka*, McGill University, Canada; *M Gallagher*, Lakehead University, Canada

Given potential applications in molecular electronics, organic thin films continue to attract a great deal of scientific attention. Furthermore, organic-inorganic semiconductor hybrids have been identified as a possible platform for future devices. Generally such a device would require thin films of functionalized organic molecules grown on silicon surfaces. To promote the growth of high quality films, the Si surface needs to be passivated. For example, the Si(111)  $\sqrt{3} \times \sqrt{3}$ -Ag surface has been shown to be weakly interacting, allowing molecules to remain mobile and form well ordered layers [1].

In this work we compare the adsorption and self-assembly of two halogenated molecules of threefold symmetry; 2,4,6-tris(4-iodophenyl)-1,3,5-triazine (TIPT), and tribromotrioxaazatriangulene (TBTANG) on the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface. The self assembly of TIPT on HOPG and Au(111)

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has been reported previously [2], and heteroatom forms of triangulene are of particular interest in molecular electronics [3].

We find that both molecules display high mobility on the  $\sqrt{3}$ -Ag surface. With increasing molecular dose, TIPT forms supramolecular domains defined by a 2.0 nm by 1.8 nm rectangular cell. The size and symmetry of the unit cell provides strong evidence that a large fraction of the monomers do not undergo de-halogenation, and that the dominant interaction within the domains is intermolecular I...H hydrogen-bonding. As the coverage approaches one monolayer, the film consists of supramolecular domains of limited extent separated by regions of disorder. STM images at lower coverage reveal that molecular adsorption increases the defect density of the underlying  $\sqrt{3}$ -Ag layer. We believe that a small fraction of the TIPT molecules de-iodinate on adsorption and that the iodine subsequently reacts with the Ag overlayer. The increased defect density limits the extent of the supramolecular domains on this surface.

In contrast, TBTANG exhibits long-range self-assembly of intact molecules. The ordered structure is characterized by several closely packed rows of molecules. Within the rows the repeating motif is two-molecules linked together by Br...Br interactions. With increasing coverage, the  $\sqrt{3}$  surface remains unaffected and the self assembled layer extends over the entire surface.

- [1] Yokoyama, T. *et al.*, *J Chem Phys* **142**, 204701 (2015).
- [2] Gatti, R. *et al.*, *J. Phys. Chem. C* **118**, 25505–25516 (2014).
- [3] Nakatsuka, S. *et al.*, *Angewandte Chemie* **129**, 5169–5172 (2017).

#### 4:20pm **SS+AS+BI+MI+NS-ThA-7 Electron Interactions with Alkanethiol Self-assembled Monolayers on Au(111)**, *Jodi Grzeskowiak*, University at Albany-SUNY; *C Ventrice, Jr.*, SUNY Polytechnic Institute

Self-assembled monolayers (SAMs) are often used for applications such as molecular electronics, selective deposition, and various forms of surface modification. Advanced lithography within the semiconductor industry is adopting ever shorter wavelengths of light such that the interaction of secondary electrons with the organic resist is becoming the primary mechanism for photo-initiated electro-chemical solubility changing reactions. In order to study the interaction of low energy electrons with thin organic films, measurements have been performed on electron decomposition of alkanethiol molecules grown on Au(111) substrates. SAMs have been grown via both solution and vapor phase methods. These monolayers arrange into two distinct phases commonly referred to as lying down and standing up. The lying down phase is a physisorbed layer that is only weakly interacting with the substrate via Van der Waals forces. Conversely, the standing up phase is a chemisorbed species that is more strongly bound to the substrate. Various surface analysis techniques were used to characterize the monolayers before and after electron exposure. Low energy electron diffraction (LEED) was used to determine the structure of the SAM and the rate of decomposition. Temperature programmed desorption (TPD) in combination with mass spectrometry was used to evaluate the thermal stability and bonding strength of the attached SAMs and the decomposition products from electron exposure.

#### 4:40pm **SS+AS+BI+MI+NS-ThA-8 Measuring the Electronic Properties of Organic Single Crystals**, *Sujitra Poolpanratana*, *E Bittle*, *C Hacker*, *S Robey*, National Institute of Standards and Technology (NIST); *R Ovsyannikov*, *E Giangrisostomi*, Helmholtz-Zentrum Berlin, Germany

Organic and molecular-based compounds have found commercial application in consumer-based electronics. Organic semiconductors can be integrated onto device structures in different physical forms such as single crystals, polycrystalline thin-films, or amorphous thin-films. The structural order of the molecular solid profoundly influences the electronic properties, that in turn controls important properties, such as the transport gap and binding energy of the highest occupied molecular orbital (HOMO) [1, 2], that govern how an electronic device operates. Photoemission can play a vital role in illuminating these important electronic properties. While there are numerous photoemission spectroscopic measurements of organic semiconductors in thin-film structures, far fewer attempts have been made to determine the “fundamental” electronic properties for pristine organic single crystals.

Here, we present results of photoemission measurements for single crystalline (SC) dinaphthothienothiophene (DNNT). DNNT is a small molecule-based thienoacene and has demonstrated carrier mobilities approaching  $10 \text{ cm}^2/(\text{V s})$  [3], is air-stable [4] and durable against accelerated temperatures and humidity conditions.[5] While there are

many device studies that establish DNNT and other related thienoacenes for a variety of applications, detailed electronic and chemical structure studies are lacking. Electronic “band” structure measurements using a novel angle-resolved time-of-flight electron spectrometer is performed on SC-DNNT, and multiple highest occupied molecular orbitals are resolved of varying widths. Modest dispersion of the frontier HOMO is observed, and this result will be discussed in context of the charge carrier behavior of DNNT reported in the literature.

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#### 5:00pm **SS+AS+BI+MI+NS-ThA-9 Surface Functionalization of Porous Substrates via Initiated Chemical Vapor Deposition**, *Christine Cheng*, *M Gupta*, University of Southern California

Porous materials are used in various applications including separation membranes, paper-based microfluidics, and flexible electronics. Tuning surface properties of porous materials enhances the versatility of existing materials, giving them new functions and applications. However, traditional surface modification methods are typically solvent-based, which limits the range of substrates that can be coated. In this work, initiated chemical vapor deposition was used to continuously modify the surface of large areas of porous substrates in an all-dry vacuum process. A superhydrophobic polymer was deposited onto a porous substrate and the coating was characterized using contact angle goniometry, X-ray photoelectron spectroscopy, and scanning electron microscopy to study the uniformity of the coating along the entirety of the substrate. The superhydrophobicity of the coated porous substrate is attributed to the deposited polymer and the roughness of the substrate. Addition of a perfluorinated liquid to the superhydrophobic porous substrate formed a slippery liquid-infused porous surface. A hydrophilic polymer was deposited on top of the superhydrophobic polymer to demonstrate the facile stacking of polymer layers with different chemistries using this process.

#### 5:20pm **SS+AS+BI+MI+NS-ThA-10 Atomic-Scale Understanding of Anatase Nanocatalyst Activation**, *William DeBenedetti*<sup>1</sup>, *E Skibinski*, *M Hines*, Cornell University

Our ability to predict the chemical reactivity of nanocatalysts has been stymied by our lack of atomic-scale understanding of nanocatalyst surface structure. Specifically, do nanocatalyst surfaces adopt a bulk-terminated structure or do they reconstruct to minimize their surface free energy, thereby lowering their chemical reactivity as observed in ultra-high vacuum? Furthermore, do nanocatalysts processed at higher temperature maintain their low-chemical-reactivity, reconstructed surfaces when used at low temperatures and under typical operating conditions?

Using a new technique for the growth of highly aligned anatase (001) nanocatalysts, we will show that solution-synthesized anatase is terminated by a monolayer of fluorine, which acts as an atomic-scale protective coating against adventitious contamination. We will also show that carboxylic acid solutions, the most common TiO<sub>2</sub> functionalization chemistry, causes a spontaneous reorganization of a reconstructed nanocatalyst, leading to a five-fold increase in the number of reactive sites. This surface reorganization is not observed when carboxylic acids are dosed from the gas phase, indicating that experiments in ultra-high vacuum environments lead to trapped states that may not be relevant to nanocatalysts in ambient conditions. *Ab initio* calculations show that although the carboxylic acid termination is slightly less effective at removing surface stress than the reconstructed surface, it is more effective in lowering the surface free energy. These findings suggest that bulk-terminated metal oxide nanocatalysts may be common under ambient operating environments, even after high-temperature processing or if reactants are rinsed off.

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



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5:40pm **SS+AS+BI+MI+NS-ThA-11 Mechanistic view of Solid-Electrolyte Interphase Layer Evolution at Li-metal Anode, Venkateshkumar Prabhakaran**, Physical Sciences Division, Pacific Northwest National Laboratory; *M Engelhard, A Martinez*, Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory; *G Johnson*, Physical Sciences Division, Pacific Northwest National Laboratory; *S Thevuthasan*, Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory; *V Murugesan*, Physical Sciences Division, Pacific Northwest National Laboratory

A molecular-level understanding of structural and chemical transformations of electrolyte at solid-electrolyte interfaces (SEI) is critical for rational design of electrochemical materials. Despite numerous studies, evolution of the transient and metastable species which dictates the cascade of interfacial reactions are still not clear. The challenge is to establish the chemical homogeneity within interface to clearly delineate the origin of various decomposition reaction products and their energetic pathways. Soft landing of mass-selected ions is ideally suited for building the interface with selected constituent which can alleviate the complexity associated with diverse and correlated processes within SEI layer.<sup>1-4</sup> Herein, we report the development and first demonstration of new capabilities that combine ion soft landing with *operando* infrared reflection-absorption spectroscopy (IRRAS) to study the decomposition of counter anions and solvent molecules on bare lithium metal surfaces. Specifically, we discreetly deposited sulfonyl imide based electrolyte anion (TFSI) and solvated Lithium cations without corresponding counter ions onto bare lithium metal using soft landing approach and monitored their decomposition using *in-situ* IRRAS and *ex-situ* x-ray photoelectron spectroscopy (XPS). *Operando* IRRAS and XPS measurements captured the signatures of transient species arising from decomposition of electrolyte anions and solvent molecules in real time. We will discuss, our unique approach of building interface with precise control over the constituents and subsequently detect the spectroscopic signatures of transient species during decomposition processes.

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## Thin Films Division

### Room 104B - Session TF+AS+EL+EM+NS+PS+SS-ThA

#### IoT Session: Thin Films for Flexible Electronics and IoT

**Moderators:** Jesse Jur, North Carolina State University, Siamak Nejati, University of Nebraska-Lincoln

2:20pm **TF+AS+EL+EM+NS+PS+SS-ThA-1 Ultraflexible Organic Electronics for Bio-medical Applications, Tomoyuki Yokota, T Someya**, The University of Tokyo, Japan

**INVITED**

Recently, flexible electronics has much attracted to realize bio medical application for their flexibility and conformability [1-3]. To improve these characteristics, reducing the thickness of the device is very effective [4]. We have developed ultra-flexible and lightweight organic electronics and photonics devices with few micron substrates. We fabricated the 2-V operational organic transistor and circuits which has very thin gate dielectric layers. The gate dielectrics were composed of thin aluminium oxide layer and self-assembled monolayers (SAMs). Due to the very thin substrate and neutral position, our device shows the highly flexibility and conformability. The device doesn't be broken after crumpling.

And also we fabricated highly efficient, ultra-flexible, air-stable, three-color, polymer light-emitting diodes (PLEDs) have been manufactured on

one-micrometer-thick parylene substrates. The total thickness of the devices, including the substrate and encapsulation layer, is only three micrometers, which is one order of magnitude thinner than the epidermal layer of the human skin. The PLEDs are directly laminated on the surface of skin and are used as indicators/displays owing to their amazing conformability as their superthin characteristics. Three-color PLEDs exhibit a high external quantum efficiency (EQE) (12, 14, and 6% for red, green and blue, respectively) and large luminance (over 10,000 candelas per square meter at 10 V). The PLEDs are integrated with organic photodetectors and are used as pulse oximeter.

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3:00pm **TF+AS+EL+EM+NS+PS+SS-ThA-3 Molecular Surface Chemistry for Improved Interfaces in Organic Electronics, Jacob W. Ciszek**, Loyola University Chicago

Organic optoelectronic devices (OLED, OFETs, etc.) contain at least one, if not multiple instances of overlayers deposited onto organic semiconductors. The generated interface is inherently flawed with issues such as non-ohmic contact, overlayer delamination, or deposition induced damage arising. Traditionally, this is addressed by physical vapor deposition of yet another layer or by reengineering the materials in the device stack. In contrast, a reaction based approach allows for a wider range of function to be installed via molecular components in an organized and oriented manner, all while take advantage the inherent reactivity of the organic molecules which comprise the semiconducting layer. We have developed this approach via a "click-like" Diels-Alder chemistry whereby prototypical acene films (tetracene or pentacene) can be appended with a variety of small molecules to form an interfacial layer only ~5 Å thick. This chemistry is then applied towards improving the metal on semiconductor contact. As a demonstration of principle, Diels-Alder chemistry is utilized to form covalent bonds linking the organic semiconductor with a deposited metal contact thereby eliminating the poor adhesion present in this system. Application of the chemistry towards contact potential shifts is presented, while work towards sensing applications concludes the talk.

3:20pm **TF+AS+EL+EM+NS+PS+SS-ThA-4 Investigation of Low Temperature ALD-deposited SnO<sub>2</sub> Films Stability in a Microfabrication Environment, Tony Mairon, S Sandrez, N Vaxelaire**, CEA/LETI-University Grenoble Alpes, France

For applications such as displays (LCD, OLED) or solar cells, it is mandatory to use Transparent Conductive Oxides (TCOs) so as to allow light to extract out of the circuit or for light harvesting, respectively. In display technology, TCOs are also studied so as to replace the silicon technology developed to make the semiconducting channel in thin-film transistors. The mainstream TCO today is indium tin oxide (ITO), (90% indium oxide and 10% tin oxide). It has the advantage of having a high conductivity and a low surface resistivity, of the order of 10 ohm/square, while having a transmittance greater than 85% over the entire visible spectrum. However, it has several drawbacks, including the scarcity of indium and the high cost associated to its extraction process, which has prompted the scientific community to look for alternative TCOs. Among all TCOs, ZnO has been widely studied as a low cost single-metal oxide alternative material to ITO, as well as its multi-metal oxide derivatives using a dedicated metal dopant to control its electrical conductivity, as for instance with Al (ZnO:Al or AZO). One issue however with ZnO films lays in their relative chemical stability to water. It has been shown that films of ZnO or AZO change their physical properties when exposed to moisture: electrical conductivity decreases, roughness can increase, and optical characteristics are modified. By extension, when ZnO-based TCOs have to be finely patterned by photolithography, their high sensitivity to water-based solutions can be a severe issue. In our laboratory, we have noticed that ZnO and AZO films made by ALD at 150 °C typically are not stable in a microfabrication process: a large decrease (~ 20 %) of AZO thickness after the development step of photoresists used to pattern the TCO film has been noticed. One way to stabilize ZnO-based compounds is to anneal the films at high temperatures. However for some dedicated applications that use fragile substrates (plastic films for flexible organic electronics for instance), such post annealing processes at high temperature (typ. > 150 °C) cannot be applied. An alternative is to explore alternative materials to AZO: we found out that SnO<sub>2</sub> ALD (150 °C) shows

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very promising features regarding the stability under a microfabrication environment, while having good electrical and optical characteristics.

**4:00pm TF+AS+EL+EM+NS+PS+SS-ThA-6 Dopant Distribution in Atomic Layer Deposited ZnO:Al and In<sub>2</sub>O<sub>3</sub>:H Films Studied by Atom Probe Tomography and Transmission Electron Microscopy**, Y Wu, B Macco, Eindhoven University of Technology, The Netherlands, Netherlands; D Giddings, T Prosa, D Larson, CAMECA Instruments Inc.; S Kölling, P Koenraad, Eindhoven University of Technology, The Netherlands; F Roozeboom, Erwin Kessels, Eindhoven University of Technology, The Netherlands, Netherlands; M Verheijen, Eindhoven University of Technology, The Netherlands

Transparent conductive oxides (TCOs) are ubiquitous in many of today's electronic devices, including solar cells. Atomic layer deposition (ALD) is a promising method to prepare high quality TCO films due to its well-known virtues – i.e., precise growth control, excellent conformality and uniformity – combined with its damage-free character. Here we report on two types of TCO films that we have studied by a combination of atom probe tomography (APT) and high-resolution transmission electron microscopy (TEM). The aim was to get more insight into how the dopants are distributed in the films.

The first study was carried out on ZnO:Al prepared by alternating cycles of Zn(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> and H<sub>2</sub>O with cycles of Al(CH<sub>3</sub>)<sub>3</sub> and H<sub>2</sub>O in a supercycle fashion at 250 °C. For this material it is known that the maximum conductivity achievable is limited by the low doping efficiency of Al. To better understand the limiting factors for the doping efficiency, the 3-dimensional distribution of Al atoms in the ZnO host material matrix has been examined at the atomic scale by the aforementioned techniques [1]. Although the Al distribution in ZnO films prepared by so-called “ALD supercycles” is often presented as atomically flat δ-doped layers, in reality a broadening of the Al-dopant layers was observed with a full-width-half-maximum of ~2 nm. In addition, an enrichment of the Al at grain boundaries was seen.

The second study involved In<sub>2</sub>O<sub>3</sub>:H prepared by InCp and a mixture of O<sub>2</sub> and H<sub>2</sub>O at 100 °C. This material provides a record optoelectronic quality after post-deposition crystallization of the films at 200 °C. Since both the H dopant incorporation and the film microstructure play a key role in determining the optoelectronic properties, both the crystal growth and the incorporation of H during this ALD process were studied [2]. TEM studies show that an amorphous-to-crystalline phase transition occurs in the low temperature regime (100-150 °C), which is accompanied by a strong decrease in carrier density and an increase in carrier mobility. Isotope studies using APT on films grown with D<sub>2</sub>O show that the incorporated hydrogen mainly originates from the co-reactant and not from the InCp precursor. In addition, it was established that the incorporation of hydrogen decreased from ~4 at. % for amorphous films to ~2 at. % after the transition to crystalline films.

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**4:20pm TF+AS+EL+EM+NS+PS+SS-ThA-7 Roll-to-Roll Processable OTFT Sensors and Amplifier**, Kai Zhang, University of Oxford, Department of Materials, UK; C Chen, B Choubey, H Assender, University of Oxford, UK

The high flexibility and relatively low cost of organic electronics are gradually providing more possibility for their application. Compared with conventional silicon based electronics, organic electronics have relatively short lifecycles and processor speed, but they are more promising in the market of wearable and flexible devices, for example, wearable health care devices, simple memory devices and flexible displays. In recent years, some flexible and wearable sensors have been developed, e.g. skin-touching sensors embedded in a sports suit can detect the change of heart rate, blood pressure, ion concentration of perspiration, or infrared radiation from the human body.

In most sensors based on organic thin film transistors (OTFT) made to date, the semiconductors are employed directly to detect analytes. However, (1) the lifecycles of this design is short due to the low stability of organic semiconductors; and (2) any modification for selectivity needs to be compatible with the semiconductor.

In this paper, we present sensors based upon an extended floating gate in order to separate the sensory area from the semiconductor. Transistors are manufactured, using our roll-to-roll vacuum webcoating facility, using a high-throughput all evaporation process (Ding et al., 2016, Taylor et al.,

2015). We have demonstrated the principle of operation of a floating gate sensor integrated with the vacuum-deposited OTFT, by means of a simple strain sensor, using ferroelectric PVDF on the extended floating gate to directly act as a sensory material. To amplify the sensor signal further, a series of current mirrors and differential amplifiers have been designed based on the properties of single OTFTs. The combination of organic amplifier and OTFT sensor will be helpful to transduce sensing signal to a suitable level for wireless signal reading from flexible devices.

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**4:40pm TF+AS+EL+EM+NS+PS+SS-ThA-8 Functionalization of Indium Gallium Zinc Oxide Surfaces for Transparent Biosensors**, X Du, S John, J Bergevin, Gregory Herman, Oregon State University

Amorphous indium gallium zinc oxide (IGZO) field effect transistors (FETs) are a promising technology for a wide range of electronic applications including implantable and wearable biosensors. We have recently evaluated the functionalization of IGZO back channel surfaces with a range of self-assembled monolayers (SAM) to precisely control surface chemistry and improve stability of the IGZO-FETs. The SAMs evaluated include, n-hexylphosphonic acid (n-HPA), (3,3,4,4,5,5,6,6,6-nonafluorohexyl) phosphonic acid (FPA), and (3-aminopropyl) trimethoxysilane (APTMS). A comparison of the surface chemistry is made for bare and SAM functionalized IGZO back channel surfaces using X-ray photoelectron spectroscopy and electronic device measurements in air and phosphate buffer solution (PBS). We find significantly improved device stability with the SAMs attached to the IGZO back channel surface, both in air and PBS. We related this to the reduction of traps at the back channel surface due to SAM passivation. To further evaluate the IGZO-FETs as biosensors we have immobilized glucose oxidase (GOx) to the APTMS functionalized IGZO back channel surface using glutaraldehyde. We find that both the FPA functionalized and the GOx immobilized surfaces are effective for the detection of glucose in PBS. Furthermore, the GOx immobilized IGZO-FET based glucose sensors have excellent selectivity to glucose, and can effectively minimize interference from acetaminophen/ascorbic acid. Finally, we will discuss fully transparent IGZO-FET based glucose sensors that have been fabricated directly on transparent catheters. These results suggest that IGZO-FETs may provide a means to integrate fully transparent, highly-sensitive sensors into contact lenses.

**5:00pm TF+AS+EL+EM+NS+PS+SS-ThA-9 Large Area Atmospheric Pressure Spatial ALD of IZO and IGZO Thin-film Transistors**, C Frijters, I Katsouras, A Illiberi, G Gelinck, Holst Centre / TNO, Netherlands; Paul Poodt, Holst Centre / TNO and SALDtech B.V., Netherlands

Atmospheric pressure Spatial ALD is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. An emerging application for Spatial ALD is flat panel (OLED) display manufacturing. Examples include oxide semiconductors and dielectric layers for use in thin-film transistors (TFT's), and thin-film encapsulation for flexible OLED displays. As today's displays are fabricated on glass plate sizes in the order of several square meters, a remaining challenge is the development of large-area Spatial ALD deposition technology that is able to combine high throughput with uniform performance across very large areas.

We are developing large area Spatial ALD technology, and as a first step between the lab and the display fab, we have installed a large area Spatial ALD sheet-to-sheet tool which can handle up to 400x325 mm<sup>2</sup> sized substrates. With this tool we are able to deposit uniform films across a deposition width of 400 mm and thickness non-uniformities of ~ 1%. The whole tool is operated under an atmospheric pressure but inert N<sub>2</sub> environment. The tool can be used to deposit a variety of materials using both thermal and plasma-enhanced Spatial ALD.

We will present about the fabrication and performance of 30 cm x 30 cm TFT backplanes with InZnO<sub>x</sub> (IZO) and InGaZnO<sub>x</sub> (IGZO) oxide semiconductors deposited by spatial ALD. The IZO and IGZO films were deposited by plasma enhanced Spatial ALD using co-injected In-, Ga- and Zn-precursors and an atmospheric pressure N<sub>2</sub>/O<sub>2</sub> plasma. The deposition

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process has been optimized in terms of film composition and electrical properties on a lab-scale reactor before being translated to the large area spatial ALD reactor. We will report on the yield and performance of the 30 cm x 30 cm TFT backplanes, including electrical properties such as the field effect mobility,  $V_{on}$  and bias stress stability and compare it with state-of-the-art sputtered IGZO TFT's. Finally, the challenges in up-scaling Spatial ALD to plate sizes of 1.5 m and beyond will be discussed.

5:20pm **TF+AS+EL+EM+NS+PS+SS-ThA-10 Thin Film Ink-Jet Printing on Textiles for Flexible Electronics**, *Jesse Jur, I Kim, H Shahariar*, North Carolina State University

Inkjet printing of thin film flexible electronics on textiles is an emerging field of research with advances in wearable technology. In this study we describe for the first-time a reliable and conformal inkjet printing process of printing particle free reactive silver ink on textile surfaces. Reactive silver ink is printed on fibers with eclectic polymers ranging from polyester and polyamide, and different structures of textiles such as knitted, woven, and nonwoven fabrics. The conductivity and the resolution of the inkjet-printed tracks are directly related to the fiber structures in the fabrics. Multiple passes of printing layers are needed to confirm the percolation of the metal network on porous, uneven surfaces. The conformity and the electrical conductivity of the inkjet-printed conductive coating on PET textiles are improved by in-situ heat curing the substrate during printing and surface modification, for example, by atmospheric oxygen plasma treatments. The in-situ heat curing potentially minimizes wicking of the ink into the textile structures. We have achieved the minimum sheet resistance of 0.2 Ohm/sq on polyester knit fabric, which is comparable to the conductive thick-paste used in the screen-printed process, as well as other traditional physical and chemical deposition processes on textile fabrics/yarns. Additionally, we have constructed textile knit structures which changes electric percolation depending on structural deformations of the knit loops, providing positive and negative gauge factors upon stretching. The printed patterns are post-treated with diluted silicone/UV curable aliphatic water-soluble polyurethane coating to improve the durability during washing. These findings open up the possibility of integrating inkjet printing in the scalable and automated manufacturing process for textile electronic applications.

5:40pm **TF+AS+EL+EM+NS+PS+SS-ThA-11 Flexography Oil Patterning for In-line Metallization of Aluminium Electrodes onto Polymer Webs: Commercial Roll to Roll Manufacturing of Flexible and Wearable Electronics**, *Bryan Stuart, T Cosnahan, A Watt, H Assender*, University of Oxford, Department of Materials, UK

Vacuum metallisation of aluminium through shadow masks has been commercially used for decades for depositing electrodes on rigid semiconductor devices, however recent developments have enabled large area, continuous deposition of patterned metallization in the aesthetic printing industry and has the potential for electrode interconnects for devices on flexible substrates such as Polyethylene Terephthalate (PET) and Polyethylene Naphthalene (PEN). Flexible polymer webs of PET were coated (*See Supplementary Figure*) with 50 nm thick, 165 um wide aluminium electrodes by commercially compatible manufacturing at roll-to-roll web speed of 2.4 m min<sup>-1</sup> showing tremendous potential for large scale manufacturing of wearable electronic devices in transistors, low level energy generation (Thermoelectric generators), energy storage (thin film batteries) or display technologies (LED displays) [1].

The in-line patterning process relies on adaptation of flexography ink printing which typically transfers ink to a rubber patterned plate for printing images onto polymer webs. The flexibility of the printing plate accommodates for irregularities in the surface of the substrate making this process desirable for large area manufacturing. Metallization has been used to deposit aluminium onto a flexography applied pattern by replacing ink with a low vapor pressure oil (e.g. Perfluoropolyether, Krytox®). The radiative heating of aluminium metallization causes simultaneous evaporation of the oil pattern, thereby rapidly forming the desired metal pattern onto the un-patterned regions. Currently we are scaling-up the oil flexography/metallization process into an industrial-scale roll-to-roll coater with potential web widths of 350 mm and roll speeds of 100 m min<sup>-1</sup>, in order to increase web speeds, and to expand the range of materials deposited and the functional devices to which they are applied.

This paper reports on in-line pattern deposition of aluminium and other materials as applied to functional devices, for example organic thin film transistors and thermoelectric devices. In particular we are able to demonstrate how the process can be compatible with other functional layers. We will report our studies of electrode precision (shapes/sizes) by

patterned metallization and our first studies of sputtering with flexography patterning. The long term view is integration of this technology along the R2R production path for single pass/high speed production of low cost and flexible integrated circuits.

## References

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# Thursday Evening Poster Sessions, October 25, 2018

## Nanometer-scale Science and Technology Division Room Hall B - Session NS-ThP

### Nanometer-scale Science and Technology Division Poster Session

**NS-ThP-1 Intermolecular Interactions in Self-Assembled Monolayers on Metal Surfaces Characterized by Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy**, *J Schultz, P Whiteman, Nan Jiang*, University of Illinois at Chicago

In order to fully characterize molecular assemblies at the single molecular scale, advanced analytical surface techniques have to be employed. We carried out scanning tunneling microscopy (STM) experiments on two molecules (N-N'-bis(2,6-diisopropylphenyl)-perylene-3,4:9,10-bis(dicarboximide) (PDI) and subphthalocyanine (SubPc)), which are both self-assembled on noble metal substrates. The STM experiments were complemented by tip-enhanced Raman spectroscopy (TERS), surface-enhanced Raman spectroscopy (SERS) and density functional theory (DFT) calculations. In particular, we have interrogated the lifting of an accidental vibrational degeneracy of a mode of PDI on Ag(111) and Ag(100) surfaces, with the most strongly perturbed mode being that associated with the largest vibrational amplitude on the periphery of the molecule. In the other hand, the alignment between experimental TERS of SubPc on surface and DFT calculated Raman spectrum of gas phase SubPc was quite good, which indicates that the interaction between SubPc molecules in the monolayer is very weak. New two-dimensional molecular superstructures were discovered to consist of several distinct molecular binding configurations. Both TERS and SERS experiments of SubPc yielded nearly identical vibrational spectra for both binding configurations, consistent with their small adsorption energies (<0.2 eV) as calculated by DFT. Our results demonstrate the necessity of advanced Raman techniques such as TERS when precisely probing molecule-molecule and molecule-substrate interactions.

**NS-ThP-2 Nanoscale Detection of Surface Plasmon-driven Hot Electron Flux on Au/TiO<sub>2</sub> Nanodiodes with Atomic Force Microscopy**, *Hyunhwa Lee*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea; *H Lee*, Institute for Basic Science (IBS), Republic of Korea; *J Park*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Electrons with high kinetic energy (1-3 eV) can be generated in metals during surface reaction processes. These energetic electrons are called "hot electrons". A way to detect these hot electrons is by using metal-semiconductor Schottky diode. It was proposed that enhanced light absorption with localized surface plasmon resonance results in amplified hot electron generation by utilizing Au/TiO<sub>2</sub> Schottky diodes. In this scheme, the surface morphology of the metal thin film was modified to a connected gold island structure that exhibits surface plasmons.<sup>[1,2]</sup>

To probe the enhanced hot electron flows by surface plasmon, we fabricated patterned Au islands on TiO<sub>2</sub> diodes using e-beam evaporator, [3] and measured the local photocurrent with the conductive probe atomic force microscopy under back illumination of the light. The gold pattern has triangle shape with the length of the hypotenuse of 150 nm and the thickness of 20 nm. We found that the photocurrent depends on the wavelength of laser, and the bias between Au and TiO<sub>2</sub>. The photocurrent measured at the edge of the Au islands was higher than that on the flat area of Au islands. The result indicates the localized surface plasmon resonance leads to enhancement of hot electron flux.

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**NS-ThP-3 Surface Functionalization of 2D Mo<sub>2</sub>C**, *Yang Zeng, P McBreen, T Zhang*, Laval University, Canada

A preliminary study of the surface reactivity of 2D - $\alpha$ -Mo<sub>2</sub>C crystallites grown on a copper foil was performed using X-ray photoelectron spectroscopy. Different sample preparation protocols for the as-received materials were explored in order to remove hydrocarbon surface

contamination. Annealing in vacuum and in argon led to the formation of graphitic layers while annealing in O<sub>2</sub> led to almost complete disappearance of the Mo signal. Gentle argon ion sputtering proved effective at removing the hydrocarbon contamination to reveal pristine molybdenum carbide. XPS spectra were recorded following the exposure of the prepared sample at room temperature to furfural. The results are commented on in relation to deoxygenation and olefin metathesis surface chemistry.

**NS-ThP-4 a-Si:H Spacer Lithography Using Different Mandrels (Al, SiN<sub>x</sub>, and Photoresist) and Etching Processes (RIE, ECR and ICP)**, *Andressa Rosa, J Diniz, UNICAMP, Brazil*

Semiconductors nanowires are essential for obtaining present and future electronic devices (transistors) and integrated circuits (microprocessors), which require technologies with dimensions smaller than 50 nm and 10 nm, respectively<sup>1,2</sup>. In this context, Spacer Lithography (SL) or Self-Aligned Double Patterning (SADP) methods for the definition of silicon nanowires (SiNW<sub>s</sub>), for sub-150 nm width dimensions, were developed. These methods are based on: i) hydrogenated amorphous silicon (a-Si:H) spacers (two thickness values of 60 nm and 150 nm) deposited by ECR-CVD (Electron Cyclotron Resonance (ECR) - Chemical Vapor Deposition (CVD)) at room temperature; ii) three different types of mandrels, aluminum - Al, deposited by sputtering; silicon nitride - SiN<sub>x</sub>, obtained by ECR-CVD; and photoresist, deposited by spinner; and iii) three different etching processes (RIE (Reactive Ion Etching), ECR and ICP (Inductively Coupled Plasma).

Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to obtain the SiNW widths and the shapes of tridimensional (3D) structures as shown a Figure 1. The Table 1 shows the results of the SiNW width values extracted from SEM images and confirmed by AFM analyses, in related to a-Si:H thickness (60 nm or 150 nm), mandrel materials (Al, SiN<sub>x</sub> or Photoresist) and etching processes (RIE, ECR or ICP). Furthermore, it is presented the comparison between the original a-Si:H thickness, after deposition and before etching process, and the SiNW width, after the etching, to detect if the lateral anisotropic etching of a-Si:H has occurred (or not), to obtain SiNW less wide than expected. From the results, it can be conclude that our method for the formation of semiconductors nanowires sub-150 nm wide is effective and feasible for 3D devices prototyping. Besides that, RIE and ECR processes present lateral etching, obtaining SiNWs with wide less than the a-Si:H spacer thickness.<sup>3</sup> This result is interesting for the nanostructure formation without the traditional methods (e.g., EBL or 193i).<sup>2</sup> It is important to notice that, the ICP process enable the SiNWs formation with width similar to the a-Si:H spacer, indicating that process is anisotropic.

<sup>1</sup> Koike, K. et al. *Proc. SPIE 10586, Advances in Patterning Materials and Processes XXXV*, 105861F (13 March 2018);

<sup>2</sup> Bunday, B. et al. *Proc. SPIE 10585, Metrology, Inspection, and Process Control for Microlithography XXXII*, 105850I (22 March 2018);

<sup>3</sup> Rosa, A. M. et al. *IEEE 30th Symposium on Microelectronics Technology and Devices (SBMicro)* (2015).

**NS-ThP-5 Optimization of Stitching Multiple Fields of View for Large Scale Two Photon Lithography**, *Steven Kooi*, Massachusetts Institute of Technology

We explore multiple methods for the optimization of high accuracy overlapping of writing fields of view in a home-built two photon microscope. Stage feedback, interferometry and active optical marker tracking methods are compared and combined to provide the highest precision overlapping to allow for the fabrication of mm sized two and three dimensional photonic structures from individual fields of view written by galvo scanning two photon lithography. Optimized structures are large enough to be characterized by optical transmission, reflection and absorption measurements. These optical measurements are compared to theoretical predictions to quantify the structure fidelity. Additionally, cross sectional imaging is used to locally probe the intersectional areas where multiple fields of view meet.

**NS-ThP-6 Fabrication of Carbon Nanotube-Based Electronic Devices with the Dielectrophoresis Method**, *Joevente Kimbrough, S Chance, B Whitaker, Z Duncan, K Davis, A Henderson, Q Yuan, Z Xiao*, Alabama A&M University

We report the deposition and alignment of semiconducting carbon nanotubes with the alternating electric field-directed dielectrophoresis (DEP) method and the fabrication of carbon nanotube-based electronic devices with the DEP-aligned semiconducting carbon nanotubes (CNTs). Semiconducting carbon nanotubes, which were dispersed ultrasonically in

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solutions, were deposited and aligned onto a pair of gold electrodes 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 aligned carbon nanotubes and fabricated devices were imaged using the scanning electron microscope (SEM), 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.

## **NS-ThP-7 Fabrication and Electrical Characterization of a Flagella-Scaffolded Metallic Nanocluster Network, Marko Chavez, P Edwards, M El-Naggar, V Kresin, University of Southern California**

Bacteria produce rotary filamentous appendages, known as flagella, for propulsion through their environment in response to various chemical signals. The flagella, of nanoscale width and of microscale length, can be easily isolated from the microorganisms at low cost and in large quantities. Once isolated, these nanofilaments of uniform size distribution can be deposited onto desired surfaces in controlled quantities and can act as novel templates for nanostructures. Flagella placed on a surface ahead of ionic, size-selected metallic cluster deposition could act as scaffolds in the construction of nanocluster networks. These organized nanocluster networks could then be used to investigate the various unique quantum and nanoscale properties exhibited by finite-size systems. These include enhanced surface plasmon resonance, catalytic applications, charge tunneling junctions, and Josephson current in potential superconducting arrays.

## **NS-ThP-8 High-contrast Infrared Polymer Photonic Crystals Fabricated by Direct Laser Writing, Yanzen Li, D Fullager, S Park, University of North Carolina at Charlotte; D Childers, USC Conec, Ltd.; G Boreman, T Hofmann, University of North Carolina at Charlotte**

Direct laser writing has been established as a prototyping tool for the rapid fabrication of optical materials with nanometer-sized features. So far, however, highly reflective photonic crystals have been predominately obtained from 3D polymer templates manufactured by direct laser writing which were subsequently inverted using high index materials. The incorporation of high index materials enhances the reflectivity of a given 3D structure considerably, but it inevitably increases the complexity of the fabrication process. Here we demonstrate the successful fabrication of one-dimensional photonic crystals by 3D direct laser writing using only a single polymer to obtain refractive index values approaching that of a gold reference in the near-infrared spectral range. The necessary periodic variation of refractive index is achieved by utilizing partially filled layers wherein integrated sub-wavelength-sized pillars are utilized as a scaffold while simultaneously providing index contrast to that of solid polymer layers. Bruggemann effective medium theory and simulated reflectivity profiles were then used to optimize the photonic crystals' design to operate at a desired wavelength of 1.55  $\mu\text{m}$ . After fabrication, the structures of the photonic crystals were compared to the nominal geometry via inspection of SEM micrographs and showed true-to-form fabrication results. A good agreement between the model-calculated and measured FTIR reflection and transmission data is observed demonstrating the ease of predictive design with this method.

## **NS-ThP-9 Controlled Water-repellent Behavior by Modulating the Density of Nanoscale Si Nanopillar Structure Fabricated with Bio-template and Neutral Beam Etching Technique, Daisuke Ohori, S Samukawa, Tohoku University, Japan**

Si NP structures have a great potential for thermoelectric and cooling device applications. However, current fabrication techniques are too complicated. Furthermore, it is difficult to modulate the properties of the NP by those methods. In this work, we proposed an excellent method to fabricate the NP structure. The water-repellent characteristic of the fabricated Si nanopillar (NP) structure was investigated, and we try clearing the contact angle of density dependence for Si-NPs structure.

12 nm in diameter Si-NPs structure with various density ranging from 1.6  $\times 10^{11}/\text{cm}^2$  (low-density) to 7.1  $\times 10^{11}/\text{cm}^2$  (high-density) were fabricated. These samples were fabricated with a unique technique of a bio-template mask and a neutral beam etching. The bio-template mask is a protein shell with an iron oxide core, called ferritin. The density of the Si-NPs can be easily adjusted by modulating the distance between ferritins. The ferritin arrangement was carefully adjusted by controlling the length of the decorated poly(ethylene glycol) (PEG); a spin-coating was carried out for this arrangement process. Thereafter, an etching process was done by a

neutral beam etching (NBE) technique. The NBE process could realize the damage-less etching on the surface/interface utilizing a bottom electrode that neutralizes Si ion in pulsed-plasma. The NBE process could realize the damage-less etching on the surface/interface utilizing a bottom electrode that neutralizes ion in pulsed-plasma. NBE can also minimize a UV irradiation to the sample which is beneficial to reduce the occurring lattice defects.

We measured the contact angle for all samples under the conditions that were the as-etch and removed  $\text{SiO}_2$  layer. For the as-etched condition, the contact angle of the low-density and high-density samples were 4.6 and 9.1 deg, respectively. Meanwhile, the contact angle of Si wafer with a  $\text{SiO}_2$  layer was 48.1 deg. After the removal of the  $\text{SiO}_2$  layer, the contact angle of the low-density, high-density samples, and Si wafer became 112, 104, 89.8 deg, respectively. This indicates that the removal of the  $\text{SiO}_2$  layer also helps to improve the contact angle, especially the Si-NPs samples.

## **NS-ThP-10 An Empirical Model of Fences Ligation during Ion Beam Processing, Anthony De Luca, J Guerrero, C Ligaud, Cea, Leti, Minatex, France**

For many years integrated circuits and microstructure devices fabrication, getting smaller features in order to achieve higher density has been a challenge with lithography and dry plasma etching technology improvements. Now, the fabrication of new microsystems need the introduction of materials (like Pt, Ni, Mn, Fe, Co, etc ...) incompatible with stand plasma etching. Leading to new stringent etch requirement, the Ion Beam Etching Process enables to address these technological issues.

In this paper, the ion beam milling process is not presented as a simple technological step after lithography and before stripping steps. We will discuss about a complete technological step including lithography, etching and stripping. All the applications presented need metallic compounds or metallic alloys stack etching for microsystem applications. We will present an empirical model based on experiments to describe fences formation during ion beam etching.

Different design with squared and rounded patterns were tested. Isolated and array of patterns were processed to simulate the impact of design and the role of etching surface in fences formation. All the design were also used for different metallic stacks and metal simple layer in order to understand the impact of material in fences formation.

## **NS-ThP-11 Towards Molecular-Level Control of Reactions on Organic Semiconductor Surfaces, Gregory Deye, J Ciszek, Loyola University Chicago; J Chen, J Vicente, Ohio University; S Dalke, S Piranej, Loyola University Chicago**

Presently, it is an enormous challenge to react organic surfaces with a molecular-level of control, and this largely because current methods, including UV-ozone and electron irradiation, are inherently crude. Unsurprisingly, the precedence of reactions on organic (molecular) surfaces is minimal as these materials do not have the long rich history of inorganic surfaces. As a consequence, the factors defining reactivity have not been effectively evaluated. In contrast with inorganic surfaces which are strongly held together by metallic or covalent bonding, organic surfaces are only held together by relatively weak van der Waals interactions. Furthermore, reactions on organic surfaces are highly anisotropic, where molecular orientation within the lattice is cornerstone to the reactivity of a surface. We examine these and other factors by exposing acene thin films to reactive vapors under a controlled parameter space. Reaction extent was determined using polarization modulation infrared reflection absorption spectroscopy and x-ray photoelectron spectroscopy, and surface morphology was evaluated using atomic force microscopy and scanning electron microscopy. We show that with only mild thermal activation, a surface reaction extended into the subsurface, which we attribute to the weak intermolecular interactions comprising the surface. Classical reaction models were evaluated for their predictive ability and it was found that surface reactions most closely resembled solution/gas phase precedence, while diffusion into the surface plays a small role. Finally, reactivity on organic surfaces are profoundly influenced by defects in a manner not that dissimilar to that of their inorganic counterparts. This work demonstrates the important factors guiding reactivity on organic surfaces, and offers insights into controlling chemical functionalization on the molecular-level.

## **NS-ThP-12 The TESLA JT SPM, Markus Maier, D Stahl, A Piriou, M Fenner, J Koebler, K Winkler, T Roth, Scienta Omicron GmbH, Germany**

The TESLA JT SPM provides access to more than 5 days SPM measurement time at temperatures down to 1K ( $^4\text{He}$  operation) with magnetic fields larger than  $B > 3\text{T}$ . Careful thermal design of the bath cryostat and JT

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cooling stage as well as the integrated UHV magnet lead to exceptionally low LHe consumption of only 11 liters LHe for 120 hours, specifically also during magnet operation and field variation. The external JT Helium supply allows for  $^3\text{He}$  operation and significantly lower temperatures in the range of 500mK.

The microscope head is a proven, highly stable design developed specifically for high magnetic field environments. It offers the full range of SPM measurements modes, including Scienta Omicron's leading QPlus AFM technology.

Safe and independent tip/sample exchange under optical control is one of several key ease-of-use features delivering dependable high performance SPM and successful scientific work.

In contrast to a conventional wet magnet concept, the dry split-pair magnet provides for optical access enabling various optical experiments and even in-situ evaporation into the SPM at low temperatures.

We will discuss the technical concept and will show performance evaluation measurements at T=1K that prove stability below 1pm as well as energy resolution on superconductors.

Specifically, continuous STM and QPlus AFM imaging at varying temperatures during magnetic field ramping without increasing the LHe consumption differentiate the concept from traditional  $^4\text{He}$  and  $^3\text{He}$  systems and open up new experimental possibilities.

**NS-ThP-13 Recent Developments of Home-made UHV SPM Systems and their Applications, Qing Huan, R Wu, L Yan, D Bao, R Ma, Z Wu, Institute of Physics, CAS, China; Z Gao, X Chen, University of Chinese Academy of Sciences, China; J Ren, Institute of Physics, CAS, China; L Dong, A Wang, H Yang, Y Xing, L Wu, J Yan, Y Wang, L Bao, S Du, H Gao, Institute of Physics, CAS, China**

Scanning probe microscope (SPM) is a powerful tool for studying physical and chemical processes at single molecular/atomic level. The first part of this report will introduce our R&D progresses on UHV-SPM systems, which includes the update of a 4-probe STM, Variable-temperature STM, Low-temperature SPM combined with MBE and optical accesses, and Low-temperature SPM combined with PLD et. al. The second part will mainly introduce some research works on graphene, organic functional molecules and so on which are carried out on these home-made systems.

**NS-ThP-14 Novel In-situ Diagnostic tools to Analyze Chemical Composition and Energy Spectrum of Vapor in Thin Film Deposition Process, Mikhail Strikovski, S Kolagani, Neocera LLC**

The device potential of multicomponent films in various electronic, magnetic and optical applications critically depends on (i) the chemical composition and (ii) the kinetic energy of the atomic species arriving at the film growth surface. We present two novel methods and instrumentation that allow analysis and control of both composition and energy spectrum of the deposition species. Pulsed Laser Deposition (PLD), a well-known deposition method for multi component materials has been chosen to demonstrate these in-situ diagnostics, providing researchers and engineers an immediate feedback in real-time.

The first tool, called Low Angle X-ray Spectrometer (LAXS), executes quantitative analysis of multiple X-ray spectra emitted by the film-substrate system under the impact of a high-energy electron beam. As the film thickness increases, LAXS follows the evolution of the x-ray spectrum dynamically, and applies special analytical algorithm to find film composition. To validate LAXS, we have chosen multi-elemental compound Y-Ba-Cu-O and demonstrated the efficiency of the technique in identifying the deposition conditions that result in the stoichiometric  $\text{YBa}_2\text{Cu}_3$  cation composition needed for optimum superconducting properties. In another example using Zn-Ti-Cr continuous compositional spreads, LAXS provides a 2D- map of the resulting compositions that the user can correlate with the distribution of physical properties of interest.

The second tool is the Ion Energy Spectrometer (IES), a differential retarding field energy analyzer, which probes kinetic energy distribution of ions at the growth substrate. Depending on a number of system variables, actual energetics of ions arriving at the growth surface is a critical process parameter that needs careful optimizations. As an example, we analyze the energy spectrum of  $\text{CeO}_2$  as a function of oxygen partial pressure in a typical PLD case. Ions of energy as high as  $>100$  eV are present, while majority of the ions are distributed in the 5 - 40 eV range. By varying oxygen background pressure, the IES spectrum is fine-tuned to have a spectral maximum at  $\leq 10$  eV- desirable for non-thermally activated, yet soft film growth. The IES also provides several operational modes, including quick acquisition of Time-Of-Flight spectrum.

**NS-ThP-15 Towards Automated High Throughput Drug Delivery with Plasmonic Nanopipettes, Naihao Chiang, Y Gong, L Scarabelli, N Wattanatorn, C Zhao, J Belling, University of California at Los Angeles; N Cho, Nanyang Technological University; S Jonas, P Weiss, University of California at Los Angeles**

The emergence of robust genome editing methods and their application to hematopoietic stem and progenitor cells (HSPCs) are increasingly being employed to produce more sophisticated gene therapies. We are developing a new gene-delivery platform which provide an optimized environment that promotes survival and facilitates the efficient delivery of targeted endonucleases to HSPCs for improving the development of gene therapies. Specifically, we are combining scanning probe microscopy (SPM) with plasmonics. We are developing a recipe for constructing plasmonic-active gold nanopipettes with controllable localized surface plasmon resonances (LSPR) for adapting different laser excitations. When a nanopipette is placed in close proximity to a stem cell, a low power laser will be used to excite the LSPR at the pipette's tip. The highly localized and amplified electromagnetic field from the LSPR will create a nanometer-size pore along the cell's outer membrane without physically penetrating the cells. The ability of performing the proposed experiments at the single-cell level, without severely damage the cells, gives us a direct access to understand the effectiveness of our procedures, and therefore provide new insights for the field of nanomedicine and gene-therapy.

**NS-ThP-16 High Fidelity and Sustainable Anti-reflective Moth-eye Nanostructures and Large Area Sub-wavelength Applications, Shuhao Si, Technische Universität Ilmenau, Germany; M Hoffmann, Ruhr-Universität Bochum, Germany**

The eyes of moths own a feature of unique significance that they reflect little or no light. The dome-like patterns in a depth of approximately 200 nm with pitches of about 200 nm function as a surface with graded refractive index to reduce the reflections.

In recent years, the booming of large screen TVs and smart phones brings increasing attentions for the AR moth-eye structures in sub-wavelength for panels. The AR moth-eye structures applied on smart phone glass displays require finer high resolution and well-oriented patterns, as well as much higher ability to sustain finger frictions and environmental contamination. However, the ideal moth-eye like structure is acknowledged to be parabolically curved domes, which has been rarely systematically demonstrated, and the reported methods suffer from the long-term sustainability. Formed by coating, those reported nanoparticles spheres can be easily peeled off from the surface inevitably by scratching or sticking in either hard or soft pressing from the first steps. The sustainability and reproducibility, thus the reduction of total cost of ownership, are strongly hindered as a consequence. Therefore, such critical issues have not been properly tackled.

An attempt has been made in this work to focus on the sustainability and reproducibility of the moth-eye structures fabricated in profile of parabolically curved domes. A master defining the resolution of the sub-wavelength structures is prepared, commonly by means of EBL. The transfer of large area moth-eye nanostructures is conducted by soft UV-NIL. The next critical step is to etch the substrate for sloping sidewalls, i.e. in an isosceles trapezoid from a cross-sectional view. After that, the silicon substrate is thermally oxidized, in which way the domes can be achieved taking advantage of the variation of oxidation rate at the structure corner, sidewall and bottom. By this step, a template featuring highly ordered moth-eye nanostructures in profile of parabolically curved dome of sub-wavelength resolution is well defined. The moth-eye patterns will be transferred onto the target glass substrate though soft UV-NIL and subsequent processing. The dome structures are made eventually in the substrate via covalent bonding, rather than physical adhesion in case of nanoparticle spheres. Loss of nanoparticles due to pressing, sticking, scratching and so on is hardly an issue.

The moth-eye nanostructures patterned in glass are expected to show improved reflectivity of the incident sunlight in sub-wavelength application of portable electrical devices such as smart phone glass displays. Soft UV-NIL enables its potential for direct large area replications.

**NS-ThP-17 Fano Resonances at Interference of Electron Waves in Geometrically Inhomogeneous Semiconductor 2D Nanostructures, Victor Petrov, Institute of Radio Engineering and Electronics, Russian Academy of Sciences, Moscow, Russia, Russian Federation**

Fano resonances (FRs) in a semiconductor 2D nanostructure (NS) geometrically inhomogeneous along the propagation of the electron wave (EW) (the x-axis) are theoretically investigated. As is known, FRs [1] arise

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from interference of EWs propagating along two channels: one of them in the continuous energy spectrum, and the other - a quasistationary state against the background of this spectrum. The considered symmetric along the z-axis NS consisted of three sequentially arranged rectangular quantum wells (QWs) in which the motion of the particle was limited along the z-axis: QW<sub>1</sub> of width L<sub>1</sub> at x < -a, QW<sub>2</sub> of width L<sub>2</sub> at -a < x < a and QW<sub>3</sub> of width L<sub>1</sub> at x > a. It was assumed that L<sub>1</sub> < L<sub>2</sub>. In this case, the potential along the x-axis abruptly changed at the points x = -a and x = a, and in each QW a series of quantum-size subbands (QSSs) was formed. Thus the energy QSSs E<sub>(1),n</sub> in QW<sub>1</sub> and E<sub>(3),n</sub> in QW<sub>3</sub> was the same for the same width of this QWs. In a wide QW<sub>2</sub> the distance between QSSs E<sub>(2),m</sub> was less than the distance similar number of QSSs in QW<sub>1</sub> and QW<sub>3</sub> (figures 1,2,3 in round brackets indicate the number of the QW, and n and m - number of QSSs, respectively, in QW<sub>1</sub>, QW<sub>3</sub> and QW<sub>2</sub>). Therefore, in QW<sub>2</sub> formed longitudinal rectangular QW along the x-axis of width 2a, due to the different energy position of the QSSs in QW<sub>1</sub>, QW<sub>3</sub> and QW<sub>2</sub>. These QWs also formed QSSs E<sub>(2),t</sub> due to the restriction of motion in them along the x-axis. These QSSs were the quasistationary states providing the formation of FRs in the considered NS. We calculated the dependence of the NS transmission coefficient |T(E<sub>x</sub>)|<sup>2</sup> for the electron wave of the unit amplitude propagating from the QW<sub>1</sub> along the lower QSS E<sub>(1),1</sub>, on its longitudinal energy E<sub>x</sub> in the range E<sub>(1),1</sub> < E<sub>x</sub> < E<sub>(1),2</sub>. The widths of the QWs L<sub>1</sub> and L<sub>2</sub> in the symmetric on the z-axis NS were chosen so that in this range of variation of E<sub>x</sub> in QW<sub>2</sub> there exist at least two longitudinal QWs of different depths with quasistationary states: QW<sub>x,1</sub>, formed by the QSSs E<sub>(1),2</sub>, E<sub>(2),2</sub> and E<sub>(3),2</sub>, and lying higher in energy QW<sub>x,2</sub>, formed by the QSSs E<sub>(1),2</sub>, E<sub>(3),2</sub> and E<sub>(3),2</sub>. In this case, the wave propagation to QW<sub>2</sub> was possible only through this overlying QSS, since the transition from the QSS E<sub>(1),1</sub> in QW<sub>1</sub> to the E<sub>(2),2</sub> QSS in QW<sub>2</sub> was forbidden by the symmetry of the NS. At the same time, the wave propagation in the channel in the continuous spectrum and in the quasistationary state with the corresponding energy was possible in QW<sub>2</sub>. Further, the interfering waves propagated in QW<sub>3</sub> also along one lower QSS with energy E<sub>(3),1</sub> = E<sub>(1),1</sub>. Thus, when changing E<sub>x</sub>, depending on |T(E<sub>x</sub>)|<sup>2</sup>, FRs appeared.

[1] U. Fano, Phys. Rev. **124**. 1866 (1961).

**NS-ThP-18 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<sup>1</sup>, A Hanbicki, M Rosenberger, C Hellberg, S Sivaram, K McCreary, I Mazin, B Jonker, Naval Research Laboratory

**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. Stephen Hellberg, S.V. Sivaram, K.M. McCreary, I.I. Mazin, and B.T. Jonker

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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 heterostructure property is an interlayer exciton (ILE), a spatially indirect, electron-hole pair with the electron in one TMD layer and the hole in the other.

In this report [1], we use state-of-the-art preparation techniques [2] to create MoSe<sub>2</sub>/WSe<sub>2</sub> heterostructures encapsulated in hBN. We observe ILE emission 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 work was supported by core programs at NRL and the NRL Nanoscience Institute, and by the Air Force Office of Scientific Research #A0ARD 14IOA018-134141. 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.

[1] Hanbicki, Aubrey T., Hsun-Jen Chuang, et al. "Double Indirect Interlayer Exciton in a MoSe<sub>2</sub>/WSe<sub>2</sub> van der Waals Heterostructure." ACS Nano 12 (5) 2018: 4719-4726.

[2] Matthew R Rosenberger, Hsun-Jen Chuang, et al. "Nano-"Squeezee" for the Creation of Clean 2D Material Interfaces" ACS applied materials & interfaces 10 (12) 2018: 10379-10387

**NS-ThP-19 Pycroscopy – A Community-driven Approach for Analyzing and Storing Materials Imaging and Spectroscopy Data**, S Somnath, C Smith, R Vasudevan, Sergei Kalinin, S Jesse, Oak Ridge National Laboratory

Materials science is undergoing profound changes, driven by continual improvements to instrumentation that have resulted in an explosion in the data volume, dimensionality, complexity, and variety, in addition to increased accessibility to high-performance computing (HPC) resources, and more sophisticated computer algorithms than ever before. However, the software supplied with the instruments such as microscopes typically do not provide access to advanced data analysis routines. In addition, such software store measurement data in proprietary file formats and are very expensive to license. These proprietary software and file formats not only impede data analysis but also hinder continued research and instrument development, especially in the era of "big data". Therefore, moving to the forefront of data-intensive materials research requires general and unified data curation and analysis platforms that are HPC-ready and open source.

We have developed the Universal Spectroscopy and Imaging Data (USID) model, which is an instrument-agnostic data schema capable of representing data of any size, dimensionality, or complexity acquired on a regular grid of positions or random positions as in compressed sensing. This USID schema is stored in standardized hierarchical data format files (HDF5) that can be manipulated using any programming language, scale well from kilobyte to terabyte sized datasets. Consequently, USID files are curation-ready and therefore both meet the guidelines for data sharing issued to federally funded agencies and satisfy the implementation of digital data management as outlined by the United States Department of Energy. The generalized data representation allows data processing to be generalized to a single version of the algorithm regardless of the instruments or even modalities.

We have developed a free and open-source python package called Pycroscopy for analyzing, visualizing and storing data in USID HDF5 files. Our instrument-independent data format has also greatly simplified the correlation of data acquired from multiple instruments, necessary for comprehensive studies of materials. Unlike many other open-source packages that focus on analytical or processing routines specific to an instrument, USID can be readily adopted for different techniques within and beyond microscopy. Furthermore, the generality of Pycroscopy provides material scientists access to a vast and growing library of community-driven data processing and analysis routines that are desperately needed in the age of big data. In summary, Pycroscopy can greatly accelerate materials research and discovery through the realms of big, deep, and smart data.

**NS-ThP-20 Auto-dispersing Cellulose Nanoparticles with High Uniformity via Self-assembly in Ionic Liquids**, Y Ahn, Seung-Yeop Kwak, Seoul National University, Republic of Korea

In this study, auto-dispersing nanospheres with diameters of 20 nm were successfully fabricated via molar mass control and self-assembly of cellulose molecules in ionic liquids. We showed how to prepare cellulose nanoparticles with extremely decreased size and improved dispersion in water. Without extra treatment, the particles could be stably dispersed in the aqueous media longer than a month due to their positive charge on nanoparticle surfaces. The comprehensive analysis demonstrated that the molecular mobility and imidazolium at the reducing ends simultaneously played important roles in increasing the crystallinity and the size uniformity.

**NS-ThP-21 The Silicon Atomic Layer Etching by Two-step PEALD Consisting of Oxidation and (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> formation**, E Song, Korea Institute of Materials Science, Republic of Korea; J Ahn, Korea Maritime and Ocean University, Republic of Korea; Jung-Dae (J.-D.) Kwon, Korea Institute of Materials Science, Republic of Korea; S Kwon, Pusan National University, Republic of Korea

The process of precise silicon etching on the atomic scale was investigated by examining the formation of an (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> thin film as an intermediate phase followed by the removal of this layer by sublimation. An amorphous (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> thin film was formed on a Si substrate via a two-step plasma-enhanced atomic layer deposition (PEALD) process consisting of an oxidation step involving an O<sub>2</sub> plasma and a transformation step to deposit an (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> thin film using an NH<sub>3</sub> / NF<sub>3</sub> plasma, where the deposited thin film was removed by a sublimation process. Because the thickness of the

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$(\text{NH}_4)_2\text{SiF}_6$  thin film could be linearly controlled by altering the number of PEALD cycles, the etching depth could be successfully controlled on the sub-nanometer scale.



## 2D Materials Focus Topic

Room 201B - Session 2D+EM+MN+NS-FrM

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

Moderator: Xiang Zhang, University of California, Berkeley

8:20am **2D+EM+MN+NS-FrM-1 Interfacial Strength and Surface Damage Characteristics of Two-dimensional h-BN, MoS<sub>2</sub> and Graphene**, *Frank DelRio*, National Institute of Standards and Technology; *B Tran Khac, K Chung*, University of Ulsan, South Korea

Two-dimensional (2D) materials such as single- and multi-layer hexagonal boron nitride (h-BN), molybdenum disulfide (MoS<sub>2</sub>), and graphene have attracted intensive interest due to their remarkable material properties. In this study, the film-to-substrate interfacial strengths and surface damage characteristics of atomically-thin h-BN, MoS<sub>2</sub> and graphene were systematically investigated via atomic force microscopy (AFM)-based progressive-force and constant-force scratch tests and Raman spectroscopy. The film-to-substrate interfacial strengths of these atomically-thin films were assessed based on their critical forces (*i.e.*, normal force where the film was delaminated from the substrate) as determined from progressive-force scratch tests. The evolution of surface damage with respect to normal force was further investigated using constant-force tests. The results suggested three different steps in the evolution of surface damage. At relatively low normal force, no significant change in topography and friction force was observed, which points to elastic deformation in the scratched area. As normal force increased, the formation of defects in the film and plastic deformation in the substrate were noted. At this stage, although the films have not yet failed, their topography, friction force, crystalline quality, and mechanical strengths were affected, which notably degraded their tribological performance. At normal forces above the critical force, delamination of the film from the substrate occurred. The compressive strain-induced buckling in front of the

AFM tip was the primary source of mechanical instability. As the compressive strain increased, the atomic bonds were compressed, and eventually ruptured. As the number of layers increased, the tribological performance of h-BN, MoS<sub>2</sub>, and graphene were found to significantly improve due to an increase in the interfacial strengths and a decrease in the surface damage and friction force. In all, the findings on the distinctive surface damage characteristics and general failure mechanisms are useful for the design of reliable nanoscale protective and solid-lubricant coating layers based on these 2D materials.

8:40am **2D+EM+MN+NS-FrM-2 Optical and Optoelectronic Properties in 2D Homo- and Hetero-junctions**, *Juan Xia*, Nanyang Technological University, Singapore, China

It is well-known that the optical and electronic structures of two-dimensional transition metal dichalcogenide (2D TMD) materials and perovskites often show very strong layer-dependent properties<sup>1</sup>. It is less well-known however is that the properties can also be tuned by stacking order, which allows us to build electro and optical devices with the same material and the same thickness. Detailed understanding of the inter-layer interaction will help greatly in tailoring the properties of 2D TMD materials for applications, e.g. in p-n junction, transistors, solar cells and LEDs. Raman/Photoluminescence (PL) spectroscopy and imaging have been extensively used in the study of nano-materials and nano-devices. They provide critical information for the characterization of the materials such as electronic structure, optical property, phonon structure, defects, doping and stacking sequence<sup>2</sup>.

In this talk, we use Raman and PL techniques and electric measurements, as well as simulation to study TMD samples (Figure 1). The Raman and PL spectra also show clear correlation with layer-thickness and stacking sequence. Electrical experiments and ab initio calculations reveal that difference in the electronic structures mainly arises from competition between spin-orbit coupling and interlayer coupling in different structural configurations<sup>3</sup>. Similar phenomena could also be found in TMD heterostructures.

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9:00am **2D+EM+MN+NS-FrM-3 Sequential Edge-epitaxy: Towards Two-dimensional Multi-junctions Heterostructures and Superlattices**, *Humberto Rodriguez Gutierrez*, University of South Florida **INVITED**

Atomically thin layers are known as two-dimensional (2D) materials and have attracted a growing attention due to their great potential as building blocks for a future generation of low-power and flexible 2D optoelectronic devices. Similar to the well-established 3D electronics, the development of functional 2D devices will depend on our ability to fabricate heterostructures and junctions where the optical and electronic properties of different compounds are brought together to create new functionalities. Vertical heterostructures can be produced by selective van der Waals stacking of different monolayers with distinct chemical composition. However, in-plane lateral heterostructures, where different materials are combined within a single 2D layer, have proven to be more challenging. During the formation of the hetero-junction, it is important to minimize the incorporation of undesired impurities and the formation of crystal defects at the junction that will impact the functionality of the 2D device. When fabricating periodic structures it is equally important to develop the ability to control the domain size of each material. In this talk, we will review different techniques that have been used to create 2D lateral heterostructures of transition metal dichalcogenide compounds. Emphasis will be made in our recently reported one-pot synthesis approach, using a single heterogeneous solid source, for the continuous fabrication of lateral multi-junction heterostructures of TMD monolayers. In this method, the heterojunctions are sequentially created by only changing the composition of the reactive gas environment in the presence of water vapor. This allows to selectively control the water-induced oxidation and volatilization of each transition metal precursors, as well as its nucleation on the substrate, leading to sequential edge-epitaxy of distinct TMDs. This simple method have proven to be effective for continuous growth of TMD-based multi-junction lateral heterostructures, including selenides, sulfides and ternary alloys. Basic devices with field effect transistor configuration were fabricated to study the electrical behavior of these heterojunctions, their diode-like response, photo-response as a function of laser power as well as photovoltaic behavior of the heterojunctions will be discussed.

9:40am **2D+EM+MN+NS-FrM-5 Interpretation of  $\pi$ -band Replicas Observed for Mono- and Multi-layer Graphene Grown on 4H SiC(0001)**, *T Balasubramanian, M Leandersson, J Adell, C Polley*, Lund University, Sweden; *Leif Johansson, R Yakimova, C Jacobi*, Linköping University, Sweden

Graphene has made a major impact on physics due to its large variety of properties. The peculiar band structure of free standing graphene, showing linear dispersion and a Dirac point at the Fermi energy, makes it attractive for various applications. Large-scale epitaxial films have been grown on Si-terminated SiC substrates. However, the electronic structure is influenced when the graphene is laid upon a substrate whose lattice symmetry does not match that of graphene [1,2]. Six replicas oriented around each Dirac cone were observed already in the first ARPES experiments [1] of graphene grown on SiC(0001), and later reported [2] to have around 40 times lower intensity than a main Dirac cone. They were found to have the same relative separation and orientation as the rosette spots observed around the 0<sup>th</sup> and 1x1 SiC and Graphene spots in the low energy electron diffraction (LEED) pattern and were explained [2] to have similar origin, *i.e.* to originate from photoelectron diffraction.

In two later ARPES investigations [3,4] additional weaker replicas were reported to exist along the  $\Gamma$ -K direction in the Brillouin zone of Graphene. One of them showed the existence [3] only for 1 ML but not 2 ML samples while the other reported [4] the existence in both 1 ML and 3 ML graphene samples. The origin of these replicas were in both cases attributed to a modulation of the ionic potential in the graphene layer/layers induced by the charge modulation of the carbon layer at the interface, *i.e.* the carbon buffer layer. Thus to an initial state effect instead of the earlier proposed final state effect. In both those experiments un-polarized HeI radiation was utilized, so the symmetry of the  $\pi$ -band replicas was not determined. We therefore investigated monolayer and multilayer graphene samples using linearly polarized synchrotron radiation, which allowed us to exploit the so called dark corridor [5] to directly determine the symmetry of the replica cones. Our ARPES data therefore clearly show the origin of these additional replicas observed using He-I radiation and moreover reveal the existence of some weaker replicas not earlier reported. An interpretation of our ARPES data in terms of final state photoelectron diffraction effects is shown to account for the location and symmetry of the  $\pi$ -band replicas observed.

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# Friday Morning, October 26, 2018

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10:00am **2D+EM+MN+NS-FrM-6 Effect of SiC(0001) Substrate Morphology and Termination on Multilayer Hexagonal Boron Nitride Epitaxy by Plasma-Enhanced CBE**, *Daniel J. Pennachio, N Wilson, E Young, A McFadden, T Brown-Heft*, University of California at Santa Barbara; *K Daniels, R Myers-Ward, K Gaskill, C Eddy, Jr.*, U.S. Naval Research Laboratory; *C Palmstrøm*, University of California at Santa Barbara

Despite the prevalent use of hexagonal boron nitride (hBN) in 2D devices as a gate dielectric, tunnel barrier, or substrate, the quality of hBN thin films are typically lacking relative to flakes exfoliated from bulk crystals. To address the challenges of hBN epitaxy, this work studies the growth of hBN on single-crystal epitaxial graphene on SiC(0001) via plasma-enhanced chemical beam epitaxy (PE-CBE). As PE-CBE is conducted in an ultra-high vacuum environment, hBN nucleation, composition, and morphology were able to be examined using a combination of *in-situ*, *in-vacuo*, and *ex-situ* characterization techniques to gain insight into the formation of high-quality hBN films and hBN/graphene heterostructures.

It was found that utilization of high growth temperature ( $>1400^{\circ}\text{C}$ ) and nitrogen plasma flux ( $5 \times 10^{-6}$  Torr background pressure) resulted in improved multilayer hBN film morphology over lower temperature ( $1300^{\circ}\text{C}$ ) depositions and CBE growths without nitrogen plasma flux. PE-CBE also produced more stoichiometric films than CBE without plasma at temperatures above  $1400^{\circ}\text{C}$ , as determined by *in-vacuo* X-ray photoelectron spectroscopy (XPS). *In-situ* reflection high energy electron diffraction (RHEED) showed streaky diffraction patterns persisting throughout several nanometers of PE-CBE hBN growth, indicative of a smooth, epitaxial film. Crystallinity and epitaxial arrangement of hBN nuclei were examined by *in-vacuo* and *ex-situ* scanning probe microscopy (SPM).

Scanning probe spectroscopy provided information on the electrical properties of the hBN films relative to bulk values.

The epitaxial alignment of the hBN/graphene/SiC(0001) heterostructure was studied by RHEED and by comparing nuclei edge alignment, as measured with SPM or scanning electron microscopy, to the substrate lattice orientation. It was found that the rotational alignment of the hBN nuclei depended on the substrate surface morphology. Nuclei on the  $(6\sqrt{3} \times 6\sqrt{3})R30^{\circ}$  SiC surface reconstruction, a graphene-like buffer layer, aligned directly to the buffer layer, while hBN nuclei on  $4^{\circ}$  off-cut epitaxial graphene substrates showed preferential alignment to substrate macrosteps rather than the graphene lattice. These  $\sim 25\text{nm}$  high macrosteps were then examined by cross-sectional transmission electron microscopy (TEM), which showed that the epitaxial graphene and hBN conformally blanketed the macrostep facets despite the macrostep's effect on nuclei orientation. The macrostep-directed nucleation outlined in this work provides a potential route to controlling the hBN/graphene rotational alignment during van der Waals epitaxy, an important variable for modulating electronic properties in this 2D system.

10:20am **2D+EM+MN+NS-FrM-7 Nanoelectromechanical Drumhead Resonators from 2D Material Bimorphs**, *Sun Phil Kim, J Yu, E Ertekin, A van der Zande*, University of Illinois at Urbana-Champaign

Atomic membranes of monolayer 2D materials represent the ultimate limit in size of nanoelectromechanical systems. Yet, new properties and new functionality emerge by looking at the interface between layers in heterostructures of 2D materials. In this talk, we demonstrate the integration of 2D heterostructures as nanoelectromechanical systems and explore the competition between the mechanics of the ultrathin membrane and the incommensurate van der Waals interface. We fabricate electrically contacted, 5-6  $\mu\text{m}$  circular drumheads of suspended heterostructure membranes of monolayer graphene on monolayer molybdenum disulfide ( $\text{MoS}_2$ ), which we call a 2D bimorph. We characterize the mechanical resonance through electrostatic actuation and laser interferometry detection. The 2D bimorphs have resonance frequencies of 5-20 MHz and quality factors of 50-700, comparable to resonators from monolayer or few layer 2D materials. The frequencies and eigenmode shape of the higher harmonics display split degenerate modes showing that the 2D bimorphs behave as membranes with asymmetric tension. The devices display dynamic ranges of 44 dB, but there is a strong dependence of the dissipation on the drive. Under electrostatic frequency tuning, devices display small tuning of  $\sim 20\%$  compared with graphene

resonators  $> 100\%$ . In addition, the tuning shows a recoverable kink that deviates from the tensioned membrane model for atomic membranes, and corresponds with a changing in stress of  $0.014\text{ N/m}$ . One model that would account for this tuning behavior is the onset of interlayer slip in the heterostructure, allowing the tension in the membrane to relax. Using density functional theory simulations, we find that the change in stress at the kink is much larger than the energy barrier for interlayer slip of  $0.0001\text{ N/m}$  in a 2D heterostructure, but smaller than the energy barrier for an aligned bilayer of  $0.034\text{ N/m}$ , suggesting local pinning effect at ripples or folds in the heterostructure. Finally, we observe an asymmetry in tuning of the full width half max that does not exist in monolayer materials. These findings demonstrate a new class of NEMS from 2D heterostructures and unravel the complex interaction and impact of membrane morphology, and interlayer adhesion and slip on the mechanics of incommensurate van der Waals interfaces.

10:40am **2D+EM+MN+NS-FrM-8 Atomically-precise Graphene Etch Masks for 3D Integrated Systems from 2D Material Heterostructures**, *Jangyup Son*, University of Illinois at Urbana-Champaign; *A van der Zande*, University of Illinois at Urbana-Champaign

Atomically-precise fabrication methods are critical for the development of next-generation technologies in which electronic, photonic, and mechanical devices approach the atomic scale. In no area is this challenge more apparent than in nanoelectronics based on two-dimensional (2D) heterostructures, in which van der Waals (vdW) materials, such as graphene, hexagonal boron nitride (hBN), and transition metal dichalcogenides (TMDs), are integrated stacked to form functional electronic devices with nanometer thicknesses. A major challenge in the assembly of vdW heterostructure devices is the difficulty of patterning and individually connecting each molecular layer.

In this presentation, we demonstrate the use of graphene as a highly selective, atomically-thin etch mask and etch stop in van der Waals heterostructures. We also show the advantages of graphene etch masks (GEM) through advanced device demonstrations. We demonstrate that most inorganic 2D materials, such as hBN, TMDs, and black phosphorus (BP), are efficiently etched away by exposing those to  $\text{XeF}_2$  gas at room temperature. In contrast, instead of getting etched, atomically-thin monolayer graphene is chemically functionalized (*i.e.* fluorographene (FG)) under  $\text{XeF}_2$  exposure due to the formation of  $sp^3$  bonds by the addition of fluorine atoms onto the graphene surface. Based on this, we used exfoliated (and CVD) graphene layer as etch mask for patterning other 2D layers in micro (and macro) scale vdW heterostructures. We also demonstrate the use of this selective etching and GEM in mainly two different applications: 3D-integrated heterostructure devices with interlayer vias and suspended graphene mechanical resonators. First, we fabricate an electrical device having buried contacts in a 2D material heterostructure. Holes were etched through the top layer of hBN in an encapsulated BN-G-BN heterostructure to locally expose the buried graphene layer and contacts were fabricated by evaporating metal electrodes on the exposed graphene regions. The resulting encapsulated graphene device shows a low contact resistance of  $\sim 80\text{ ohm}\cdot\text{mm}$  ( $n = -2 \times 10^{12}\text{ cm}^2$ ) at room temperature, leading to high carrier mobility of  $\sim 140,000\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , which is comparable to the electrical properties of state-of-the-art edge contacted graphene devices. Second, we fabricate a suspended graphene membrane by vapor phase etching of a BP thin film supporting graphene. We show that the graphene membrane behaves as a nanomechanical resonator with a frequency of 5.24 MHz and quality factor of  $\sim 255$ , comparable to graphene NEMS prepared on conventional substrates.

11:00am **2D+EM+MN+NS-FrM-9 Insights into the O Atom Adsorption and O<sub>2</sub> Dissociation on Halogenated Graphene Surfaces**, *Reynaldo Geronia*, University of the Philippines Diliman; *A Padama*, University of the Philippines Los Baños, Philippines; *J Ocon*, University of the Philippines Diliman, Philippines; *P Chuang*, University of California, Merced

Oxygen reduction reaction (ORR) usually depends on precious metal-based catalysts like platinum and its alloys to facilitate its sluggish kinetics. The high cost of these materials however limits the employment of ORR-based technologies in commercial applications like fuel cells and metal-air batteries. Interestingly, recent works have demonstrated that doped metal-free carbon catalysts, such as graphene-based materials, can facilitate adsorption of ORR intermediate species [1]. This motivates us to investigate the interaction of oxygen atom and oxygen molecule on halogenated graphene systems.

In this work, we performed density functional theory (DFT) based calculations to investigate the stability of coplanar and non-coplanar halogen (X = F, Cl, Br, I) doped monovacant graphene systems. The stability of halogenated-graphene is strongly influenced by the size of halogen dopant as well as the geometry of the vacancy [2]. The calculated adsorption properties of atomic [3] and molecular oxygen on halogenated graphene systems, on the other hand, signifies the possibility of O<sub>2</sub> dissociation. We note that the dissociation of the molecule results to the distortion of the geometric structure of the substrate. This leads mostly to the formation of dangling and bridging C-O bonds along the edge of the graphene monovacancy which could have facilitated the dissociation of the molecule. Depending on the halogen, adsorption of oxygen can strengthen or weaken existing C-X bonds, due to differences between the abilities of oxygen and halogens to induce charge transfer and to participate in  $\pi$  bonding with carbon. These findings are expected to increase our understanding of novel graphene-based materials, which are currently being developed with the aim of reducing the use of noble metals as catalysts in fuel cells.

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## Biomaterial Interfaces Division

### Room 101B - Session BI+AS+NS-FrM

#### Characterization of Biological and Biomaterial Surfaces

**Moderator:** Bill Theilacker, Medtronic

8:20am **BI+AS+NS-FrM-1 Novel Insights into Skin Biology and Permeation of Actives using ToF-SIMS and 3D OrbiSIMS.**, *David Scurr*, The University of Nottingham, UK

**INVITED**

This work presents the use of mass spectrometry imaging (specifically ToF-SIMS and 3D OrbiSIMS) as an emerging tool for skin analysis, offering the ability to perform chemical histology and monitor the distribution of xenobiotic compounds, namely antibacterial, cosmetic and pharmaceutical agents. Both 2D and 3D spatial distribution profiles of analytes within skin are achievable for both topically applied compounds following permeation and inherent compounds present in native tissue. Data acquired using the 3D OrbiSIMS can identify a significant number of biological molecules, unavailable using ToF-SIMS, including subtle chemical variations within single skin strata and / or individual cells.

Individual tape stripped layers of human *stratum corneum*, both native and following application of a topical compound can be imaged using ToF-SIMS and 3D OrbiSIMS. The sensitivity of these techniques has also enabled the detection of analytes from native tape stripped samples highlighted differences in the lipid composition of the *stratum corneum* relating to both intrinsic and extrinsic aging effects<sup>[1]</sup>. In particular, a significant increase in the presence and a localised spatial distribution was observed for cholesterol sulfate, which has been shown to play a key role in desquamation.

In conducting an analysis of native *ex vivo* porcine tissue we were successfully able to detect and spatially map chemical biomarkers of both the *stratum corneum* and underlying epidermis. In addition, using a gas cluster ion beam (GCIB), the 3D distribution of analytes throughout the epidermis could be visualised for both pharmaceutical and cosmetic topical products following Franz cell experiments. These methods can be used to illustrate enhanced topical delivery, for example in the use of supramolecular gels encapsulating ascorbic acid and microneedles applied prior to the application of imiquimod used for cosmetic and pharmaceutical purposes respectively.

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9:00am **BI+AS+NS-FrM-3 Multivariate Analysis of ToF-SIMS Data using Mass Segmented Data Matrices: Polymers and Biointerfaces**, *R Madiona*, La Trobe University, Australia; *N Welch*, CSIRO Manufacturing, Australia; *D Winkler*, La Trobe University, Australia; *J Scoble*, CSIRO, Australia; *B Muir*, CSIRO, Australia; **Paul Pigram**, La Trobe University, Australia

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is continuously advancing. The data sets now being generated are growing dramatically in complexity and size. More sophisticated data analytical tools are required urgently for the efficient and effective analysis of these large, rich data sets. Standard approaches to multivariate analysis are being customised to decrease the human and computational resources required and provide a user-friendly identification of trends and features in large ToF-SIMS datasets.

We demonstrate the generation of very large ToF-SIMS data matrices using mass segmentation of spectral data in the range 0 – 500 m/z in intervals ranging from 0.01 m/z to 1 m/z. No peaks are selected and no peak overlaps are resolved. Sets of spectra are calibrated and normalized then segmented and assembled into data matrices. Manual processing is greatly reduced and the segmentation process is universal, avoiding the need to tailor or refine peak lists for difficult sample types or variants.

ToF-SIMS data for standard polymers (PET, PTFE, PMMA and LDPE) and for a group of polyamides are used to demonstrate the efficacy of this approach. The polymer types of differing composition are discriminated to a moderate extent using PCA. PCA fails for polymers of similar composition and for data sets incorporating significant random variance.

In contrast, artificial neural networks, in the form of self organising maps (SOMs) deliver an excellent outcome in classifying and clustering different and similar polymer types and for spectra from a single polymer type generated using different primary ions. This method offers great promise for the investigation of more complex bio-oriented systems.

9:20am **BI+AS+NS-FrM-4 Can you dig it? ToF-SIMS Tissue Depth Profiling**, *Daniel Graham*, *T Angerer*, *L Gamble*, University of Washington

ToF-SIMS has been shown to provide detailed chemical information about cells and tissues with excellent lateral resolution. This has enabled looking at the 2D chemical distribution of lipids and other biological molecules within tissues and cells. Since cells and tissues are three dimensional constructs, it is of interest to be able to characterize their chemical composition in 3D. With the use of gas cluster ion beams (GCIBs) ToF-SIMS can attain very fine z-resolution (<10 nm) in depth profiles, however the use of ToF-SIMS for 3D imaging of biological samples is limited. This is likely due to the complexity of the materials and artifacts often encountered because of the presence of salts. In this work we use ToF-SIMS 3D depth profiling to optimize accurate reconstruction of depth profiles of planarian worm cross-sections. For this, dual beam depth profiles with a 25 keV Bi<sup>3+</sup> liquid metal ion gun (LMIG) for imaging and 10 keV Argon 1000 clusters for sputtering were acquired using an Iontof 5 system. Data reconstruction was carried out using the NBToolbox

(<https://www.nb.uw.edu/mvsa/nbtoolbox>) ZCorrectorGui. It is well known that due to the fixed angle to of the analysis beam, the sequential images taken at each layer of the profile shift as a function of depth. Adjusting the beam steering during data acquisition and image shifting post data acquisition are used to account for this image shifting and more accurately reconstruct a 3D representation of the data. Areas with distinct structural features were chosen for depth profiles in order to aid in ascertaining the accuracy of the 3D data reconstruction. These studies will help establish the viability of 3D data reconstruction of complex biological samples and could be instrumental in being able to localize chemical distributions throughout tissues and cells.

9:40am **BI+AS+NS-FrM-5 Characterization of Biologic Release and Transformation Processes of Clay-sorbed Ammonia using ToF-SIMS and XPS**, *Liuqin Huang*, *W Liu*, State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, China; *Z Zhu*, Pacific Northwest National Laboratory; *H Dong*, Miami University  
Ammonia (NH<sub>4</sub><sup>+</sup>) sorption by clay minerals, either through surface chemisorption or interlayer intercalation, can efficiently reduce the migration of NH<sub>4</sub><sup>+</sup>, which plays an important role in retention of NH<sub>4</sub><sup>+</sup>-based fertilizers in soil. Microbial metabolisms may affect the stability of clay-sorbed NH<sub>4</sub><sup>+</sup> as NH<sub>4</sub><sup>+</sup> is a main nutrient and/or substrate for cells. More interestingly, microbial processes may form new N species (e.g., organic N), which still closely associate with clays but are hardly distinguished from NH<sub>4</sub><sup>+</sup> by bulk analysis. However, the release and transformation processes of clay-sorbed NH<sub>4</sub><sup>+</sup> by microbial activity was poorly understood. Time-of-Flight secondary ion mass spectrometry (ToF-SIMS) is a powerful surface

analysis tool, which can provide elemental, isotopic and molecular information on the clay surface where microbes attack. In this study,  $\text{NH}_4^+$  was first adsorbed by five typical soil clays, including smectite (SWy-2), smectite-illite mixlayer clays (S-I 30:70, 50:50 and 60:40) and kaolinite (KGa-1). Spectral PCA analysis based on both negative and positive revealed that the surface of raw clays (no  $\text{NH}_4^+$  sorption) was abundant with  $\text{SiO}/\text{AlO}$ -,  $\text{Cl}$ -, and  $\text{Na}$ -related clusters but was coated mainly by  $\text{NH}_4^+$ - and  $\text{PO}$ -related clusters after  $\text{NH}_4^+$  sorption, which was consistent with the increase of N content in the clay minerals after  $\text{NH}_4^+$  sorption as determined by elemental analysis of bulk samples. After these  $\text{NH}_4^+$ -containing clays were added as the sole N source for the growth of a common soilacidogenic bacteria (*Burkholderia glathei*), ToF-SIMS data revealed that the signal of  $\text{NH}_4^+$ - and  $\text{PO}$ -related clusters that dominant on clays in abiotic controls almost disappeared, while complex organic C and N-related clusters (e.g., CH and CN clusters) were abundant on bio-reacted clays, providing direct molecular evidence that the  $\text{NH}_4^+$  was easier released by microbial attack but the released  $\text{NH}_4^+$  assimilated into organic N and closely associated with the clay minerals. The ToF-SIMS results were also supported by more  $\text{NH}_4^+$  release into solution (detected by spectrophotometry) but less reduction of total N on the clay particles (detected by an elementary analyzer) after microbial metabolisms than in abiotic controls. In addition, X-Ray photoelectron Spectroscopy (XPS) was used to quantify N species with different chemical states on the clay mineral surfaces, and the data confirmed the existence of a substantial part of organic N adsorbed on the clay surface. Thus, our results suggested that microbial processes enhanced the release of clay-sorbed  $\text{NH}_4^+$ , and the released  $\text{NH}_4^+$  can be transformed into organic N and preserved by forming clay-organic association.

10:00am **BI+AS+NS-FrM-6 Novel Insights into Drug Release by a Functionalized Biomaterial and Dispersion into Bone using Surface Analytical Techniques**, *Marcus Rohnke, C Kern, B Mogwitz, S Ray*, Justus-Liebig University Giessen, Germany; *J Thomas*, IFW Dresden, Germany  
Bone is a complex composite material with similarities to hierarchically structured functional materials. In the case of a fracture or the need for a replacement (e.g. hip prosthesis) filler or replacement materials are necessary. Next generation bone implants are functionalised with drugs to stimulate bone healing locally or to provoke antibiotic effects. Here we focus on the release and dispersion of the anti-osteoporotic agent  $\text{Sr}^{2+}$  from strontium enriched bone cement. The knowledge of the release and dispersion kinetics of the drug plays an eminent role for the performance optimisation of the biomaterial.

Due to practical and technical reasons it is almost impossible to track the drug release kinetics, drug dispersion and the degradation of the implant material in vivo. Here we apply time of flight secondary ion mass spectrometry (ToF-SIMS) depth profiling to obtain the diffusion coefficient of  $\text{Sr}^{2+}$  in the mineralised areas of healthy and osteoporotic rat bone in post mortem examinations. For data evaluation of the depth profiles in mineralised bone we applied a simple diffusion model. The obtained diffusion coefficient for trabecular osteoporotic bone is with  $1.76 \times 10^{-10} \text{ cm}^2/\text{s}$  more than two decades higher than that for healthy bone ( $2.91 \times 10^{-12} \text{ cm}^2/\text{s}$ ). In cortical bone no significant difference in the diffusion coefficient (healthy  $1.33 \times 10^{-12} \text{ cm}^2/\text{s}$ , osteoporotic  $4.17 \times 10^{-12} \text{ cm}^2/\text{s}$ ) could be found. The varying diffusion coefficients can be explained by the different bone nanostructure, which was investigated by focused ion beam scanning electron microscopy (FIB-SEM) and high-resolution transmission electron microscopy (HR-TEM).

The data of cement dissolution experiments into water in combination with inductively coupled plasma mass spectrometry (ICP-MS) analysis account for dissolution kinetics following Noyes-Whitney rule. For dissolution in A-MEM cell culture media the process is kinetically hindered and can be described by Korsmeyer-Peppas kinetics. An adsorbed protein layer on top of the cement surface, which was detected by ToF-SIMS, is responsible for the kinetic inhibition. Based on the results of various analytical experiments we developed a two-phase model and performed a finite element calculation for the release and dispersion of  $\text{Sr}^{2+}$  in bone. The validity of the applied model is proven by animal experiments. We compared the calculated images to mass spectrometric images of bone cross sections and achieved good conformity. It appears that drug removal via the vascular system is negligible. This is a good basis for predictions of drug mobility in bone.

10:20am **BI+AS+NS-FrM-7 Spatial Distributions of Epithelial Growth Factors in Hydrogels Studied by ToF-SIMS and TIRF Microscopy for the Development of Biocompatible Multiple-protein Delivery Systems for Wound Healing**, *Shohini Sen-Britain*, State University of New York, Buffalo; *W Hicks*, Roswell Park Comprehensive Cancer Center; *J Gardella Jr.*, State University of New York, Buffalo

This work reports the use of ToF-SIMS imaging, TIRF microscopy, and depth profiling to visualize and map the interactions of (hydroxyethyl)methacrylate (HEMA)-based hydrogels with mixtures of growth factors that are often secreted by the epithelium during wound healing. During re-epithelialization, hydrogels can act as both tissue scaffolds at the interface between healing epithelium and surrounding connective tissue, and as delivery vehicles of therapeutic proteins that expedite the wound healing process.

The spatial distribution of multiple growth factors at hydrogel surfaces can influence biocompatibility and release kinetics, orientation and conformation of the individual growth factors. Hydrogels interact with mixtures of growth factors in vivo and also when they are developed into multiple-protein delivery systems. To address these concerns, this work presents 2D and 3D spatial distributions of fluorophore-labeled growth factors varying in size, secondary structure, and hydrophobicity at the hydrogel surfaces to model the interface between porous, phase segregated drug delivery systems and complex macromolecular mixtures. HEMA hydrogel blends incorporating methyl methacrylate (HEMA/MMA) and methacrylic acid (HEMA/MAA) cause increased hydrophobicity or hydrophilicity at the hydrogel surface, respectively. They also present phase segregation and porous topography at the surface. Depth profiling shows that smaller proteins, such as epidermal growth factor (EGF) permeate deeper into porous regions than larger proteins such as keratinocyte growth factor (KGF) and platelet-derived growth factor (PDGF). SIMS and TIRF imaging shows that proteins with more hydrophobic character such as PDGF and EGF localize at phase segregated regions containing MMA, while those with more hydrophilic character such as KGF localize at phase segregated regions containing MAA or HEMA. Biological ramifications of these results regarding biocompatibility and multiple-protein delivery systems are the focus of future work.

## Nanometer-scale Science and Technology Division Room 102B - Session NS+AM+AS+MN+PC+PS+SS+TR-FrM

### SPM – Probing Chemical Reactions at the Nanoscale

**Moderators:** Phillip First, Georgia Institute of Technology, An-Ping Li, Oak Ridge National Laboratory

8:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM-1 Using Self-Assembly to Engineer Electronic Properties in 1D and 2D Molecular Nanostructures**, *Michael F. Crommie*, University of California at Berkeley Physics Dept.

**INVITED**

Control of chemical reactions at surfaces has created new opportunities for on-surface synthesis of low-dimensional molecular nanostructures. By designing precursor molecules it is possible to engineer new bottom-up structures with atomic precision and predetermined electronic properties. We have used this technique to confirm recent predictions that quasi-1D graphene nanoribbons (GNRs) have well-defined electronic topology. This means that when “topologically non-trivial” GNRs are fused to “topologically trivial” GNRs then a singly-occupied, topologically-protected interface state occurs at the boundary between them. This has allowed us to engineer new GNRs with unique electronic structure. We have also engineered molecular precursors to control the behavior of 2D polymers. By tuning the coupling reaction between monomers it is possible to create 2D covalent organic frameworks (COFs) that exhibit novel electronic superlattice behavior.

9:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM-3 Chemical and Electronic Structure of Aniline Films on Silica Surfaces**, *Christopher Goodwin*, University of Delaware; *A Maynes*, Virginia Polytechnic Institute and State University; *Z Voras*, University of Delaware; *S Tenney*, Center for Functional Nanomaterials Brookhaven National Laboratory; *T Beebe*, University of Delaware

The use of silica as a substrate for polyaniline is highly appealing since silica is a common component in photovoltaics. To this end we have developed a vacuum technique for the deposition and functionalization of silica with aniline, without the need for wet chemistry. To study the chemistry of the reaction, X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary

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Ion Mass Spectroscopy (TOF-SIMS), and Atomic Force Microscopy (AFM), among other techniques, have been used. To determine the electronic structure of the resulting films, scanning tunneling microscopy and evaluation of valence band data collected by XPS was performed. By controlling the temperature of the gas-phase reaction, two states of aniline were found to exist on the silica surface. Our interest is in determining how the two states affect the electronic band structure of the surface.

9:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM-4 Electric Field Driven Chemical Reaction of Individual Molecular Subunits by Scanning Tunneling Microscopy, Tomasz Michnowicz**, Max Planck Institute for Solid State Research, Germany, Deutschland; *B Borca*, Max Planck Institute for Solid State Research, Germany; *R Pétuya*, Donostia International Physics Centre, Spain; *M Pristl*, *R Gutzler*, *V Schendel*, *I Pentegov*, *U Kraft*, *H Klauk*, Max Planck Institute for Solid State Research, Germany; *P Wahl*, University of St Andrews, UK; *A Arnau*, Donostia International Physics Centre, Spain; *U Schlickum*, *K Kern*, Max Planck Institute for Solid State Research, Germany  
Understanding of elementary steps and control in chemical reactions on the atomic scale might improve significantly their efficiency and applicability. Scanning tunneling microscopy (STM) allows both investigating and stimulating chemical reactions of individual organic subunits, for example via the tunneling current, electric field or a mechanical interaction. Here we present a study of an STM stimulated desulfurization process of the thiophene functional group embedded in a tetraceno-thiophene (TCT) molecule on a Cu(111) surface. Precise positioning and applying stimuli with the STM tip apex allows determination of a two-step process responsible for this chemical reaction. High resolution STM images, supported by the DFT calculations, help us to correlate the first reaction step to the breaking of one of the carbon-sulfur bonds and the second to the breaking of the second carbon-sulfur bond. The latter reaction also results in a significant increase of the bond strength of the broken thiophene part to Cu surface atoms. The chemical reaction is triggered by positioning the tip apex above the thiophene part and applying a threshold voltage that depends linearly on the tip-molecule distance. This linear dependence is a hallmark of an electric field driven process. In addition, conduction measurements through single TCT molecules before and after the reaction have been performed. Compared to the intact molecule we observed a 50% increase of conductance after the chemical reaction, which is in agreement with the finding of a much stronger bond formation between the molecule and Cu surface atoms.

9:40am **NS+AM+AS+MN+PC+PS+SS+TR-FrM-5 Characterising Conjugated Polymers for Organic Electronics by High-resolution Scanning Probe Microscopy, Giovanni Costantini**, University of Warwick, UK

The structure of a conjugated polymer and its solid-state assembly are without a doubt the most important parameters determining its properties and performance in (opto)-electronic devices. A huge amount of research has been dedicated to tuning and understanding these parameters and their implications in the basic photophysics and charge transporting behaviour. The lack of reliable high-resolution analytical techniques constitutes however a major limitation, as it hampers a better understanding of both the polymerisation process and the formation of the functional thin films used in devices.

Here, by combining vacuum electrospray deposition and high-resolution scanning tunnelling microscopy (STM) we demonstrate the ability of imaging conjugated polymers with unprecedented detail, thereby unravelling structural and self-assembly characteristics that have so far been impossible to determine.

Applying this novel technique to prototypical DPP- and thiophenes-containing polymers, we show that sub-molecular resolution STM images allow us to precisely identify the monomer units and the solubilising alkyl side-chains in individual polymer strands. Based on this, it becomes possible to determine the molecular number distribution of the polymer by simply counting the repeat units. More importantly, we demonstrate that we can precisely determine the nature, locate the position, and ascertain the number of defects in the polymer backbone. This unique insight into the structure of conjugated polymers is not attainable by any other existing analytical technique and represents a fundamental contribution to the long-discussed issue of defects as a possible source of trap sites. Furthermore, the analysis of our high-resolution images, also reveals that the frequently assumed all-trans-conformation of the monomers in the polymer backbone is actually not observed, while demonstrating that the main driver for backbone conformation and hence polymer microstructure is the maximization of alkyl side-chain interdigitation.

10:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM-6 Probing Electrical Degradation of Lithium Ion Battery Electrodes with Nanoscale Resolution, Seong Heon Kim**, Samsung Advanced Institute of Technology, Republic of Korea; *S Park*, *H Jung*, Samsung Advanced Institute of Technology, Republic of Korea

The high performance of lithium-ion batteries (LIBs) is in increasing demand for a variety of applications in rapidly growing energy-related fields, including electric vehicles. To develop high-performance LIBs, it is necessary to thoroughly understand the degradation mechanism of LIB electrodes. The investigation of the electrical conductivity evolution during cycling can lead to a better understanding of the degradation mechanism in cathode and anode materials for Li-ion batteries. Here, we probed the electrical degradation of LIB electrodes with nanoscale resolution via quantitative and comparative scanning spreading resistance microscopy (SSRM). First, the electrical degradation of  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA) particles which are representative LIB cathode materials was studied [1].

After 300 charge/discharge cycles, stepwise-increasing resistance distributions toward the centers of the secondary particles were observed. These distributions correspond to the degenerated granular structures of the secondary particles caused by the formation of micro-cracks. Second, the electrical degradation of LIB anodes, the blended Si-C composites with graphite (Gr) particles, was investigated using SSRM [2]. From the SSRM measurements, it was obviously demonstrated that the electrical conductivity of the Si-C composite particles is considerably degraded by 300 cycles of charging and discharging, although the Gr particles maintain their conductivity. Our approach using SSRM techniques can be a good tool to study the electrical properties of various LIB electrode materials with nanoscale resolution.

[1] S.Y. Park, W.J. Baek, S.Y. Lee, J.A. Seo, Y.-S. Kang, M. Koh, S.H. Kim, Probing electrical degradation of cathode materials for lithium-ion batteries with nanoscale resolution, *Nano Energy* 49 (2018) 1–6.

[2] S.H. Kim, Y.S. Kim, W.J. Baek, S. Heo, D.-J. Yun, S. Han, H. Jung, Nanoscale electrical degradation of silicon-carbon composite anode materials for lithium-ion batteries, Submitted.

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