Electronic Materials and Photonics
Room 102A - Session EM+NS+PS+SS+TF-MoM

Growth and Devices Technology of Group III-Nitrides

Moderators: Nikolaus Dietz, Georgia State University, Shalini Gupta, Northrop Grumman ES

8:20am **EM+NS+PS+SS+TF-MoM1 Development of AlGaN based UV Laser Diodes***, **Ronny Kirste**,* Adroit Materials*; B. Sakar, A. Franke,* NCSU*; J. Tweedie,* Adroit Materials*; Z. Bryan, I. Bryan,* NCSU*; S. Mita,* Adroit Materials*; R. Collazo, Z. Sitar,* NCSU **INVITED**

UV laser diodes are widely desired for many important applications such as chemical and biological sensing, non-line of sight communications, and DNA tagging. Design and fabrication of AlGaN based laser diodes is the most promising pathway for next generation UV lasers but challenges for these devices are many including low n- and p-conductivity, absorbing injection layers, and non-ohmic contacts. Here, we present recent advances in the growth and fabrications of UV laser diodes. The presentation will cover the most important steps that are necessary to achieve electrically injected UV laser diodes. These include: AlGaN epitaxy, doping, fabrication, and design.

As an advancement over most existing approaches, we pursue the growth of our device structures on single crystalline AlN substrates which allows for low dislocation densities < 10^4 cm^2. Any such device fabrication is started with the growth of an AlN homoepitaxial layer. It is demonstrated that this epitaxial layer can be grown with a dislocation density that follows that of the substrate and no interface between layer and substrate is observed in TEM, which indicates true homoepitaxy. Subsequent growth of AlGaN layers with Al content ranging 50-85% is shown to be pseudomorphic. An excellent control of the AlGaN surface morphology is demonstrated using a supersaturation scheme and bilayer steps as needed for highly efficient MQWs are achieved. MQWs for emission at wavelengths ranging 240-280 nm are discussed and optically pumped lasing in this region is demonstrated. The chosen approach to grow on AlN is validated by realizing MQWs with an IQE exceeding 90%. In order to achieve electrically injected UV lasing, Al-rich AlGaN is doped and free electron concentrations for the n-cladding with 80% Al-content is shown to be around $8\text{x}10^{18}$ cm^{-3}. In contrast, p-doping of AlGaN is much more challenging because of the high activation energy of the Mg acceptor. Consequently, achievable free hole concentration and conductivity of the p-cladding are low. We discuss how these epitaxial layers can be used for realizing laser diodes. Experimental work is supported by simulations and used to direct the UV laser design. Finally, we present electrical data and electroluminescence spectra from fully fabricated diodes and discuss the future challenges that need to be addressed to demonstrate the first electrically injected UV laser diode.

9:00am **EM+NS+PS+SS+TF-MoM3 Low-Temperature PA-ALD Growth Technology for Group III-Nitride Nano-heterostructures and their (Opto)Electronic Device Applications***, **Necmi Biyikli**, A. Haider, S. Kizir, P. Deminskyi, M. Yilmaz, S. Bolat, A. Celebioglu, A.K. Okyay, T. Uyar,* Bilkent University, Turkey*; F. Buyukserin, S. Altuntas,* TOBB University of Economics and Technology, Turkey*; I. Yilmaz, K. Khaled,* Turgut Ozal University, Turkey **INVITED**

Being initially developed for an entire different area of use, atomic layer deposition (ALD) became a widespread tool to grow functional films and conformal ultra-thin coatings for numerous applications. Based on self-limiting surface reactions, ALD enabled the low-temperature growth of various materials including dielectrics, semiconductors, and metals. Featuring the capability to deposit wafer-scale uniform semiconductor films at relatively low-temperatures with sub-monolayer thickness control and ultimate conformality makes ALD attractive for the semiconductor community. Towards this end, precursors and growth recipes are developed to deposit crystalline thin films for compound and elemental semiconductors. Conventional thermal ALD techniques as well as plasma-assisted and radical-enhanced ALD techniques have been exploited to achieve decent film quality compatible with device applications.

In this presentation, we give an overview of our research efforts on plasma-assisted ALD-based nanoscale semiconductor research focusing on III-nitrides. We have combined our low-temperature thin-film growth recipes with various nanoscale templates and exploited the conformality feature of ALD technique to fabricate nitride nanostructures. Electrospun polymeric nanofibers have been used to produce flexible polymer/III-nitride core-shell structures which might be used for flexible optoelectronics. In addition, hollow-core multi-shell III-nitride nano-heterostructures are demonstrated as well. Anodized alumina (AAO) templates were utilized to fabricate large-area ordered III-nitride nanostructures including radial heterostructures. Extensive growth and fabrication recipe development and materials characterization details will be presented.

The synthesized III-nitride nanoscale semiconductor materials might find applications in a vast amount of applications including physical and chemical sensing, piezo-electric energy harvesting, photocatalysis, nanoscale and flexible (opto)electronics. As proof-of-principle device demonstrations, we have shown nanofibrous GaN/InN-based photocatalysis, GaN/InN-based chemical (gas) sensing, and nanoscale GaN-based UV photodetectors.

9:40am **EM+NS+PS+SS+TF-MoM5 Structural Qualities of GaN Grown on AlN Buffer Layer by MEPA-MOCVD***, **Daniel Seidlitz**, I. Senevirathna, A. Fali, Y. Abate, N. Dietz,* Georgia State University*; A. Hoffmann,* Technical University Berlin, Germany

This study focusses on the influence of Aluminum nitride (AlN) buffer layers on the structural and optoelectronic properties of subsequent overgrown Gallium nitride (GaN) layers, using Migration Enhanced Plasma-Assisted Metal Organic Chemical Vapor Deposition (MEPA-MOCVD).

One challenge in group-III nitride growth is the lattice mismatch between the substrate (e.g. sapphire (Al_2O_3), silicon or silicon carbide) and the group III-Nitride layer as for example GaN. Lattice mismatch imposes compressive strain/stress and influences the crystal quality of subsequent grown group-III nitrides. Inserting an AlN interlayer between the sapphire substrate and the GaN epilayer, transitions the oxygen surface chemistry to a nitrogen surface chemistry, separating surface chemistry related defects from lattice mismatch induced defects, which leads to an improved crystalline quality of the overgrowning GaN layer.

All group III-Nitride layers are grown on sapphire substrates using MEPA-MOCVD. The system design allows the growth of GaN at lower temperatures by using plasma activated nitrogen species (N*/NH*/NHx*) as nitrogen precursor, which are generated by a radio-frequency hollow cathode plasma source (MEAglow^{TM}) scalable from 20W up to 600W. The tunable nitrogen plasma source enables to control the kinetic energies of the active nitrogen species in the afterglow region to be directed at the growth surface, where they interact with metalorganic (MO) precursors. The growth process parameter set includes: reactor pressure, growth temperature, pulsed injection of MO- and nitrogen plasma fluxes, plasma species and their energies.

The structural properties of the AlN buffer layers (e.g. local ordering, grain size, surface topography) are analyzed by Atomic Force Microscopy (AFM) and Raman spectroscopy. The film thickness and optoelectronic properties of the AlN and GaN layers are studied Fourier Transform infrared (FTIR) and reflectance spectroscopy. Results are presented on the structural and optoelectronic properties of the GaN layers as function of the process parameters and the properties of the underlying AlN buffer layer.

10:00am **EM+NS+PS+SS+TF-MoM6 Optical and Electrical Characteristics of Gamma-ray Irradiated AlGaN/GaN Heterostructures***, **MinPrasad Khanal**, B. Ozden, K. Kim, S. Uprety, V. Mirkhani, L. Shen, K. Yapabandara, A.C. Ahyi, M. Park,* Auburn University

AlGaN/GaN high electron mobility transistors (HEMTs) show their potential immunity toward high energy radiation related damages, making them promising candidates for the radiation hard electronics. The degradation in performance of these devices under radiation exposed environment might be due to different possible effects in the device structure such as strain/stress, generation of dislocation, carrier removal and reduction in two-dimensional-electron-gas (2DEG) concentration.The AlGaN/GaN epi structures grown on 6 inch Si wafer were used and irradiated with 120 MRad doses of gamma-ray produced from ^{60}Co source. The semi-transparent (with 10-15 nm thickness) Ni Schottky diodes and circular HEMT devices were fabricated using un-irradiated and gamma-ray irradiated AlGaN/GaN epi structures. In the case of HEMT devices, Ti/Al/Ni (30/180/40 nm thickness) for the ohmic contact and Ir (15 nm thickness) for the gate contact formation were deposited using dc magnetron sputtering system. Spectroscopic photo current-voltage (IV) measurements both with sub-band gap and above band-gap illumination, micro-Raman/photoluminescence spectroscopy, and transistor characterizations were performed. The spectroscopic photo IV measurements were carried out by applying the variable wavelength ultra-violet (UV) and visible light from Xenon lamp source under reverse bias condition. Sub-bandgap illumination (800 nm-400 nm) provided the information about sub-bandgap energy levels of defects by relating the change in photocurrent level in response to the applied light spectrum. On the other hand, above bandgap illumination (280 nm-400 nm) utilizes the fact that the penetration depth of a light varies as a function of wavelength. The result showed reduction in photocurrent on the gamma-ray irradiated samples in comparison to the un-irradiated samples, revealing the possibility of creation of extra defects, and hence, decreasing the carrier concentration in the 2DEG. Micro-Raman and photoluminescence (PL) spectroscopic analysis on both the samples were also performed and the results show no substantial change in their spectra, supporting the conclusion from previous scientific reports of radiation resistance of the HEMTs on their bulk structure level. Decrease in drain current and transconductance were observed from the transistor IV measurements, indicating a possible reduction in carrier concentration. It can be concluded that the reduction on photocurrent, drain current level and transconductance after the gamma-ray irradiation are due to the possible creation of some extra defects and decrease of carrier concentration on 2DEG channel.

10:40am **EM+NS+PS+SS+TF-MoM8 Seeded Regrowth for Production of AlN and GaN Substrates by HVPE***, **Jacob Leach**, K. Udwary, G. Dodson, K. Gentry, P. Quayle, T. Schneider, H. Splawn, K. Evans,* Kyma Technologies, Inc. **INVITED**

Freestanding GaN and freestanding AlN remain the substrates of choice for the highest performing vertical high voltage switching devices (>1200V) and UV optoelectronics, respectively. However, the cost of these substrates remains high, availability remains low, and the crystalline quality of these substrates varies depending on the growth technique employed. In particular, the electrical quality of GaN substrates and the UV transparency of AlN substrates depend on the specific growth conditions utilized and it remains a challenge to maintain high crystalline quality while simultaneously realizing high electrical quality or UV transparency. We proposed the use of hydride vapor phase epitaxy (HVPE) as a cloning technique to replicate the high crystalline quality of existing solvothermally grown GaN or physical vapor transport (PVT) grown AlN substrates while maintaining high electrical and optical quality. In this talk, we report Kyma's recent results in the use of the HVPE replication technique for realizing both AlN and GaN substrates.

Nanometer-scale Science and Technology
Room 101D - Session NS-MoM

Nanopatterning and Nanofabrication + 3D

Moderators: Keith Brown, Boston University, Indira Seshadri, IBM Research Division, Albany, NY

8:20am **NS-MoM1 Fabrication and Characterization of Carbon Nanotube-Based Electronic Devices***, **Zhigang Xiao**, S. Budak, A. Kassu, X. Crutcher, T. Strong, J. Johnson, R. Hammond, J. Gray, A. Reynolds, R. Moten,* Alabama A&M University

Single-walled carbon nanotubes (SWCNTs) are used widely in fabricating nanoelectronic devices because of their unique electrical properties. We report the fabrication of carbon nanotube field-effect transistors (CNTFETs)-based inverter and ring oscillator electronic circuits using the dielectrophoresis (DEP)-aligned single-walled carbon nanotube mesh networks. The electrical property of the fabricated CNTFET-based devices was measured. The CNTFET-based inverter shown excellent electrical transfer characteristics, while the CNTFET-based ring oscillator demonstrated oscillation characteristics, denoting that the CNTFET-based circuits can function well for the application of electronic circuits. The DEP-based fabrication of carbon nanotube electronic circuits is wafer-scale, and compatible with the integrated circuit (IC) fabrication.

8:40am **NS-MoM2 Multi-Material Two Photon and Direct Write Lithography for Photonics, Phononics and Mechanics***, **Steven Kooi**,* Massachusetts Institute of Technology

A combination of two-photon (2PL), holographic and direct write lithography, in positive and negative tone photoresists as well as photopatternable hydrogel materials, is used to produce nano and microscale structures for photonic, phononic and mechanical applications. The lithographic processes are described as well as the conversion of the 3D structures into higher index of refraction materials (Si, Ge and metals) for photonic applications and engineered modulus materials for phononic and mechanical applications by atomic layer deposition, chemical vapor deposition, chemical etching and ion etching techniques. Standard piezo stage scanning two-photon lithography is used to produce 3D structures as well as an upgraded design that incorporates galvo-scanning mirrors that greatly increase the writing speed and area.

The conversion of polymeric structures to higher index materials allows us to access more interesting and measurable optical properties in the visible wavelength range. Optical measurements include reflectivity to characterize optical bandgaps and to evaluate structural uniformity and quality. In addition, near field scanning optical microscopy (NSOM) techniques are used to follow light propagation through engineered photonic structures. These results are compared to theoretical predictions of optical properties and are used to evaluate not only the defect density in the printed structures, but also the quality of the multi-step conversion process. The 3D structures are also characterized by serial focused ion beam (FIB) milling and imaging.

Phononic and mechanical 3D structures are also produced by the same lithographic techniques. These materials are tested by light scattering techniques to evaluate phononic properties as well as static and dynamic mechanical measurements to investigate size and structure dependent mechanical properties. 2PL is also used to produce periodic structures that are used in laser-induced shock wave imaging experiments. These experiments are designed to study the influence of the periodic structures on the propagation and/or mitigation of shock waves.

9:00am **NS-MoM3 Applications of 2-photo 3D Stereolithography to Aerial Microrobots and Air-Microfluidics***, **Igor Paprotny**,* University of Illinois at Chicago **INVITED**

Additive manufacturing, commonly called 3D printing, is currently revolutionizing manufacturing worldwide. Two-photon polymerization has in the last decade been used as an novel 3D stereolithography method that enables the fabrication of microscale structures with a resolution on the order of 100s nanometers. The ability to 3D print microscale structures enables development of novel microelectromechanical systems (MEMS) that transcend traditional top-down micromachining processes. This talk will review the theory of 2-photon polymerization and the applications of this method to microstereolithography. I will also review two novel applications of this technique to MEMS devices fabricated in the Micromechatronic Systems Laboratory at the University of Illinois at Chicago. One application is the investigation of microscale flight, where two-photon stereolithography is used to develop test structures and devices that hover upon application of a localized thermal gradient. New results, enabled by our ability to 3D print 'microflier' designs with varying geometry, show similarity to flight performance observed in microscale flying insects. This talk will also describe the application of two-photon microstereolithography to air-microfluidics, where the creation of microfluidic channels with complex geometries have tremendous applications to the development of lab-on-a-chip sensors for air quality and gas measurements. Several examples of such air-microfluidics circuits are presented and discussed.

9:40am **NS-MoM5 Elucidating Proximity Effects during Direct-Write Synthesis of Complex 3D Nanostructures***, **Brett Lewis**,* University of Tennessee*; J.D. Fowlkes,* Oak Ridge National Lab*; R. Winkler,* Graz Centre for Electron Microscopy, Austria*; H. Plank,* Graz University of Technology, Austria*; P.D. Rack,* University of Tennessee

Cutting edge 3-dimensional nanofabrication techniques are essential for the future technological advancement in many fields and applications ranging from metamaterials to memory devices. One technique to realize truly flexible 3D nanoprinting is focused electron beam induced deposition (EBID), which uses a focused scanning electron beam to decompose precursor molecules adsorbed onto a substrate surface. The electron/precursor/solid intersection generates a deposit composed of the desired material and shape dictated by the prescribed scanning parameters. EBID has the advantage of being compatible with a wide range of materials, substrates and complex geometries at the nanoscale.

In this work, we will overview the relevant electron/precursor/solid interactions and present a systematic study of the geometric dependence of unwanted proximity effects that occur during the deposition process. Notably, we present a solution designed to minimize proximal deposition by appropriately adjusting the scanning parameters and beam conditions dependent on the desired final geometry. Specifically, we have developed a computer aided design (CAD) program that automatically calibrates the scanning pattern by calculating the predicted contribution from nearest neighbor elements. Our program has been demonstrated for use with platinum and gold structures grown from the organometallic precursors *MeCpPt(IV)*Me_3 *and Me2Au(acac)* and *the principles can easily be adapted to other material systems. Furthermore, we will demonstrate a laser-*

assisted process which significantly reduces contamination in the nanoscale deposits.

10:00am **NS-MoM6 Surface Textures with Asymmetric Wetting and Optical Properties Enabled by Two-Photon Direct Laser Writing**, ***Nick Lavrik,*** Oak Ridge National Laboratory*; C. McKown,* UT/ORNL Bredesen Center

Over the last decade, advances in direct laser writing (DLW) using two-photon polymerization have led to development and proliferation of user friendly commercially available tools that extend the concept of additive manufacturing into the nanoscale and enable a researcher with facile and flexible means of fabricating arbitrary complex 3D elements with submicron fidelity. Using one of such recently emerged tools, namely a Photonic Professional GT system (Nanoscribe GmbH), we have explored various asymmetric motifs with the purpose of creating surface textures with unique wetting and optical properties. Starting with simple bio-inspired elements, such as arrays of deformed pillars and fish scale elements, we design and create surface textures that exhibit asymmetric contact angle hysteresis as well as strongly anisotropic reflectivity.

The unique flexibility in creating intricate 3D elements offered by two-photon DLW allows us to elucidate relationships between the subtle variations in the surface topology and changes in the targeted functionalities. Examples of model systems based on asymmetric textures with characteristics promising for a number of applications will be discussed. This talk will also discuss how two-photon DLW can be integrated with and augmented by more conventional wafer scale processing and thin film technologies. Of our particular attention are fabrication sequences that combine two-photon DLW with ALD and thermal post-processing with the goal of creating asymmetric textures represented by more diverse classes of materials beyond crosslinked photopolymers.

10:40am **NS-MoM8 New 3D Structuring Process, by Ion Implantation and Selective Wet Etching**, ***Lamia Nouri****, N.P. Posseme, S.L. LANDIS, F.G. GAILLARD, F.M. MILESI,* CEA, LETI, MINATEC Campus, France

Silicon patterning is a one of the most important steps in nano/micro fabrication, especially for mico/nano electro-mechanical systems (MEMS/NEMS), optoelectronic devices etc ... The fabrication schemes that microelectronics had boosted for decades for the production of integrated circuits, (based essentially on layering and planar patterning stacks of semiconductors, metals, and dielectrics) do not meet the new structuration’s requirements. Indeed, for the new emerging fields which may involve complex 3D patterns, the structuration becomes more challenging and requires several complex and expensive patterning processes such as gray-scale electron beam lithography, laser ablation, focused ion beam lithography, two photon polymerization and dry etching techniques.

In this work, we propose a straightforward technique for realizing 3D structuration intended for silicon based materials (Si, SiN, SiOCH …). This structuration technique is based on ion implantation and selective wet etching .

In a first step a pattern is performed by lithography on a substrate, then ion implantation is performed through the resist mask in order to create localized modifications in the material, thus the pattern is transferred into the subjacent layer. Finally, after the resist stripping, a selective wet etching is carried out to remove selectively the modified material regarding the non-modified one. The type of implanted ions and wet etching baths depend on the morphology of the substrate.

In this study we have demonstrated the feasibility of this new 3D structuration process on Silicon and SiOCH. The mechanisms understanding involved during both implantation and wet etching processes will be presented through characterizations by photoluminescence spectroscopy, Raman spectroscopy and Secondary Ion Mass Spectrometry (SIMS) for silicon samples, and ellipso-porosimetry, Fourier Transform InfraRed spectroscopy (FTIR) for SiOCH samples.

11:00am **NS-MoM9 Design and Realization of 3D Printed AFM Probes***, N. Alsharif, A. Burkatovsky, C. Lissandrello, A.E. White,* ***Keith Brown,*** Boston University

Atomic force microscopy (AFM) is an enabling tool for nanoscience due to its ability to image surfaces with sub-nanometer resolution. One drawback, however, is that the AFM probe must be chosen to complement the material properties of the system of interest – *e.g.* stiff probes are ideal for imaging hard surfaces while soft probes are needed for softer biological materials. Furthermore, the conventional lithography techniques that are used to fabricate AFM probes can only generate limited architectures from a narrow subset of materials. In analogy to the impact rapid prototyping has made on macroscopic manufacturing, nanoscale 3D printing can in principle be used to construct AFM probes in a manner that allows important properties such as spring constant and vibrational resonance frequency to be rationally chosen. Moreover, since it is possible to fully control the 3D structure of a probe, additional properties such as higher harmonic resonance frequencies and deflection sensitivity can be independently adjusted. Here, we demonstrate that functioning AFM cantilevers that are compatible with commercial AFM systems can be 3D printed and used for imaging. In particular, a series of bisegmented probes with consistent spring constants but different resonance frequencies were designed, printed, and evaluated using an AFM. Their properties were found to be consistent with finite element mechanical simulations and comparable to commercially available probes. In addition, we found that the second harmonic mode could be tuned to an integer multiple of the principle harmonic, in a manner that could provide multimode imaging with resonance enhancement. This work opens the door for complex non-rectilinear cantilevers that provide uniquely tuned force-distance relationships or harmonic behavior.

11:20am **NS-MoM10 Evaluating the Reproducibility of Atomically Precise Dopant Structures***, J. Koepke, D. Scrymgeour, R.J. Simonson, M. Marshall,* Sandia National Laboratories*; J. Owen,* Zyvex Labs*; D. Ward, R. Muller, M. Carroll, S. Misra,* ***Ezra Bussmann,*** Sandia National Laboratories

Moore’s law extrapolates to microelectronic devices with atomic size features around 2020 [1]. Anticipating engineering of nanoelectronics at this scale, techniques to tune dopant profiles in silicon have evolved to the ultimate limit of single-atom control. A single atom transistor [2], a device with just one P dopant atom placed in the channel with atomic selectivity, was recently fabricated via hydrogen resist scanning tunneling microscopy (STM) lithography. Despite the promise of atomically precise dopant placement, there are significant challenges to fabrication based on STM lithography such as scale-up, robustness, yield, and reproducibility.

This talk describes techniques to evaluate and optimize the yield and reproducibility of patterning and incorporation for single dopant placement. The hydrogen resist STM lithography method uses electrons from the STM tip to selectively desorb hydrogen atoms from the Si(100) – 2×1:H surface. Dosing the sample with PH_3 and annealing selectively incorporates P dopants into the regions patterned with the STM tip. The key challenges for fabricating the dopant arrays are alignment of the STM tip to the dimer rows of the Si(100) surface, choice of lithographic window size and patterning conditions, and identification of the incorporated dopant after dosing and annealing the sample. Scaling the arrays to larger sizes requires reproducible STM tips that pattern consistently and very low alignment error. Using the precise alignment of the STM tip to the dimer rows of Si(100) surface, we have improved lithography yield for patterning windows for single dopant incorporation from 10% to 40%. We have developed image analysis capability to rapidly identify the dopant atoms in order to verify the results of the array fabrication and provide feedback to the lithography and dosing conditions for process optimization. Comparing results of dopant incorporation with modeling enables fine tuning of the PH_3 dosing and incorporation conditions to improve the single dopant yield.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. Data collected using a ZyVector™ STM Lithography Control System from Zyvex Labs.

[1] International Technology Roadmap for Semiconductors, http://www.itrs2.net/.

[2] Fueschle, *et al.*, *Nat. Nano*. **7**(4), 242 (2012).

Monday Morning, November 7, 2016

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+AS+MI+NS+SS-MoM

Advances in Scanning Probe Microscopy

Moderators: Saban Hus, Oak Ridge National Laboratory, Chanmin Su, Bruker Nano

8:20am **SP+AS+MI+NS+SS-MoM1 Ultrafast Imaging of Polarization Switching in Ferroelectrics via Complete Information Acquisition in SPM**, ***Suhas Somnath***, *A. Belianinov, S.V. Kalinin, S. Jesse,* Oak Ridge National Laboratory

SPM imaging can be represented as an information channel between the dynamic processes at the tip-surface junction and the observer. Current SPM techniques use heterodyne detection methods such as lock-in amplifiers which result in significant loss in vital information such as information from higher eigenmodes, mode-mixing, and other non-linear phenomena in the tip-surface interaction. We present a new technique called General-mode (G-mode) where we capture the complete broad-band response of the cantilever at sampling rates of 1-100 MHz. The availability of the complete cantilever response facilitates the application of various physical models as well as multivariate statistical methods to extract information that has been unavailable from current SPM techniques. Polarization switching in ferroelectric and multiferroic materials underpins the next generation of electronic devices such as tunneling devices, field effect transistors, and race-track memories. The switching mechanisms in these materials are highly sensitive to the local defects and structural imperfections at the micro and nanometer scale, which have undesirable effects on ferroelectric domains. These considerations necessitated the development of Piezoresponse Force Microscopy (PFM) imaging and spectroscopy techniques to measure and manipulate local polarization states. However, the current state-of-art PFM spectroscopy techniques suffer from serious compromises in the measurement rate, measurement area, voltage and spatial resolutions since they require the combination of a slow (~ 1 sec) switching signal and a fast (~ 1 – 10 msec) measurement signal. Furthermore, these techniques only capture the narrow-band cantilever response. We report on a fundamentally new approach that combines the full cantilever response from G-mode with intelligent signal filtering techniques to directly measure material strain in response to the probing bias. Our technique enables precise spectroscopic imaging of the polarization switching phenomena 3,500 times faster than currently reported methods. The improved measurement speed enables dense 2D maps of material response with minimal drift in the tip position.

This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

8:40am **SP+AS+MI+NS+SS-MoM2 Development of Synchrotron X-ray Scanning Tunneling Microscopy**, ***Nozomi Shirato,*** Center for Nanoscale Materials at Argonne National Laboratory*; H. Chang,* Ohio University*; M. Cummings,* Advanced Photon Source at Argonne National Laboratory*; S.W. Hla,* Center for Nanoscale Materials at Argonne National Laboratory*; V. Rose,* Advanced Photon Source at Argonne National Laboratory

Advancements of scanning probe microscopy have been contributing to broaden fundamental understating of surface physics. By combining high intense X-ray beam as a probe and a functionalized tip as a detector, synchrotron X-ray scanning tunneling microscopy has been developed in Advanced Photon Source at Argonne National Laboratory. The recent studies demonstrated the technique has capabilities to extract chemical information with sensitivity at the atomic limit [1] and localized magnetic contrast by utilizing polarized beams [2]. Furthermore, at Argonne, in order to fully exploit potentials of the microscope, a dedicated beamline is under construction. The soft X-ray beamline has the energy range of 400 to 1600 eV and is equipped with a polarizer and focusing optics. The capabilities of the beamline will benefit the communities to explore chemical, magnetic and electronic properties of materials at atomic resolution.

References

[1] N. Shirato et al., Nano Letters 14, 6499 (2014).

[2] A. DiLullo et al., J. Synchrotron Rad. 23, 574 (2016).

9:00am **SP+AS+MI+NS+SS-MoM3 Development and Integration of a Universal SPM head: Design Criteria and Challenges***, B. Guenther,* Sigma Surface Science GmbH, Germany*; J. Hilton,* Mantis Deposition*; A. Feltz,* Sigma Surface Science GmbH*;* ***Andreas Bettac***, Sigma Surface Science GmbH, Germany

Recently we have developed an SPM microscope head that merges the needs for high resolution STM/QPlus^1-AFM and at the same time satisfies the requirements for integration into different cryogen environments including tip and sample handling.

The new SPM head was integrated into different platforms, e.g. in a UHV Helium Flow Cryostat system for temperatures <10K and in a ^{3}He Magnet Cryostat UHV system for high magnetic fields (±12T) and temperatures <400mK.

This contribution focuses on design aspects and challenges for the new SPM head with respect to spatial restrictions, sample sizes/standards, QPlus and STM signal shielding as well as on first results (STM, STS and QPlus) obtained with the different instrumental setups.

[1] F. J. Giessibl, Applied Physics Letters 73 (1998) 3956

9:20am **SP+AS+MI+NS+SS-MoM4 How Soft Is a Protein? Stress-Strain Curve of Antibody Pentamers with 5 pN and 50 pm Resolutions***,* ***Alma Perrino***[*], Instituto de Ciencia de Materiales de Madrid, CSIC, c/ Sor Juana Ines de la Cruz 3, 28049 Madrid, Spain*; R. Garcia,* Instituto de Ciencia de Materiales de Madrid, CSIC,, Spain

Understanding the mechanical functionalities of complex biological systems requires the measurement of the mechanical compliance of their smallest components. Here, we develop a force microscopy method to quantify the softness of a single antibody pentamer by measuring the stress-strain curve with force and deformation resolutions, respectively, of 5 pN and 50 pm [1]. The curve shows three distinctive regions. For ultrasmall compressive forces (5-75 pN), the protein's central region shows that the strain and stress are proportional (elastic regime). This region has an average Young modulus of 2.5 MPa. For forces between 80 and 220 pN, the stress is roughly proportional to the strain with a Young modulus of 9 MPa. Higher forces lead to irreversible deformations (plastic regime). Full elastic recovery could reach deformations amounting 40% of the protein height. The existence of two different elastic regions is explained in terms of the structure of the antibody central region. The stress-strain curve explains the capability of the antibody to sustain multiple collisions without any loss of biological functionality.

[1] Alma P. Perrino and R.Garcia. How soft is a protein? Stress-Strain curve of antibody pentamers with 5 pN and 50 pm resolutions. *Nanoscale,* 10.1039/C5NR07957H (2016)

9:40am **SP+AS+MI+NS+SS-MoM5 AVS Medard W. Welch Award Talk: Action Spectroscopy: Characterizing Molecules at Surfaces and its Dynamics***,* ***Maki Kawai***[†], Institute for Molecular Science, Japan*; Y. Kim,* RIKEN Surface and Interface Science Laboratory, Wako, Saitama, Japan*; K. Motobayashi,* Nagoya Institute of Technology, Japan*; H. Ueba,* Toyama University, Japan **INVITED**

STM is a useful tool for spectroscopy utilizing its ultimate spatial resolution. Electronic and vibrational information that STS and inelastic electron tunneling spectroscopy (IETS) carries is not only the reflection of the static spectroscopic information but also related to dynamical phenomena as motion or reaction of molecules induced by the excitation of molecular states. Action spectroscopy is the method to related the action of molecules induced and is utilized to identify the quantum states of the molecules. Dynamical information includes as how molecular vibrations can couple with the relevant dynamical processes [1,2]. I will present typical eamples of how the fundamental excitation of vibration modes is coupled with chemical reactions at surfaces.

References:

[1] Y. Kim, K. Motobayashi, T. Frederiksen, H. Ueba and Maki Kawai, Profress in Surface Science 90 (2015) 85-143, and the references within.

[2] K. Motobayashi, Y. Kim, M. Ohara, H. Ueba and Maki Kawai, Surf. Sci. 634 (2016) 18-22.

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[*] **NSTD Student Award Finalist**

[†] **Medard W. Welch Award Winner**

10:40am **SP+AS+MI+NS+SS-MoM8 Near-Field Spectroscopy and Imaging of Single Nanoparticles***, **Yohannes Abate**, D. Seidlitz, A. Fali, S. Gamage, V.E. Babicheva, V.S. Yakovlev, M.I. Stockman,* Georgia State University*; R. Collazo, D. Alden,* North Carolina State University*; N. Deitz,* Georgia State University **INVITED**

We investigate nanoscale phase separation on single InGaN QDs and nanostructures by using high-resolution s-SNIN (scattering type scanning near-field infrared nanoscopy) technique in the mid-IR spectral region. We fabricated patterned nanolayers down to few atomic layers thick that allow determination of the near-field infrared response of InGaN/InN/GaN heterostructures quantitatively. We first calibrate the near-field IR amplitude contrast as a function of composition and thickness of the semiconductor nanolayers and QDs. We then use this quantitative leads to identify phase separation in single QDs. An advanced theoretical model is developed to guide the experimental results. Unlike previous models that consider the probe conical tip as approximate point dipoles or spheroids, our model considers the full geometry of the tip and all the sample and substrate layers.

11:20am **SP+AS+MI+NS+SS-MoM10 Atomically-resolved Three-dimensional Structures of Electrolyte Aqueous Solutions near a Solid Surface***, **Daniel Martin-Jimenez**, E. Chacon,* Instituto de Ciencia de Materiales de Madrid, CSIC, Spain*; P. Tarazona,* IFIMAC Condensed Matter Physics Center, UAM, Spain*; R. Garcia,* Instituto de Ciencia de Materiales de Madrid, CSIC, Spain

Atomic-resolution three-dimensional images of electrolyte solutions near a mica surface demonstrate the existence of three types of interfacial structures [1-3]. At low concentrations (0.01-1 M), cations are adsorbed onto the mica until charge neutrality is reached. The cation layer is topped by a few hydration layers while anions are excluded from the mica surface [4]. At higher concentrations, the interfacial layer extends several nanometers into the liquid. It involves the alternation of cation and anion planes. Classical Fluid Density Functional calculations show that water molecules are a critical factor for stabilizing the structure of the ordered interfacial layer. The interfacial layer compatibilizes a crystal-like structure with liquid-like ion and solvent mobilities. At saturation, some ions precipitate and small ionic crystals are formed on the mica. The three-dimensional images have been acquired at 300 K.

[1] E. T. Herruzo, H. Asakawa, T. Fukuma, and R. Garcia, *Nanoscale* **5**, 2678-2685 (2013).

[2] K. Kobayashi *et al.The Journal of Chemical Physics* **138**, 184704 (2013)

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[4] M. Ricci, P. Spijker and K. Voitchovsky *Nat. Commun.* **5**, 4400 (2014).

11:40am **SP+AS+MI+NS+SS-MoM11 Super-resolution Optical and Chemical Imaging of Organic Thin Films using Tip-enhanced Near-Field Optical Microscopy***, A.L. Heilman, R. Hermann, **Michael Gordon**,* University of California at Santa Barbara

Sub-diffraction-limited (super-resolution) optical and chemical characterization of organic surfaces using a custom-built tip-enhanced near-field optical microscope with side-on and attenuated total reflectance (ATR) excitation and collection will be discussed. ATR illumination is combined with an Au optical antenna tip to show that (i) the tip can quantitatively transduce the optical near-field (evanescent waves) above the surface by scattering photons into the far-field, (ii) the ATR geometry enables excitation and characterization of surface plasmon polaritons (SPPs), whose associated optical fields can enhance Raman scattering from coumarin-6 (C6) and copper phthalocyanine (CuPc) films, and (iii) SPPs can be used to plasmonically excite the tip for super-resolution chemical imaging of patterned C6 and CuPc via tip-enhanced Raman spectroscopy (TERS). ATR-illumination TERS is quantitatively compared with the more conventional side-on illumination scheme using both experiment and FDTD optical simulations. In both cases, spatial resolution was better than 40 nm and tip on/tip off Raman enhancement factors were >6500. ATR illumination was shown to provide similar Raman signal levels at lower 'effective' pump powers due to additional optical energy delivered by SPPs to the active region in the tip-surface gap. Additional observations, such as the distance scaling of Raman enhancement and inelastic scattering generated by the plasmonic tip, as well as tip-enhanced photoluminescence imaging of patterned phthalocyanine films at spatial resolutions better than 20-30 nm, will be presented.

Nanometer-scale Science and Technology
Room 101D - Session NS-MoA

Nanophotonics, Plasmonics, and Energy

Moderators: Stephane Evoy, University of Alberta, Canada, Wei Wu, University of Southern California

2:00pm **NS-MoA2 The Effects of N Incorporation in GaAsSb/GaAs Core-shell Nanowires***, **Prithviraj Deshmukh**, P. Kasanaboina,* NCA&T State University*; C. Reynolds Jr., Y. Liu,* North Carolina State University*; S. Iyer,* NCA&T State University

Bandgap tuning beyond 1.3 µm in GaAsSb based nanowires by incorporation of dilute amount of N is reported, for realizing nanoscale optoelectronic devices in the telecommunication wavelength region. Vertical GaAs/GaAsSbN/GaAs core-shell configured nanowires are grown on Si (111) substrates using plasma assisted molecular beam epitaxy. Effects of N incorporation and thickness of the shell layers on the micro-photoluminescence spectral peak shifts have been studied. Annealing in N_2 ambient led to enhanced spectral intensity, which is attributed to the annihilation of defects. Shifts and changes in the spectral shapes of the Raman spectra prior to and after annealing have been used to ascertain the nature of the defects being annihilated during the growth. I-V measurements also provided further support to the annihilation of predominantly point defects on annealing. Results from the transmission electron microscopy study on the planar defects will also be presented.

2:20pm **NS-MoA3 Exploitation of Microwave Interaction and Photoconductive Effects in TiO_2 Nanotube/Nanowire Arrays for Use in Light Harvesting and Sensing Devices***, **Karthik Shankar**,* University of Alberta and The National Institute for Nanotechnology, Canada*; M.H. Zarifi, S. Farsinezhad, M. Daneshmand,* University of Alberta, Canada **INVITED**

Nanostructures made of semiconducting metal oxides such as TiO_2, ZnO, SnO_2, WO_3, etc. have a remarkably versatile application spectrum, serving applications in sensing, catalysis, photocatalysis and solar cells. Metal oxide nanostructures abound in electronic defects originating in their high surface area and the method of fabrication. Such defects include dangling bonds, grain boundaries and color centers which in turn may act as shallow or deep trapping sites for electrons and/or holes. These defects have been more or less uniformly been viewed negatively in the literature for their deleterious effects on light harvesting and charge transport. However, a recently emerging view is that the defects also provide an opportunity to engineer sensitivity and much-needed selectivity in sensor designs, particularly with regards to the detection and quantification of small molecules.

We used highly ordered TiO_2 nanotube arrays (TNA) grown by low-cost electrochemical anodization as platforms to perform the selective sensing of alcohols without the use of external binding receptors. TNA membranes were placed in the active coupling gap of a microwave ring-type resonator [1]. By monitoring the resonator's Quality factor (Q) and resonance frequency (f_0) as a function of time following light illumination of the nanotube membrane, we were able to distinguish between the methanol, ethanol and isopropanol [2].

Our work also brings in focus a hitherto underexplored topic in nanomaterials - namely the leveraging of the interactions of microwaves and semiconductor nanostructures to build better sensors and diagnostic platforms [2]. Extension of this concept enabled us to detect a molecular monolayer by monitoring the interactions of microwaves with semiconductors, and also enabled us to use the molecular monolayer to tune the electronic interactions of the surface of wide bandgap TiO_2 with external analytes in the service of VOC sensing as well as extremely low-level photodetection.

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1. Zarifi MH, Mohammadpour A, Farsinezhad S, Wiltshire BD, Nosrati M, Askar AM, Daneshmand M and Shankar K, TRMC Using Planar Microwave Resonators: Application to the Study of Long-lived Charge Pairs in Photoexcited Titania Nanotube Arrays, *Journal of Physical Chemistry C*, 119 (25), 14358-14365, 2015.

2. Zarifi MH, Farsinezhad S, Abdolrazzaghi M, Daneshmand M and Shankar K, Selective microwave sensors exploiting the interaction of analytes with trap states in TiO2 nanotube arrays, *Nanoscale*, DOI: 10.1039/c5nr06567d, 2016.

3:00pm **NS-MoA5 Next Generation Photovoltaics from Solution-processed Quantum Dot Assemblies***, **Joseph Luther**,* National Renewable Energy Laboratory **INVITED**

Quantum confined semiconductor nanocrystals called quantum dots (QDs), are promising materials for next-generation photovoltaic technologies and other various optoelectronic applications. QDs offer several key benefits over bulk semiconductors. Researchers are actively exploiting these benefits to produce prototypes for the next generation of photovoltaic devices. New synthetic routes that employ cation-exchange reactions to produce well-controlled and stable lead chalcogenide materials will be discussed. Similarly, the effects of metal halide treatments of PbSe QD solids will be explored in various approaches. These metal halides improve the surface properties of the QD assemblies, result in conductive QD solids, and the resulting QD solids have a significant reduction in the carbon content compared to typical QD film treatments using thiols and organic halides. Even when the QDs are coupled in arrays through the utilization of recent developments in surface ligand modification, they still exhibit quantum confinement and possess intriguing ensemble properties that can be exploited in thin films, as the active layer of solar cells. The future challenges of QDs in solar cells will be discussed in relation to device physics measurements that can probe the working principles behind state of the art devices. The method developed here produces QD solar cells that perform well even at film thicknesses approaching one micron, indicating improved carrier transport in the QD films.

4:00pm **NS-MoA8 Negative Index and Hyperbolic Metamaterials: Into the Ultra-Violet***, **Henri Lezec**,* National Institute of Standards and Technology (NIST) **INVITED**

Artificial metamaterials – metallo-dielectric composites tailored on deep-subwavelength scale – enable implementation of electromagnetic responses not found in nature, leading to potentially useful applications as well as yielding new insights into the fundamental nature of light. Here we show how we have leveraged ultrasmooth planar nanoplasmonic waveguides deposited by ion-beam-assisted sputter deposition to implement easy-to-fabricate bulk metamaterials operating at visible and near-ultraviolet wavelengths and having refractive indices ranging from highly anisotropic and positive [1] to quasi-isotropic and negative [2]. Exploiting these structures to tailor the flow of light in exotic ways, we realize devices ranging from high-contrast, near-field nanoparticle optical sensors working in the visible, to the first implementation of a Veselago flat lens [3] functioning in the near ultraviolet. Substituting Al for Ag as the constituent plasmonic metal of choice, we investigate the extension of bulk metamaterial operation into the far-ultraviolet, for lithographic applications beyond the diffraction limit.

[1] T. Xu and H.J. Lezec, Nat. Comm. 5, 4141 (2014). [2] T. Xu, A. Agrawal, M. Abashin, K.J. Chau, and H.J. Lezec, Nature 497, 470 (2013). [3] V.G. Veselago, Sov. Phys. Usp. 10, 509 (1968).

4:40pm **NS-MoA10 Probing Sub-5 nm Gap Plasmon Using Collapsible Nano-fingers***, **Boxiang Song**, W. Wu,* University of Southern California

Plasmonic nanostructures are of great interests recently due to their ability to concentrate light to small volume. They have many potential applications in optical communication, disease diagnosis, and chemical sensing. Therefore it is extremely important to investigate the plasmonic hot spots both theoretically and experimentally. While it is theoretically predicted that the optimal hot spot is a sub-5 nm gap between two metallic particles , due to the difficulties in fabrication of sub-5 nm structures, most of the studies on hot spot behaviors at that scale are theoretical only. Therefore, it is essential to find a way to fabricate hot spots with sub-5 nm gap sizes deterministically and reliably as the experimental platform to probe and utilize those hot spots.

Recently, we have successfully fabricated gap plasmonic structure with precisely controlled nano-gap by using collapsible nano-fingers. First, a nano-finger array in flexible polymer (i.e. nanoimprint resist) is fabricated using nanoimprint lithography (NIL), and metallic caps, such as gold disks, are deposited on the top of each finger using electron-beam evaporation. Second, atomic-layer deposition (ALD) is used to coat a thin conformal dielectric layer. Finally, the nano-finger sample is dipped into Ethanol (water works too) and air-dried. When the Ethanol dries up, the capillary force makes the nano-fingers close together. The ALD-coated dielectric layer serves as the spacer to define the gaps between the metallic particles. If we use TiO2 as an example, each atomic layer of TiO2 is only about 1Å thick, which means the gap between the metallic particles can be precisely controlled with an accuracy of 2 Å and as small as 2 Å. For the first time, we can reliably achieve such small gaps deterministically and precisely. It is the ideal experimental platform to probe the rich sciences at the gap plasmonic hot spots.

As the polarized light shone on the dimer-like structure, it will trigger dipole-like charge distribution inside gold nanoparticle. Based on classical electromagnetic theory, field at gap center increases as the gap gets smaller. However, as gap size reduces, for sub-5 nm gap structure, electron tunneling between two gold nanoparticles becomes significant, which would cancel part of the charge in opposite sides and hence reduce the field. The competing factors result in an optimal gap size for the strongest optical field enhancement. But such a small gap structure has not been fabricated reliably until recently we demonstrated how to define and scale sub-5nm gaps by using collapsible nano-fingers

5:00pm **NS-MoA11 Strong Near-Field Coupling of Plasmonic Resonators Embedded in Si Nanowires***, **Dmitriy Boyuk**, L.-W. Chou, M.A. Filler,* Georgia Institute of Technology

We show that the near-field coupling strength between neighboring infrared localized surface plasmon resonances (LSPRs) supported in Si nanowires is ~5 times stronger than reported for conventional noble metals. We specifically measure the spectral response of selectively doped Si nanowire arrays with in situ infrared spectroscopy to demonstrate this effect. Discrete dipole approximation calculations are consistent with our experimental data, revealing that this behavior arises from a synergistic combination of the nanowire's anisotropic dielectric structure and the large permittivity of intrinsic Si in the infrared. Our experiments reveal that the "universal" scaling of near-field coupling interactions (i.e., independent of material, shape, dielectric environment, etc.), which underlies the so-called "plasmon ruler" widely used to measure nanoscale distances in the chemical and biological sciences, is largely a misnomer. Rather, the plasmon ruler only yields accurate measurements in isotropic dielectric environments. Complex structures, including Si nanowires, require a more thorough exploration of their near-field coupling behavior. Our findings also demonstrate that equivalent near-field interactions are achievable with a smaller total volume and/or at increased resonator spacing, offering new opportunities to engineer plasmon-based chemical sensors, catalysts, and waveguides.

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+2D+AS+NS+SS-MoA

Probing Topological States And Superconductivity

Moderators: An-Ping Li, Oak Ridge National Laboratory, Chuanxu Ma, Oak Ridge National Laboratory

1:40pm **SP+2D+AS+NS+SS-MoA1 Tuning Dirac States by Strain in Topological Insulators***, **Lian Li**,* University of Wisconsin-Milwaukee **INVITED**

Topological insulators (TIs) are distinguished by their metallic boundary states populated by massless Dirac fermions and bulk topological Z_2 index. Changes in the band topology induced by external variables such as strain, electrical field, and composition thus provide a means to tune the boundary states. As a large spin-orbit coupling is necessary to produce an inverted band gap, most TIs discovered to date are narrow gap semiconductors consisting of heavy elements. These materials typically exhibit layered crystal structure with anisotropic bonding characteristic: strong covalent bonding in-plane and weak van der Waals (vdW) bonding out-of-plane, which has been predicted to facilitate effective strain engineering of their bulk band topology.

In this talk, I will first give an overview of the opportunities and challenges in the epitaxial growth of layered TIs. Using the prototypical 3D TI Bi_2Se_3 as an example, I will show that the characteristic anisotropic bonding facilitates a spiral growth mode on virtually any substrates by molecular beam epitaxy. The coalescence of these spirals results in a high density of grain boundaries that consist of alternating edge dislocation pairs, leading to periodic in-plane stretching and compression. Using scanning tunneling spectroscopy, I will show that this local strain field strongly modifies the Dirac surface states, where in-plane compression expands the vdW gap and destroys the Dirac states.

Next, I will show our recent work on the strain engineering of Dirac edge states of epitaxial Bi bilayer films grown on three different substrates: the (111) surface of 3D TIs Bi_2Se_3, Sb_2Te_3, and Bi_2Te_3. Using scanning tunneling microscopy/spectroscopy, I will show that for moderately strained (<6%) single Bi bilayer on Sb_2Te_3 and Bi_2Te_3, edge states are observed; while on highly compressed single Bi bilayer on Bi_2Se_3 (>8%), edge states are suppressed. These findings, supported by density functional theory calculations, demonstrate the uniform control of edge states in 2D topological insulators by strain.

2:20pm **SP+2D+AS+NS+SS-MoA3 Detection of Current Induced Spin Polarization in Topological Insulators via Four-Probe Spectroscopy***, **Saban Hus**,* Oak Ridge National Laboratory*; Y. Chen,* Purdue University*; A.-P. Li,* Oak Ridge National Laboratory

Charge currents carried by the nontrivial surface states of topological insulators (TIs) exhibit a net spin polarization due to spin-momentum locking. Electrical detection of such a spin polarization is crucial for technological applications. However, in 3D TI materials the existence of a bulk conduction channel makes it difficult to quantify the density and the spin polarization of the current carried by the surface states. Here we report in-situ, spin sensitive four-probe spectroscopy measurements on Bi_2Te_2Se single crystals. A ferromagnetic probe detects the net spin accumulation on the surface states while a set of four-probe spectroscopy measurement is used for a quantitative separation of 2D and 3D conduction. We also examine the effect of surface doping by residual gas molecules on the current induced spin polarization. Even though, the additional carriers by dopants enhance the 2D conductance in TIs they reduce the net spin polarization of current carried by topological surface states.

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

2:40pm **SP+2D+AS+NS+SS-MoA4 Switching Handedness of Chiral Solitons Under Z_4 Topology***, **Tae-Hwan Kim**,* Pohang University of Science and Technology, Republic of Korea*; S. Cheon, H.W. Yeom,* Institute for Basic Science (IBS), Republic of Korea

Chirality is a ubiquitous and interesting property of asymmetry in many fields ranging from biology, chemistry to physics. Because of its topologically distinct nature, such chiral objects in condensed matter are often topologically excited states, which are protected by system's topology and can be used to carry information robustly against external perturbations. For instance, nanoscale magnetic skyrmions, spatially localized chiral spin texture with particle-like properties in ferromagnets, have been investigated intensively as topological information carriers for next generation spintronic devices. However, logic operations using topological excitations such as skyrmions are only conceptually proposed. On the other hand, chiral solitons are recently discovered as the topologically protected edge states of one-dimensional Z_4 topological insulators [1,2], which can be exploited as topological information carriers in electronic system. In this talk, I show experimentally and directly that switching between solitons with different chirality is possible by merging them with achiral solitons [3]. I will also show that this chiral switching corresponds to the realization of topological addition of the Z_4 topological number or chirality. With their distinct topologically protected chirality, chiral solitons could uniquely be applied for robust multilevel information storage and logic operation by storing, carrying, and switching three differently topological bits of information.

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3:00pm **SP+2D+AS+NS+SS-MoA5 Spectroscopic-imaging STM Studies on Dirac-Landau Levels in the Topological Surface State***, **Tetsuo Hanaguri**,* RIKEN Center for Emergent Matter Science, Japan **INVITED**

We show that spectroscopic-imaging scanning tunneling microscopy (SI-STM) is a powerful tool to investigate unique electronic features of massless Dirac electrons in a magnetic field.

In contrast to the conventional massive electron that is described by a single-component wave function, the massless counterpart demands the two-component wave function. In the case of the surface state of topological insulators, these two components are associated with the spin degrees of freedom, thereby governing the magnetic properties. Thus, it is highly desirable for spintronics applications to elucidate where and how the two-component nature emerges. We found that the two-component nature manifests itself in the internal structures of Landau orbits. We visualized the local density-of-states (LDOS) distributions associated with the Landau orbits in the topological surface state of Bi_2Se_3 using SI-STM. In the presence of the potential variation, Landau orbits drift along the equipotential lines, forming ring-like patterns in the LDOS images. The observed internal structures of the rings are qualitatively different from those of conventional massive electrons but are well reproduced by the calculation based on a two-component model Dirac Hamiltonian. Our model further predicts non-trivial energy-dependent spin-magnetization textures around the potential minimum. This is originated from the interplay between the two components and may provide a clue to manipulate spins in the topological surface state.

In addition to the Landau orbits, we succeeded in observing the Zeeman shift of the lowest Landau level from which precise *g* factor of the massless Dirac electron can be estimated. We performed experiments on two topological insulators, Bi_2Se_3 and Sb_2Te_2Se, and determined the surface *g* factors of them to be 18 and -6, respectively. Such remarkable material dependence suggests that the Zeeman effect is tunable by controlling the chemical composition, providing a new knob in manipulating the spins in the topological surface state.

4:00pm **SP+2D+AS+NS+SS-MoA8 The Rashba and Quantum Size Effects in Ultrathin Bi films***, **Toru Hirahara,*** Tokyo Institue of Technology, Japan **INVITED**

Precise characterization of physical properties in nanometer-scale materials is interesting not only in terms of low-dimensional physics but also in application to devices. Due to the reduced dimensionality and symmetry, these systems possess various interesting properties that cannot be found in the bulk. In this presentation, focusing on epitaxial ultrathin bismuth films formed on a silicon substrate, we introduce an intriguing interplay of the quantum size and Rashba effects in reciprocal space. Utilizing spin- and angle-resolved photoemission spectroscopy, we observed clear Rashba-split nature of the surface-state bands in these Bi films. However, the band dispersion did not follow the simple Rashba picture and the spin-splitting was lost where they overlapped with the bulk projection. From first-principles calculations, this was explained as a change in the nature of the band-splitting into an even-odd splitting induced by the quantum size effect [1]. Furthermore, we show that the interplay of the quantum size effect and the presence of the surface state induces a complicated change in the Fermi level position of the bulk states in bismuth, which is critical in discussing the surface-state contribution in the film properties [2,3].

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4:40pm **SP+2D+AS+NS+SS-MoA10 Understanding the Microscopic Effects of Annealing in $Ba(Fe_{1-x}Co_x)_2As_2$ Superconductor***, **Qiang Zou**, Z. Wu, Q. Zheng, S. Rajputł, D.S. Parker, A.S. Sefat, Z. Gai,* Oak Ridge National Laboratory

By hole or electron doping of the parent iron-based $BaFe_2As_2$ compound, the high-transition temperature superconductivity emerges from the suppression of the antiferromagnetic order. [1] It was widely reported that thermal-annealing significantly improves some superconducting characteristics in $Ba(Fe_{1-x}Co_x)_2As_2$, including T_c [2] The microscopic origin of such effect is still an open question. To make a connection between the global and the microscopic behavior of the materials, we did a comparison measurement on the pair of well-characterized x, we call ' as-grown' vs 'annealed' $Ba(Fe_{1-x}Co_x)_2As_2$ crystals, and using low temperature scanning tunneling microscopy and spectroscopy (STM/S). The superconducting gap maps deducted from the dI/dV maps were compared. The gap width distribution of the as-grown sample are obviously narrower than that of the annealed one. The coherent peak position also shifted to higher value for the annealed sample. The corresponding reduced-gaps of $2\Delta/k_bT_{c1}$ are about 2.3 and 5.4 for the as-grown and annealed crystals, respectively. The difference of the reduced-gaps indicates that the pairing strength of the annealed crystal is stronger than the as-grown one.

This research was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division . A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Reference

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2. Gofryk, K., et al. "Effect of annealing on the specific heat of $Ba(Fe_{1-x}Co_x)_2As_2$" *Physical Review B, 83(6), 064513*

5:00pm **SP+2D+AS+NS+SS-MoA11 Annealing Effect on the Properties of Superconducting Parent $BaFe_2As_2$ Crystal***, **Shivani Rajput**, Q. Zou, A.S. Sefat, Z. Gai,* Oak Ridge National Laboratory

Understanding of electronic interactions in a parent phase of a superconducting crystal is crucial in determining the mechanism behind high Tc superconductivity. Bulk measurements show that annealing of parent $BaFe_2As_2$ crystal at 700 ^{0}C for 30 days causes a 5 K shift in magnetic transition temperature (T_N) compared to as grown crystal. To understand the effect of annealing and details of magnetic phase transition, we investigate as-grown and annealed $BaFe_2As_2$ crystals at atomic scale using a variable temperature scanning tunneling microscopy/ spectroscopy at various temperature points across T_N. Tunneling spectroscopy exhibit a ~ 0.53 eV gap type feature above T_N, while V-shape dI/dV spectra below T_N. The dI/dV mapping measurements show that as-grown $BaFe_2As_2$ crystals are electronically inhomogeneous, and averaging the differential conductance spectra over a large area does not truly represent the electronic properties of the sample at local scale, whereas annealed sample is comparatively electronically homogeneous.

This research was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Nanometer-scale Science and Technology
Room 101D - Session NS-TuM

Nanodiamonds, Thin Films and Electronics (8:20–10:00 am)/Health and Environmental Impact of Nanotechnology (11:00 am–12:20 pm)

Moderators: Trevor Wiley, Lawrence Livermore National Laboratory, Leonidas Ocola, Argonne National Laboratory

8:00am **NS-TuM1 Formation of Dynamic Topographic Patterns during Electron Beam Induced Etching of Diamond***, **Aiden Martin,*** Lawrence Livermore National Laboratory*; A. Bahm,* FEI Company*; J. Bishop, I. Aharonovich, M. Toth,* University of Technology, Sydney

Spontaneous formation of complex geometric patterns is an interesting phenomenon that provides fundamental insights into underlying roles of symmetry breaking, anisotropy and non-linear interactions. Here we present dynamic, highly ordered topographic patterns on the surface of diamond that span multiple length scales and have a symmetry controlled by the chemical species of a precursor gas used in electron beam induced etching (EBIE).

We provide an anisotropic etch rate kinetics model that fully explains the observed patterns, and reveals an electron energy transfer pathway that has been over-looked by existing EBIE theory. We therefore propose a fundamental modification, whereby the critical role of energetic electrons is to transfer energy to surface atoms of the solid rather than to surface-adsorbed precursor molecules.

EBIE is a high resolution, direct-write nanofabrication technique in which a precursor gas and an electron beam are used to realize etching. A key advantage of EBIE is the ability to etch materials such as diamond that are resistant to conventional chemical etch processes, without introducing damage to the substrate as observed in ion sputtering techniques. As a result, EBIE has recently been used to fabricate components for photonic and electronic applications. Our findings can be harnessed to engineer specific surface patterns under various electron beam irradiation environments for controlled wetting, optical structuring and other emerging applications that require nano and micro-scale surface texturing.

A portion of this work was funded by FEI Company and the Australian Research Council (Project Number DP140102721). A portion of this work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344. I.A. is the recipient of an Australian Research Council Discovery Early Career Research Award (Project Number DE130100592).

8:20am **NS-TuM2 Towards a Gold Standard in Single Digit Detonation Nanodiamond***, N.J. Nunn, O.A. Shenderova, M. Torelli,* Adamas Nanotechnologies, Inc.*; **Gary McGuire,*** International Technology Center

Aggregates of detonation nanodiamond have long been of interest for their numerous potential applications; however, no size of detonation nanodiamond (DND) is perhaps more elusive, yet technologically important, than sub 10 nanometer (or “single-digit”) primary particles. Primary particles of DND have a number of potential applications including drug delivery, seeding in microelelctronics, polymer nanocomposites, and lubricants. Nevertheless, the challenge associated with obtaining these particle from the initial 200-300nm aggregates of purified detonation soot has made them too expensive for widespread use. Even after overcoming the initial challenge of obtaining the primary particles, they are still often limited in their use due to the assortment of chemical functional groups found on their surface. Therefore, an additional challenge is to tailor the surface chemistry of the particles without sacrificing their size by promoting re-aggregation. A final challenge is to identify useful solvents where stability and size of the functionalized particles are preserved. Here we report our work in obtaining high yields of 5nm particles of DND, progress made toward functionalizing these particles with a number of useful chemical structures including: carboxyl, hydroxyl, amine, hydrophobic chains and the dispersion of these particles in a range of solvents such as DMSO, NMP, DMF, THF, Ethylene Glycol, Synthetic Oils, alcohols, and water.

9:20am **NS-TuM5 Field Emission Electron Source Based on UltraNanoCrystalline Diamond Films for Electron Accelerators Applications***, S. Baryshev, S. Antipov, C. Jing,* Euclid TechLabs LLC*; **Anirudha Sumant,*** Argonne National Laboratory

Currently, commercially available electron sources for electron accelerators are photocathodes or thermionic cathodes. Both types puts limits onto the resulting duty cycle of an accelerator and adds into increasing its complexity, as they require additional accessories (lasers, pulser compressors etc.). Cold cathode field emission technology based on low work function metals and other materials is an attractive alternative to simplify the electron injector, however, field emission current stability and processing challenges associated with formation of an atomically sharp tip for these field emitters makes it difficult to adopt this technology for accelerator applications

Nitrogen incorporated ultrananocrystalline diamond (N) UNCD films developed at Argonne National Laboratory have demonstrated its remarkable field emission properties. The unique structure of atomically abrupt nitrogen-incorporated grain boundaries provides field emission sites with very high field enhancement and therefore eliminates the need to make sharp nano-tips thus drastically reducing processing steps to fabricate field emission source. More specifically, it delivers significant currents at electric gradients as low as ~10^5 V/cm, which is far below typical breakdown thresholds in many materials (>~10^6 V/cm), and has turn-on voltages as low as 2-5×10^4 V/cm, and have shown excellent emission current stability for extended time periods up to 1000 hrs. Small grain size and a unique grain boundary network ensure more uniform emission properties over large areas and smaller current load per emitting site (i.e., per grain boundary). Taking advantage of these unique properties of (N)UNCD, Euclid TechLabs in collaboration with Argonne conducted a case performance study of a thin film planar (N)UNCD field emitter in an radio frequency(RF) 1.3 GHz electron gun in an electron accelerator. The field emission cathode was a 100 nm thick (N)UNCD film grown on a 20 mm cathode plug. At surface gradients 45-65 MV/m, peak currents of 1-80 mA (0.3-25 mA/cm^2) were achieved. Imaging with two YAG screens confirmed emission from the planar (N)UNCD surface with beam emittance of 1.5 mm×mrad/mm-rms and longitudinal FWHM energy spread of 0.7% at 2 MeV[1]. The same technology could be adopted for industrial and scientific linear accelerators, both normal-conducting and superconducting, for isotope production for radiopharmacy; X-/gamma-ray production for medicine, non-destructive evaluation, well-logging; and materials processing.

References:

[1] S. V. Baryshev et al., Appl. Phys. Lett. 105, 203505 (2014).

9:40am **NS-TuM6 Time-resolved Small Angle X-ray Scattering during the Formation of Detonation Nanodiamond***, **Michael Bagge-Hansen,** M. Nielsen, L. Lauderbach, R. Hodgin, S. Bastea, L. Fried, D. Hansen, C. May,* Lawrence Livermore National Laboratory*; T. Graber,* Washington State University*; B.J. Jensen, R. Gustavsen, D. Dattelbaum, E. Watkins, M. Firestone,* Los Alamos National Laboratory*; J. Ilavsky,* Argonne National Laboratory*; T. van Buuren, T.M. Willey,* Lawrence Livermore National Laboratory

Most commercial nanodiamond originates from detonation of high explosives, particularly from RDX/TNT mixtures. Models suggest that the phase, crystallinity, and morphology of carbon is strongly dependent on the type of high explosive used and the exact evolution of temperature and pressure conditions during the very early stages of detonation; however, characterization of carbon condensation under the extreme conditions present at 100 ns timescales has been technically challenging. Using time-resolved, synchrotron-based small-angle x-ray scattering, we present a comparative survey of early time carbon condensation from three CHNO high explosives: HNS, Comp B (60% RDX, 40% TNT), and DNTF. We also extend this study to post-mortem TEM analysis of recovered carbon condensates. At later times, the size of particles extracted from SAXS compares favorably with our microscopy results. At early times, models predict that this array of explosives should provide graphitic, nanodiamond, and liquid carbon phases, respectively; our analysis of time resolved SAXS is remarkably consistent with these computational predictions.

This work was performed under the auspices of the US DOE by LLNL under Contract DE-AC52-07NA27344.

11:00am **NS-TuM10 Transformations and Biological Impact of Emerging Energy Storage Nanomaterials***, **Robert Hamers,*** University of Wisconsin-Madison **INVITED**

The rapid increase in mobile electronics and electric vehicle technologies is leading to a rapid escalation in the use of complex oxides as cathode materials in the lithium-ion batteries that power these devices. Economic factors are driving a trend toward mixed-oxide materials such as $Li_xNi_yMn_zCo_{1-y-z}O_2$ (“NMC”) that combine high performance with low cost. However, these materials also incorporate substantial amounts of metals such as Ni and Co that may post environmental risk, and there is not current any national infrastructure for recycling of these materials. We have been investigating the transformation of these emerging nanomaterials and the resulting biological impact as revealed through acute and chronic mortality studies and gene expression studies using *Shewanella oneidensis* and *Daphnia magna* as model organisms. Further molecular-level insights are provided by detailed investigations of NMC interactions with supported lipid bilayers. Our results show that this class of materials induces toxic effects through multiple pathways; with Shewanella with effects can be attributed almost exclusively to the redox dissolution of the NMC to form Ni^{2+} and Co^{2+} ions in solution; in contrast, ion-equivalent controls cannot reproduce the effects observed with *Daphnia magna*. These results highlight the need to develop a mechanistic understanding of the transformation of nanomaterials in the environment and the resulting impacts. Some perspectives on potential strategies for redesign to reduce adverse biological impact will be presented.

11:40am **NS-TuM12 Bio-inspired Nanosystems for Healthcare Applications***, **Elena Rozhkova**,* Argonne National Laboratory **INVITED**

Nanotechnology offers efficient solutions for virtually all areas of science and technology spanning from energy to healthcare technologies. Owing to rapid development of synthesis, nanofabrication and characterization techniques today we are able to engineer advanced hybrid nanosystems from scratch, at atomic and molecular scale, through controlled assembly of nanoparticles and molecules toward practical devices. Biological phenomena such as self-assembly, electron transfer, photosynthesis and enzyme catalysis, and magnetic field sensing have been a source of inspiration for engineers and scientists. We are using both nature's blueprints and biostructure building blocks for developing smart nano-bio hybrids and devices and then interface them with living systems of various levels of complexity towards advancing modern therapeutic, sensing, imaging and diagnostic methods.

Advanced Surface Engineering
Room 101C - Session SE+NS+TF+TR-TuM
Nanostructured Thin Films and Coatings

Moderators: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Robert Franz, Montanuniversität Leoben, Austria

8:00am **SE+NS+TF+TR-TuM1 Design and Predictive Synthesis of Thin Films and Coatings***, P.A. Salvador, **Gregory Rohrer**,* Carnegie Mellon University **INVITED**

A fundamental challenges in materials synthesis is to obtain a specific targeted composition in a functional crystal structure. For example, the synthesis of hexagonal BN is relatively easy, but synthesizing thick films of cubic BN is more difficult. In other words, we cannot currently predict exact synthesis conditions of many targeted polymorphs, and so their formation is often left to lengthy "design-of-experiments" (DOE) methodologies or, more commonly, basic trial-and-error practices. It is essential to improve the output of computational and physical experimental practices to move closer to predictive synthesis and design of coatings.

This talk will describe some recent results of a methodology called combinatorial substrate epitaxy (CSE), which we have used to understand the preferred epitaxial orientations (PEOs) of a wide range of heteroepitaxial structures and to fabricate various novel metastable materials. In this approach, the target compound is deposited on polished polycrystalline substrates, rather than commercial single crystals or buffer layers. The primary hypotheses underpinning CSE is that the each grain surface in the polycrystalline substrate can be treated as the equivalent of a single-crystal surface in a traditional DOE experiment, therefore providing every combination of substrate orientation in a single experiment. The local structure is probed in a scanning electron microscope using electron backscatter diffraction and automated orientation assignments. The method not only allows for hundreds of experiments to be carried out in a single growth run, it has the unique advantage of not being restricted to the use of commercially available single crystals.

This talk will focus on three important observations. First, when a film is grown on a polycrystal, the growth occurs by grain-over-grain epitaxy. In other words, films can grow on microcrystalline substrates in the same way they grow on millimeter scale substrates, or every grain is in an independent observation of growth. Second, there are PEOs, regardless of the substrate surface plane, and these can be easily predicted. For many of the cases we have observed, the PEO is the one that aligns the closest packed planes and directions in the eutactic (nearly close packed) arrangement of oxide ions in different structures. Third, we have already fabricated new and novel metastable coatings using this methodology, where novel substrates provide the epitaxial template to control phase formation. Observations relative to functional ceramics, including examples from the BO_2, B_2O_3, ABO_3, A_2BO_4, and $A_2B_2O_7$ families, will be described.

8:40am **SE+NS+TF+TR-TuM3 Nanoscale Atomic Arrangement in Multicomponent Thin Films Synthesized Far-from-Equilibrium***, V. Elofsson, G.A. Almyras, B. Lü, R.D. Boyd, **Kostas Sarakinos**,* Linköping University, Sweden

Synthesis of multicomponent thin films using vapor fluxes with a modulated deposition pattern is a potential route for accessing a wide gamut of atomic arrangements and morphologies for property tuning. In the current study, we present a research concept that allows for understanding the combined effect of flux modulation, kinetics and thermodynamics on the growth of multinary thin films. This concept entails the combined use of thin film synthesis by means of multiatomic vapor fluxes modulated with sub-monolayer resolution [1], deterministic growth simulations and nanoscale microstructure probes. Using this research concept we study structure formation within the archetype immiscible Ag-Cu binary system showing that atomic arrangement and morphology at different length scales is governed by diffusion of near-surface Ag atoms to encapsulate 3D Cu islands growing on 2D Ag layers [2]. Moreover, we explore the relevance of the mechanism outlined above for morphology evolution and structure formation within the miscible Ag-Au binary system. The knowledge generated and the methodology presented herein provides the scientific foundation for tailoring atomic arrangement and physical properties in a wide range of miscible and immiscible multinary systems.

[1] "*A METHOD OF CONTROLLING IN-PLANE COMPOSITIONAL MODULATION*", Patent Pending Application, PCT/EP2014/052831.

[2] V. Elofsson, G.A. Almyras, B. Lü, R.D. Boyd, and K. Sarakinos, "*Atomic arrangement in immiscible Ag-Cu alloys synthesized far-from-equilibrium*", Acta Mater. 110, 114 (2016).

9:00am **SE+NS+TF+TR-TuM4 Is *Intrinsic* Nanocrystalline Stability Practically Achievable? Insights from Investigations with Pt-Au Alloys***, **Nicolas Argibay**, T.A. Furnish, D.P. Adams, P. Lu, M. Chandross, M.A. Rodriguez, B.L. Boyce, B.L. Clark, M.T. Dugger,* Sandia National Laboratories

The existence of intrinsic thermodynamically stable nanocrystalline binary metal alloys has been proposed recently, supported by some notable demonstrations of stability through annealing of powders. There is a great deal of interest in understanding the impact of stress on this stability. In this presentation we present results of an investigation on the stress and temperature dependent nanocrystalline stability of a noble-metal alloy (Pt-Au) in the form of sputter co-deposited thin films. In situ XRD and TEM annealing revealed an extraordinary degree of thermal stability, confirming literature predictions. Tribological experiments and molecular dynamics simulations were used to further explore the impact of stress as a destabilizing factor.

9:20am **SE+NS+TF+TR-TuM5 Improved Mechanical Properties In Tungsten-Molybdenum Nanostructured Thin Films***, **Gustavo Martinez**, C.V. Ramana,* University of Texas at El Paso

Preventing materials failure and improving the performance of materials in nuclear reactors demand novel materials to serve under extreme environment conditions. For nuclear applications, tungsten (W) has been alloyed in the past with La and Re to improve its performance and properties including low fracture and high ductile to brittle transition. In this work, molybdenum (Mo) solute atoms were added to W matrix with the intention of creating interstitial point defects in the crystals that impede dislocation motion, increasing the hardness and young modulus of the material. Nanostructured W-Mo thin films with variable Mo content were deposited by the sputter-deposition. W-Mo films were stabilized in bcc structure of W. Studies showed that as grain size formation increases the residual stress distribution will reach the maximum and stabilize after a deposition temperature of 350 °C. The residual stress still continues to follow a parabolic pattern, indicating that the stresses mainly depend on grain organization rather than atomic packing. From Nano-scratch testing, it is found that depth penetration decreases with increasing sputtering temperature. The effect of Mo on the overall mechanical properties improvement in W-Mo nanostructured thin films will be presented and discussed.

Keywords: Tungsten-Molybdenum Thin Films, Mechanical Properties, Nano-Indentation

9:40am **SE+NS+TF+TR-TuM6 Hierarchical Monolith Scaffolds for Silicon Lithium Ion Battery Electrodes*, Kevin Laughlin,*** Brigham Young University

Research has shown stable high gravimetric capacity lithium ion battery anodes can be made from silicon deposited on carbon nanotubes (CNTs). High stability operation however requires nanostructuring of the silicon to alleviate stresses caused by the large expansion of the silicon upon Li alloying. At high silicon loadings even nanoscale layers of silicon result in stresses large enough to cause mechanical damage to the electrode. Here we present work on a hierarchical approach to structuring carbon nanotube based carbon monoliths that provide for electrode stress management on multiple scales.

11:00am **SE+NS+TF+TR-TuM10 Technological Developments in Coatings for Components and Cutting Tools*, Roel Tietema,*** IHI Hauzer Techno Coating B.V., Netherlands*; D. Doerwald,* Hauzer, Netherlands*; R. Jacobs, G. Negrea, I. Kolev, J. Zhu, J. Landsbergen,* Hauzer **INVITED**

Nanostructured and amorphous coatings play an important role in today's industrial applications. This is the case both in applications for cutting tools, as well as in applications for components.

In cutting tools nanostructured coatings with high hardness, including hot hardness, and ductility have been extremely helpful to increase the productivity of the machining process. On one hand superlattice multilayers have shown here great benefits and on the other hand nanocrystallites in the material have been created to give the coating materials an inherent high hardness and ductility.

In automotive coatings these material properties were leading to technological breakthroughs as well. First coatings on the market were nanostructured WC-C:H sputtered coatings, developed by Prof. Dimiggen of Fraunhofer IST. These developments were soon followed by hybrid a-C:H coatings, combining the WC-C:H developments with a multilayered structure to achieve a gradual adaptation of the Young's modulus of the relatively soft steel as base material to the very hard a-C:H-DLC top layer. In this way it has been possible to produce coatings with a very high ductility, despite the high hardness. Hardness values as applied today on components are ranging from 2000-2500 HV for a-C:H coatings up to 4000-7000 HV for ta-C coatings.

The importance of petreatment and post treatment steps for cutting tools and components, being as important as the actual coating step, will be addressed in this talk.

The main focus in this talk will be on the equipment aspects. Several technologies for cutting tools and for components will be presented. The equipment design and even the selection of most suitable process technology is however also strongly determined by the productivity. Besides technological properties of the coating there is a focus on the cost reduction of the coating per coated part. Cost reduction is main driver in many fields, especially in the field of components. Reduction of the cost of ownership leads to a tendency to use fast processes in large systems, respectively application of in-line systems.

11:40am **SE+NS+TF+TR-TuM12 Influence of Transition Metal Dopants on Target Poisoning and Oxidation Mechanisms of Reactively Sputtered γ-Al_2O_3 Thin Films*, Helmut Riedl,*** *B. Kohlhauser,* TU Wien, Institute of Materials Science and Technology, Austria*; V. Paneta,* Uppsala University, Sweden*; C.M. Koller,* TU Wien, Institute of Materials Science and Technology, Austria*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

The outstanding oxidation resistance, thermo-mechanical stability and chemical inertness of Al_2O_3 attracts particular attention in various industrial applications. Especially, in the field of protective barrier coatings there are many research activities focusing on the synthesis of the different polymorphs α- and γ-Al_2O_3 (corundum and cubic), respectively. Apart from the fact that the deposition of the thermodynamically stable α-Al_2O_3 is strongly limited by the depositing temperature, the formation of electrically isolating Al_2O_3 at the target surface leads to massive arcing processes and destabilizes the deposition process. These problems could be overcome by varying the powering method to pulsed DC and especially RF sputtering, but at the cost of decreased deposition rates and plasma densities.

Therefore, we study in detail the influence of small amounts of transition metals such as M = Cr, Nb, Mo, and W on the process stability and coating properties of reactive DC sputter deposited $(Al_{1-x}M_x)_2O_3$ thin films. To keep the influence of the alloying elements on the outstanding properties of alumina as low as possible only targets with alloying contents of x = 2 and 5 at.% are investigated. All micro-alloyed targets allow for significantly improved process stability and massively reduced arcing processes at the target as compared to the non-alloyed Al target. The morphology of all coatings deposited is highly dense, smooth and partly columnar with cubic γ-Al_2O_3 crystalline structure. The mechanical properties of the Cr, Mo, and W containing coatings are slightly enhanced by solid solution hardening in comparison to pure Al_2O_3 obtaining e.g. hardness values of about 25 GPa. In contrast, alloying contents of about 1 at.% Nb are already degrading the mechanical properties of alumina thin films. The significantly enhanced process stability when using Cr, Mo, and W alloyed Al targets, leads to coatings with improved thin film quality. Therefore, the oxidation resistance of these films even outperform the Al_2O_3 DC sputtered film.

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+AS+MI+NS+SS-TuM

Probing Chemical Reactions at the Nanoscale

Moderator: Tae-Hwan Kim, Pohang University of Science and Technology

8:00am **SP+AS+MI+NS+SS-TuM1 *In Situ* Probing of Oxygen Vacancy Diffusion Across Multilayer Oxide Heterostructures***, J. Zhu,* University of Massachusetts - Amherst*; J.-W. Lee, H. Lee,* University of Wisconsin - Madison*; R. DeSouza,* RWTH Aachen University, Germany*; C.-B. Eom,* University of Wisconsin - Madison*; **Stephen Nonnenmann,*** University of Massachusetts - Amherst

Complex oxide heterostructures display an extraordinary array of exotic collective and correlated physical phenomena that result from exploiting the strong interplay between structural and electronic degrees of freedom. Oxygen vacancies often facilitate or govern the interfacial phenomenon observed at or across well-defined discrete interfaces, ranging from domain wall pinning within ferroic systems to electron donors in conducting systems. Realization of multifunctionality within oxide heterostructures therefore necessitates a direct, proper understanding of the interrelationship exhibited by concomitant, defect-mediated transport mechanisms with adequate spatial resolution. Here we utilize a modified, *in situ* scanning probe technique to measure the surface potential across a multi-layered yttria-stabilized zirconia / strontium titanate (YSZ/STO) heterostructured film at 500 °C. Subsequent application of a classic semiconductor dopant formalism to the work function profile derived from the surface potential enables mapping of the oxygen vacancy distribution within STO with a resolution < 100 nm. The results presented herein demonstrate the promise of *in situ* scanning surface potential microscopy (SSPM) to investigate complex oxide interfacial systems multilayers that exhibit vacancy-dominated properties, under extreme environmental perturbation, on a highly localized scale.

8:20am **SP+AS+MI+NS+SS-TuM2 Study of Surface Chemistry on Various Noble Metal Surfaces by Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy*, Naihao Chiang,*** Northwestern University*; D. Chulhai,* Pennsylvania State University*; G. Goubert, L. Madison, X. Chen, E. Pozzi, M.C. Hersam, T. Seideman,* Northwestern University*; N. Jiang,* University of Illinois at Chicago*; L. Jensen,* Pennsylvania State University*; G. Schatz, R.P. Van Duyne,* Northwestern University

During the last few years, there has been an explosion of interest and activity in the field of nanoscale vibrational spectroscopy. Tip-enhanced Raman spectroscopy (TERS) combines the ability of scanning tunneling microscopy (STM) to resolve atomic scale surface features with the single molecule chemical sensitivity of surface-enhanced Raman spectroscopy (SERS). The goal is to understand and manipulate chemistry on the nanometer length scale using the properties of the collective electronic excitations in noble metal nanostructures, known as localized surface plasmon resonance (LSPR).

Two recent advances in ultrahigh vacuum (UHV) TERS which illustrate the power of this nanoscale vibrational spectroscopy will be presented. First, our current understanding of the adsorbate-surface and adsorbate-plasmon interactions involved in the UHV-TERS of the N-N'-bis(2,6-diisopropylphenyl)-perylene-3,4,9,10-bis(dicarboximide) (PDI) on various single crystal surfaces (Ag(111), Ag(100), Cu(111), and Au(111)) which probed by a Ag tip will be discussed. This study demonstrates that TERS is a substrate general technique. Additionally, the LSPR of the Ag tip-Ag sample junction is as broad as a Ag nanoparticle dimer system. Therefore, TERS on Ag tip-Ag sample systems is also excitation general.

Second, new insights into the nature of a conformational dynamics involved at room temperature will be described. We have interrogated the conformational change of *meso*-tetrakis-(3,5-di-tertiarybutylphenyl)-porphyrin (H_2TBPP) on a Cu(111) surface between two stable conformations. At room temperature, the barrier between the porphyrin ring buckling up/down conformations of the H_2TBPP-Cu(111) system is easily overcome, and our group has achieved unprecedented sub-nm resolution by simultaneous UHV-TERS and STM analysis. This topic illuminates that TERS can unambiguously distinguish the conformational differences between neighboring molecules with single molecule resolution. Furthermore, the sub-nm resolution led to the direct observation of single molecule transitions between states from one scan to the next.

8:40am **SP+AS+MI+NS+SS-TuM3 Exploring Surface-assisted Reactions Toward Functional Carbon Nanostructures***, **Xiaohui Qiu,*** National Center for Nanoscience and Technology, China **INVITED**

Understanding the dehydrogenation and dehalogenation reactions of molecular entities on surface is essential for the controlled synthesis of carbon-based nanostructures. Delicately designed precursor molecules exploit the potential of selective activation of functional groups and templating effect of substrates and promise the fabrication of nanoscale building blocks with desired geometries. Here we employed a combination of scanning tunneling microscopy, atomic force microscopy, and theoretical calculation to elucidate self-assembling of halogen-containing molecules on metal surfaces. Metallo-supramolecular assemblies are constructed via coordination bonding between metal atoms and halogen ligands. The spontaneously formed molecular scaffolds are further explored to program the structure and chemical composition of hybrid carbon architecture. We reveal the hierarchic reaction pathway of a few aromatic derivatives in an effort toward realizing carbon-based nanostructures with controllable electronic, optical and magnetic properties.

9:20am **SP+AS+MI+NS+SS-TuM5 Landscapes in Conversion of Quasi-Free-Standing Polymer Chains to Graphene Nanoribbons***, **Chuanxu Ma,*** Oak Ridge National Laboratory*; Z. Xiao,* North Carolina State University*; L. Liang,* Oak Ridge National Laboratory*; W. Lu, J. Bernholc,* North Carolina State University*; K. Hong, B.G. Sumpter, A.-P. Li,* Oak Ridge National Laboratory

Although the cyclodehydrogenation is well known as a key step in the bottom-up preparation of graphene nanoribbons (GNRs), the mechanism is still unclear. To understand and control the cyclodehydrogenation can help to create novel intraribbon heterojunctions of GNR-based structures. Here, we demonstrate the conversion of quasi-free-standing polymer chains to GNRs induced by thermal annealing and manipulations with a scanning tunneling microscope tip. Combined with the density functional theory calculations, a domino-like fashion and the hole-involved cyclodehydrogenation are proposed for the thermal annealing and tip-induced conversion of polymer chains to GNRs, respectively. Our results provide the first direct experimental evidence that the catalytic effect of the Au substrate is critical to the thermal-induced cyclodehydrogenation in forming bottom-up GNRs. Strongly localized density of states in the short GNR segment of the polymer–GNR herterojunction is observed. The significant confinement of the charge carriers is attributed to the big bandgap difference between the two segments of the heterojunction. Our findings might pave new ways to form GNR-based intraribbon heterojunctions by controlling the cyclodehydrogenation during bottom-up preparation, and shed light to the potential applications of the polymer–GNR herterojunctions.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility, and partially supported by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the US DOE.

11:00am **SP+AS+MI+NS+SS-TuM10 Imaging Single Molecule Chemistry***, **Wilson Ho,*** University of California Irvine **INVITED**

Single molecule chemistry can now be probed at unprecedented spatial resolution with a low temperature scanning tunneling microscope (STM) in ultrahigh vacuum. Advances in this field have provided new measurements and insights into the structure and function of molecules through real space imaging and high resolution vibrational spectroscopy. The combination of the STM with optical spectroscopy and femtosecond lasers has added a new dimension of time to space and enabled the probing of single molecule dynamics in light-matter interaction with better than 0.1 nm resolution. The ability to visualize single molecule chemistry has reinvigorated the study of molecules and their transformations on solid surfaces. Much of the scientific advancement and understanding in surface chemistry have derived from the well-defined conditions that have long been championed by surface science in providing unambiguous results that are appealing to the theoretical and experimental communities. Imaging single molecule chemistry has a broader impact on general chemistry due principally to direct visualization of molecules and their inner machinery at the limit of space and time.

11:40am **SP+AS+MI+NS+SS-TuM12 Atomic Force Microscopy: A Tool for Chemical Analysis of Surfaces and Molecules on Atomic Scale***, **Pavel Jelinek,*** Institute of Physics of the AS CR, Czech Republic **INVITED**

Atomic resolution and manipulation is routinely achieved by both scanning tunneling microscopy (STM) and atomic force microscopy (AFM) nowadays. Despite of large activities in development of the scanning probe technique, still some challenges remain, namely the chemical analysis on atomic and molecular level.

First, we will present a novel method extending further the chemical analysis [1,2] by means of AFM. Namely we will discuss a new methodology to measure Pauling's electronegativity of individual atoms on surfaces using AFM. Electronegativity has been an important concept in chemistry, originally defined by Pauling as "*the power of an atom in a molecule to attract electrons to itself*". However, its experimental determination on individual surface atoms was not possible so far.

Second, we will discuss the origin of sub molecular AFM/STM resolution acquired with functionalized tips. We will show that the electrostatic force can substantially affect the sub molecular contrast. We will show, that the electrostatic potential on a single molecule can be mapped out with sub molecular resolution.

[1] Y. Sugimoto et al Nature 446, 64 (2007)

[2] M. Setvin et al ACS Nano 6, 6969 (2012)

[3] P. Hapala et al, Phys. Rev. Lett. 113, 226101 (2014)

[4] J. vad der Lit et al, Phys. Rev. Lett. 096102 (2016)

[5] P. Hapala et al. Nature comm. (accepted 2016)

Surface Science
Room 104D - Session SS1+AS+HC+NS-TuM

Surface Dynamics, Non-Adiabaticity, and Theory and Modeling of Surface and Interfacial Phenomena

Moderator: Greg Kimmel, Pacific Northwest National Laboratory

8:00am **SS1+AS+HC+NS-TuM1 Graphene-Semiconductor Catalytic Nanodiodes for Quantitative Detection of Hot Electrons Induced by a Chemical Reaction***, **Hyosun Lee**[*],* KAIST & IBS, Republic of Korea*; I. Nedrygailov,* IBS & KAIST, Republic of Korea*; Y.K. Lee, C. Lee,* KAIST & IBS, Republic of Korea*; H. Choi,* Electronics and Telecommunications Research Institute (ETRI), Republic of Korea*; J.Y. Park,* Institute for Basic Science (IBS) & Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Direct detection of hot electrons produced by exothermic reactions on catalysts is an effective strategy to quantify the non-adiabatic energy transfer during the elementary steps of the surface reactions, which provides an insight of the catalytic activity.[1,2] In particular, hot electron dynamics at the surface of metal nanoparticles (NPs) with precisely controlled shape and size is a challenge as well as a key issue in the real-world catalyst system. Herein, we show a novel scheme of graphene catalytic nanodiode composed of a Pt NPs array on graphene/TiO_2 Schottky nanodiode, which allows detection of hot electron flows induced by hydrogen oxidation on Pt NPs. By analyzing the correlation between the turnover rate (catalytic activity) and hot electron current (chemicurrent) measured on the graphene catalytic nanodiodes, we demonstrate that the catalytic nanodiodes utilizing a single graphene layer for electrical connection of Pt NPs are beneficial for the detection of hot electrons due to not only atomically thin nature of graphene but also reducing the height of the potential barrier existing at the Pt NPs/graphene interface. Thereby, the graphene catalytic nanodiodes offer an effective and easy to use approach to study mechanisms of chemical energy conversion in various heterogeneous system, even including composite catalysts with carbon-based supports.

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[*] **National Student Award Finalist**

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8:20am **SS1+AS+HC+NS-TuM2 Adlayer-Structure Dependent Ultrafast Desorption Dynamics: The Coverage Dependence of Substrate–Adsorbate Energy Transfer in Carbon Monoxide on Pd(111)***, **Sung-Young Hong,*** Brookhaven National Laboratory*; P. Xu,* Stony Brook University*; N.R. Camillone, M.G. White, N. Camillone,* Brookhaven National Laboratory

We have conducted a detailed investigation of the coverage dependence of the ultrafast photoinduced desorption of CO from the (111) surface of palladium. Because the CO binding site depends on coverage, these measurements present an opportunity to examine the dependence of the substrate–adsorbate energy transfer on adsorption site. Specifically, as the CO coverage is increased, the adsorption site population shifts from all three-fold hollow (up to 0.33 ML), to bridge and near bridge (> 0.5–0.6 ML) and finally to mixed three-fold hollow plus top site (0.6 ML to saturation at 0.75 ML). We show that between 0.24 and 0.75 ML this progression of binding site motifs is accompanied by two remarkable features in the ultrafast photoinduced desorption of the adsorbates: (i) a roughly two-orders of magnitude increase in the desorption probability, and (ii) a nonmonotonic variation in the adsorbate–substrate energy transfer rate observed in two-pulse correlation experiments, with a minimum occurring at intermediate coverages. Simulations using a phenomenological model to describe the adsorbate–substrate energy transfer in terms of frictional coupling indicate that these features are consistent with an adsorption-site dependent electron-mediated energy coupling strength, η_{el}, that decreases with binding site in the order: three-fold hollow > bridge and near bridge > top site. The weakening of η_{el} largely counterbalances the decrease in the desorption activation energy that accompanies this progression of adsorption site motifs and moderates what would otherwise be a rise of several orders of magnitude in the desorption probability. Furthermore, we show that within this framework, the observed energy transfer rate enhancement at saturation coverage is due to interadsorbate energy transfer from the copopulation of molecules bound in three-fold hollows to their top-site neighbors. This conclusion is supported by comparison to desorption of CO from mixed CO+O adlayers where the O adsorbs at three-fold hollow sites and further promotes CO desorption from top sites.

8:40am **SS1+AS+HC+NS-TuM3 Evidence for a Spin Accelerated Reaction Mechanism in the Thermal Decomposition of Alkyl Radicals on the Si(100) Surface***, A.J. Pohlman, D.S. Kaliakin, S.A. Varganov, **Sean Casey,*** University of Nevada

Density functional theory and complete active space self-consistent field calculations were used to probe the thermal decomposition of alkyl radicals on the Si(100) surface. Single dimer and single row double dimer cluster models were used to mimic the Si(100) surface in the calculations, and results indicate an interdimer β-hydrogen elimination reaction is the kinetically favored thermal decomposition pathway for adsorbed alkyl radicals. This pathway occurs via a spin crossing from the initial singlet energy surface to the triplet surface mediated by spin-orbit coupling. On the triplet surface the barrier to the elimination reaction is predicted to be about 40 kJ/mol lower than on the singlet surface. Experimental thermal desorption studies of alkyl chlorides adsorbed onto the Si(100)-(2x1) surface appear to give desorption energies for alkene products that are consistent with the barriers computed for the interdimer β-hydrogen elimination spin accelerated reaction mechanism. Experimental and computational results for the adsorption/desorption energetics of several different alkyl radicals will be discussed, along with results from partial deuteration studies of adsorption of selected haloalkanes.

9:00am **SS1+AS+HC+NS-TuM4 Hyperthermal Ion Induced Hot Carrier Excitations in a Metal Probed using Schottky Diodes***, **Dhruva Kulkarni,** D.A. Field, D.B. Cutshall, J.E. Harriss, W.R. Harrell, C.E. Sosolik,* Clemson University

We present measurements on hot carrier excitations in a metal irradiated by hyperthermal energy ions.

Specifically, alkali (Na^+/Rb^+) and noble gas(Ar^{q+}) ions were used to irradiate a Schottky diode consisting of

a thin film of Ag (~25nm) grown on an n-type Si (111) wafer. Measurements of the resultant current

through the device were performed as a function of energy, angle of incidence and velocity of the incident ions. Energy loss of the incident energetic ions inside the metal film leads to the generation of

hot carriers that travel ballistically to the Schottky interface and are detected as a kinetically-induced

current or "kinecurrent" within the device. This kinecurrent is analogous to previous measurements of

"chemicurrent" [H. Nienhaus, *Surface Science*, **45**, 1-78 (2002)], which were linked to the energy

delivered to a surface by exothermic reactions that could non-adiabatically couple to the electronic

structure and generate hot carriers.

9:20am **SS1+AS+HC+NS-TuM5 H Atom Scattering, Adsorption, and Absorption in Collisions with Metal Surfaces: the crucial role of electron-hole-pair excitation***, M. Alducin,* Donostia International Physics Center, Spain*; **Daniel Auerbach,*** Max Planck Institute for Biophysical Chemistry, Germany*; M. Blanco-Rey,* Donostia International Physics Center, Spain*; O. Bünermann, Y. Dorenkamp,* Georg-August University of Göttingen*; S.M. Janke,* Max Planck Institute for Biophysical Chemistry, Germany*; H. Jiang,* Georg-August University of Göttingen*; A. Kandratsenka,* Max Planck Institute for Biophysical Chemistry*; G-J. Kroes,* Leiden Institute of Chemistry, The Netherlands*; M. Kammler,* Max Planck Institute for Biophysical Chemistry*; M. Pavenelo,* Leiden Institute of Chemistry **INVITED**

When an H atom collides with a solid surface, it can transfer some of its kinetic energy into elementary excitations of the solid like phonons and electron-hole pairs. If the atom loses enough kinetic energy, it can become bound to the solid, either on the surface or in the bulk. For a metal, the availability of a continuum of low lying electronic excitations can lead to the breakdown of the adiabatic Born Oppenheimer approximation and the facile nonadiabatic excitation of electron-hole pairs (ehp). If the H atom loses sufficient energy, it can enter a bound state with the solid, either on the surface or in the bulk.

We have used a combined theoretical and experimental approach to elucidate the relative roles of adiabatic processes (phonon excitation) and nonadiabatic processes (ehp excitation) in collisions of H atoms with metals, insulators, and graphene. The experiments use photolysis to produce nearly mono-energetic beams of H atoms with energies of 1 - 3.3 eV and high resolution energy loss measurements using Rydberg atom tagging time-of-flight analysis. The theory involves calculations of classical trajectories for H atom collisions with two techniques. In the first, we calculate energies and forces on-the-fly during the course of a trajectory using density functional theory (DFT) and ab initio molecular dynamics (AIMD). In the second, we construct a full dimensional potential energy surface (PES) using a flexible functional form fit to DFT energies and bulk properties of the solid.

The measured mean energy loss for H atoms scattering from metals is large, approximately 30% of the initial energy and there is a tail in the energy loss distribution (ELD) extending to the full energy of incidence. The measured ELD is in reasonable agreement with theory only if nonadiabatic effects are included; adiabatic theory drastically underestimates the energy loss. Scattering from insulators (where ehp excitation can be excluded) shows much smaller energy loss and results consistent with adiabatic theory.

For metals, nonadiabatic effects not only dominate the energy loss process, but also change both the magnitude and mechanism for adsorption on metals. With nonadiabatic effects, the most probable pathway to adsorption is for H atoms to penetrate the surface, lose energy in the subsurface region, and then reemerge to adsorb on the surface.

11:00am **SS1+AS+HC+NS-TuM10 Progress in Characterizing Submonolayer Island Growth: Capture-Zone Distributions, Growth Exponents, and Transient Mobility***, **Theodore L. Einstein,*** University of Maryland, College Park*; A. Pimpinelli,* Rice University*; J.R. Morales-Cifuentes,* University of Maryland, College Park*; D.L. González,* Universidad del Valle, Colombia

Analyzing capture-zone distributions (CZD) using the generalized Wigner distribution (GWD) has proved a powerful way to gain insight into epitaxial growth, in particular to access the critical nucleus size *i*, as reviewed in [1]. The CZ of an island contains all points closer to that island than to any other and is known as a Voronoi tesselation. This approach complements measurements of the growth exponent α from the scaling (with flux *F*) of island density $N \sim F^{\alpha}$ and of the distribution of island sizes. We summarize some extensive Monte Carlo simulations and experiments, especially newer ones, on various systems to which the GWD has been applied. These experiments include atomic or organic adsorbates, sometimes with impurities, and colloidal nano-particles. In some cases, most notably parahexaphenyl (6P) on sputter-modified mica [2], the value *i* extracted from CZD) differs from the [larger] values of *i* deduced from $N \sim F^{\alpha}$. Furthermore, while the scaling was good, the values of α differed considerably at small and large *F*, which was attributed to DLA and ALA dynamics [2]. To reconcile the CZD and scaling measurements, we took into account long-known transient mobility (hot precursors) using a rate-equation approach [3]. We also applied this method to data for pentacene (5A) on the same substrate. In applications of the GWD to social phenomena, notably the areas of secondary administrative units (e.g. counties or French *arrondissements*) [4], lognormal distributions (typically due to multiplicative noise) sometimes arise instead of GWD or gamma distributions; we show this also occurs for some pore-size distributions [5].

*Work at UMD supported by NSF CHE 13-05892

[1] T.L. Einstein, A. Pimpinelli, D.L. González, J. Cryst. Growth **401** (2014) 627; TLE, AP, DLG, J.R. Morales-Cifuentes, J. Physics: Conf. Ser. J. Phys.: Conf. Series **640** (2015) 012024

[2] T. Potocar et al., Phys. Rev. B **83** (2011) 075423 & later work by A. Winkler et al., see [1].

[3] JRM-C, TLE, and AP, Phys. Rev. Lett. **113** (2014) 246101.

[4] R. Sathiyanarayanan, Ph.D. thesis, UMD, 2009; R. Sathiyanarayanan and TLE, preprint.

[5] A.S. DeLoach, B.R. Conrad, TLE, and D.B. Dougherty, submitted.

11:20am **SS1+AS+HC+NS-TuM11 Hindered Translator and Hindered Rotor Models for Calculating the Entropy of Adsorbed Species***, Lynza H. Sprowl*[*]*,* Oregon State University*; C.T. Campbell,* University of Washington*; L. Arnadottir,* Oregon State University

Adsorbed species on surfaces are important for a range of applications including heterogeneous catalysis, corrosion processes, and film growth. The need for a fast and accurate way to predict equilibrium constants and rate constants for surface reactions is important for understanding reaction kinetics and for building microkinetic models of catalytic reactions. Here a method to calculate partition functions and entropy of adsorbed species is presented. Instead of using the vibrational frequencies estimated from density functional theory and the harmonic oscillator approximation to calculate the partition function for all modes of motion, we use hindered translator and hindered rotor models for the three modes of motion parallel to the surface, two translations and one rotation. The energy barriers for translation and rotation were determined using density functional theory and the nudged elastic band method for four different adsorbates on a platinum surface: methanol, propane, ethane, and methane. The hindered translator model was used to calculate the entropy contributions from the two translations parallel to the surface and the hindered rotor model was used to calculate the entropy contribution from the rotation about the axis perpendicular to the surface. When combined with the vibrational entropy contributions and the concentration related entropy contributions, this gives the total entropy of the adsorbate on the surface. The total adsorbate entropies were found to agree well with experimental results, with an average absolute value of the error of only 1.1R or 8% for the four adsorbates. This new model should be useful to future researchers in surface chemistry, since it provides more accurate predictions of standard-state entropies and partition functions, and thus more accurate equilibrium constants and rate constants for surface reactions than provided by the standard harmonic oscillator approximation.

11:40am **SS1+AS+HC+NS-TuM12 Stabilization of *X*-Au-*X* Complexes on the Au(111) Surface: A Theoretical Investigation and Comparison of *X*=Sulfur, Chlorine, Methythiolate, and Silylthiolate***, J. Lee, J.S. Boschen, T.L. Windus, P.A. Thiel, J.W. Evans,* ***Da-Jiang Liu,*** Iowa State University

The involvement of Au atoms in the self-assembled methylthiolate (CH_3S) monolayers on Au(111) has been demonstrated experimentally [1], while for S and Cl, chain-like structures with no direct Au involvement were found [2,3]. We find that for S on various coinage metal surfaces, the linear S-M-S complexes (M=Cu, Ag, Au) are prevalent. A systematical theoretical study of the X-Au-X complexes, with X=S, Cl, CH_3S, and SiH_3S, has been performed using DFT and other quantum chemistry methods. Assuming equilibration of the metal substrate, the chemical potential of X are calculated and used to predict the stability of various Au-X complexes. We find good agreement between DFT and available experimental findings. Furthermore, the van del Waals interaction is shown to play a crucial role in the self-assembly of CH_3S observed in experiments [1].

[1] P. Maksymovych, O. Voznyy, D. B. Dougherty, D. C. Sorescu, J. T. Yates Jr., *Prog. Surf. Sci.***85**, 206 (2010).

[2] V. V. Zheltov *et al.Phys. Rev. B,* **89**, 195425 (2014).

[3] H. Walen, *J. Chem. Phys.***143**, 014704 (2015).

12:00pm **SS1+AS+HC+NS-TuM13 Contrasting Phonon Confinement and Interface Stability at Fe-Ag and Fe-Cr Multilayers: Insights from *Ab Initio* Calculations***, S. Hong,* ***Talat Rahman,*** University of Central Florida

We have performed density functional theory based calculations to compare the characteristics of the interface of Fe-Ag and Fe-Cr multilayers. A perfect interface lattice match between the Fe and Ag layers was obtained by rotating fcc Ag(100) layers by 45° on bcc Fe(100). On the other hand, the Fe-Cr interface could be modeled by epitaxial layers of bcc Fe(100) and Cr(100). In Fe-Ag multilayers, we find the signature peak of Fe bulk phonons (35 meV) to be completely diminished, while the low energy peaks are remarkably enhanced, in agreement with experiment [1]. In contrast, the phonon density of state in the Fe-Cr multilayers do not show any salient feature except a slight decrease in the 35 meV peak for the Fe layer at the interface, as compared to that of the middle Fe layer, again in agreement with experiment [2]. The magnetic moment of the interfacial Fe atoms is larger than that of Fe atoms in other layers, as a result of charge transfer from Fe to Ag at the interface. As compared to the middle layers, more spin-up and less spin-down states are occupied at the interface in such a way that Fe donates a large number of spin-down electrons to Ag but receives only a few spin-up electrons from the latter because of the almost fully occupied Ag d-band. This leads to rather unstable Fe-Ag interface. On the contrary, at the Fe-Cr interface, Cr can easily give and take electrons leading to smooth interfacial coupling and stable environment.

[1] B. Roldan Cuenya et al., to be published

[2] Roldan et al, Phys. Rev. B 77, 165410 (2008).

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Surface Science
Room 104E - Session SS2+AS+HC+NS-TuM

Nanostructures: Growth, Reactivity, and Catalysis

Moderator: Bruce Koel, Princeton University

8:00am **SS2+AS+HC+NS-TuM1 Use of Size Correlations to Probe Reaction Mechanisms on Size-selected Model Catalysts***,* ***Scott Anderson,*** University of Utah **INVITED**

The ability to prepare model catalysts by deposition of mass-selected metal clusters allows the size and density of catalytic sites to be varied independently and precisely, providing a new tool for mechanistic studies. In addition, preparation of truly monodisperse samples alters the kinetics for Ostwald ripening, thus changing the cluster stability under thermal/reactive conditions. This talk will focus on use of size-dependent correlations between catalytic activity and physical properties such as cluster morphology and electronic properties, to probe the factors that control catalysis and electrocatalysis by supported Pt clusters in the <25 atom size range. The stability of the clusters, and how this varies with size under heating, adsorbate exposure, and potential cycling will also be discussed.

8:40am **SS2+AS+HC+NS-TuM3 Role of the Strong Metal Support Interaction on the Catalytic Activity of Platinum Deposited on TiO_2 Supports***,* ***R.Paul Hansen****, R.S. Phillips,* University at Albany-SUNY*; E.T. Eisenbraun, C.A. Ventrice, Jr.,* SUNY Polytechnic Institute

Several roadblocks prevent the large-scale commercialization of hydrogen fuel cells, including the stability of catalysts and their substrates and the high cost of the Pt involved in the oxygen reduction reaction (ORR). The former of these problems can be solved by replacing the traditional carbon support with a conductive metal oxide such as reduced TiO_2, which will not easily corrode and should result in longer lasting fuel cells. The Pt is necessary in the cathode of the fuel cell to overcome the slow kinetics of the ORR. In this study, Pt was deposited either by atomic layer deposition (ALD) or physical vapor deposition (PVD). The typical size of the Pt islands that were grown using these deposition techniques was 5-8 nm. One factor that can inhibit the catalytic activity of a metal catalyst on a metal oxide is the strong metal support interaction (SMSI). This is where a metal on a

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[*] **Morton S. Traum Award Finalist**

reducible metal oxide can be encapsulated by a layer of the metal oxide support material at elevated temperatures. The processing of materials through atomic layer deposition can exceed this temperature. The TiO_2 substrates used in this study were either grown by ALD, which results in a polycrystalline anatase film, or were single-crystal rutile TiO_2(110) samples prepared in ultra-high vacuum (UHV). The Pt/TiO_2 samples were tested electrochemically using cyclic voltammetry (CV) to determine the level of catalytic activity. To determine the effect of the SMSI interaction on the catalytic activity of the PVD grown samples, CV was performed on samples that were annealed in high vacuum after Pt deposition. Additional characterization was performed with scanning electron microscopy (SEM), Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), and four point probe analysis.

9:00am **SS2+AS+HC+NS-TuM4 Adsorption and Adhesion Energies of Au, Cu, and Ag Nanoparticles on CeO_2(111), MgO(100) and Other Oxide Surfaces***, **Charles T. Campbell**, S.L. Hemmingson, G.M. Feeley,* University of Washington

Heterogeneous catalysts consisting of late transition metal nanoparticles dispersed across oxide supports are ubiquitous in industrial chemistry and energy technology. We have used an ultrahigh vacuum single-crystal adsorption calorimeter to study the adsorption energies of Au, Cu and Ag gas atoms as they adsorb and grow nanoparticles on single-crystal oxide surfaces as models for real catalyst systems. These measurements allow us to determine the chemical potential of metal atoms in supported nanoparticles as a function of particle size and the support upon which they sit. The support effect manifests itself very directly on metal chemical potential via the metal / oxide adhesion energy. Our earlier studies have shown that metal chemical potential can be related to the metal nanoparticle's catalytic activity and deactivation rates through sintering, so there is a great motivation to understand how it varies with particle size and support, and how metal / oxide adhesion energies vary with the nature of the metal and the oxide support material. Through these measurements on a variety of systems, we have discovered systematic trends in these that allow predictions of adhesion energies for system which have not been measured. We have also measured the adsorption energy of isolated Cu atoms on CeO_2(111) terrace sites, which is possible at 100 K. This is the first measurement of the adsorption energy of any late transition metal atom on any oxide surface of the type used as catalyst supports in a situation where the atom sits on the surface as an isolated monomer (as opposed to sitting within a small metal cluster).

9:20am **SS2+AS+HC+NS-TuM5 Effects of Nanoparticles on Surface Resistivity: Ni on Au(111)***, **Joshua Cohen**, R.G. Tobin,* Tufts University

The change in surface resistivity due to the formation of nickel nanoparticles on gold(111) was studied by measuring the resistance of a thin film of Au as a function of Ni coverage, θ. After annealing, Au(111) configures into the herringbone reconstruction and provides a template for the periodic nucleation and growth of Ni nanoparticles. The Ni islands grow radially until θ ~ 0.3 ML, after which, subsequent Ni atoms contribute almost exclusively to a second layer [1].

Surface resistivity arises primarily from the scattering of the substrate's conduction electrons by foreign atoms or defects, and studies of the dependence of surface resistivity on coverage yield insights into growth dynamics, interadsorbate interactions, and interactions between the adsorbed atoms and conduction electrons. For randomly distributed non-interacting scatterers the resistivity change is linear in coverage. Since Ni atoms on Au(111) grow in tight ordered nanoclusters, a nonlinear dependence might be anticipated. Our results, however, show a linear dependence on coverage for Ni atoms in the first layer, as if they were independent point scatterers. At coverages above θ ~ 0.3 ML, there is no further change in resistivity, which we attribute to Ni atoms forming a second layer and making no significant contribution to the surface resistivity.

The samples were 150 nm thick epitaxial Au(111) films on mica prepared by sputtering and annealing in ultrahigh vacuum. The resistance of the film was measured as Ni was thermally evaporated on the surface. Ni coverage was determined using Auger electron spectroscopy (AES), corrected for the inelastic mean free path of the electrons.

The resistance and AES data were analyzed in terms of a growth model that allowed for variation in the coverage at which a second layer begins, the relative probabilities of first- and second-layer growth after that point, and the relative contributions of first- and second-layer Ni atoms to the surface resistivity. The results are consistent with the growth model observed with STM [1], and serve as an indirect probe of the growth kinetics of this interesting system, as well as determining for the first time the contributions of the Ni islands to the surface resistivity of the Au film.

1. Chambliss, D.D., R.J. Wilson, and S. Chiang, *Ordered Nucleation of Ni and Au Islands on Au (111) Studied By Scanning Tunneling Microscopy.* Journal of Vacuum Science & Technology B, 1991. **9**(2): p. 933-937.

9:40am **SS2+AS+HC+NS-TuM6 Three-Dimensional Control of Nanoparticle Layer Deposition by "Click Chemistry"***, **Mackenzie Williams**, A.V. Teplyakov,* University of Delaware

Our previous studies have focused on the formation of highly-controlled nanoparticle mono- and multilayers of silica and magnetic iron oxide nanoparticles through the copper(I) catalyzed azide-alkyne cycloaddition reaction. By using the specific functionalization scheme in that method, we achieved very high surface coverage and the formation of exactly one nanoparticle layer per deposition cycle, as could be observed with scanning electron microscopy (SEM) and atomic force microscopy (AFM). Formation of the triazole ring from the "click" reaction was confirmed by infrared spectroscopy and X-ray photoelectron spectroscopy (XPS), while density functional theory calculations were used to confirm spectroscopic results and investigate the reasons behind the high coverage. In the current work, a higher level of control over the nanoparticle layers is being sought. Conformal filling of the layer over high aspect-ratio features is being studied and would allow this method to be used as a viable alternative to traditional layer-by-layer techniques. Additionally, control of the spatial resolution of the nanoparticle layers upon the substrate via alternative methods of catalysis initiation is currently being investigated.

11:00am **SS2+AS+HC+NS-TuM10 Spherical Metallic Nanostructures Based on Fullerene Scaffolds with Tunable Bandgap, A Scanning Tunneling Microscopy/Spectroscopy (STM/STS) Study***, **Ehsan Monazami**,* University of Virginia*; J.B. McClimon,* University of Pennsylvania*; J.M. Rondinelli,* Northwestern University*; P. Reinke,* University of Virginia

The current literature on annealing of fullerene molecules on tungsten surfaces indicates a complete dissociation of the fullerene cage and the formation of a carbide phase. However, our measurements with high resolution STM and STS illustrate a complex intermediate reaction sequence. Upon annealing of C_{60} adsorbed on a tungsten thin film grown on MgO (001) in UHV, C_{60} does not dissociate and the spherical C_{60} shape is retained up to a temperature of at least 973 K. During the annealing, the band gap of the molecular layer decreases gradually from the wide bandgap of fullerene to a fully metallic electronic state. This transition occurs in a narrow temperature range between 600 K and 700 K. After this transition, the near-spherical particles are termed "nanospheres." This progression was observed with a series of high resolution scanning tunneling spectra and detailed spectral mapping. The bandgap variation presents an approach to achieve the formation of densely packed nanoclusters (nanospheres) with variable bandgap, which are stable at elevated temperatures. Experimental results for sub-ML fullerene coverage on tungsten show that the fullerene molecules are mobile at room temperature, but they become stationary after annealing above 500 K. This immobilization of molecules indicates a strong interaction and likely a covalent bond between the molecule and substrate that is triggered by annealing.

The progression to metallic nanospheres is hypothesized to occur either by gradual substitution of W-atoms or by wetting the molecule with W-atoms and thus formation of W-C bonds in a solid state reaction. These models were tested using density functional theory (DFT) calculations. Two simulation strategies were used. In the first, C_{60} carbon atoms were substituted by W in the molecule and the resulting electronic properties and bandgap were calculated. In the second approach, different adsorption geometries of a C_{60} molecule on the tungsten (110) surface were considered. The variation of the band gap due to different C_{60} orientations relative to the tungsten substrate and various types of hetero-fullerenes will be discussed.

11:20am **SS2+AS+HC+NS-TuM11 Facile Synthesis of Gold Nanoworms and their Excellent Surface Enhanced Raman Scattering (SERS) and Catalytic Properties***, **Waqqar Ahmed**,* COMSATS Institute of Information Technology, Pakistan*; J.M. van Ruitenbeek,* Leiden University, Netherlands

Gold nanoparticles exhibit interesting optical properties because of the surface plasmon resonance. The shape and size of gold nanoparticles can markedly influence their optical properties. A spherical nanoparticle has a single palsmon peak, while rod-shaped nanoparticles have two plasmon peaks because of their shape anisotropy. Furthermore, slight deviations from the rod morphology can markedly influence the optical properties. For example, worm-shaped gold nanoparticles can have more than two plasmon peaks. Moreover, nanoworms can display very high local field enhancements upon plasmon excitation owing to their special shape and surface roughness.

We have devised a simple, seedless, high-yield protocol for the synthesis of gold nanoworms [1]. Nanoworms were grown simply by reducing $HAuCl_4$ with ascorbic acid in a high pH reaction medium in the presence of growth directional agents. In contrast to the seed-mediated growth of gold nanorods where a seed particle grows into a nanorod, nanoworms grew by oriental attachment of nanoparticles. By varying different reaction parameters we were able to control the length of NWs from a few nanometers to micrometers. Furthermore, the aspect ratio can also be tuned over a wide range.

Owing to their special morphology, gold nanoworms are much superior than the conventional nanorods for numerous applications. For instance, we have seen that they show markedly superior SERS and catalytic properties compared to their nanorod counterparts. This is due to their high-energy rough surface and twisted shape, which not only provides an ideal platform for catalytic activities but also generates local hot-spots upon plasmon excitation. Our study shows that both catalytic and SERS properties of gold nanoworms are strongly dependent on their length.

[1] W. Ahmed, C. Glass, and J.M. van Ruitenbeek, *Nanoscale*, 6, 13222, (2014)

11:40am **SS2+AS+HC+NS-TuM12 Surface Hydrogen Enables Sub-Eutectic Vapor-Liquid-Solid Semiconductor Nanowire Growth***, S.V. Sivaram, H. Hui,* Georgia Institute of Technology*; M. de la Mata, J. Arbiol,* Catalan Institute of Nanoscience and Nanotechnology, Spain*; **Michael Filler**,* Georgia Institute of Technology

Semiconductor nanowires are emerging as indispensable nanoscale building blocks for next generation energy conversion, electronic, and photonic devices. The bottom-up vapor-liquid-solid (VLS) mechanism – whereby a liquid eutectic "catalyst" droplet collects precursor molecules (or atoms) from the vapor and directs crystallization of the solid nanowire – is a nearly ubiquitous method for nanowire synthesis. While VLS growth below the bulk metal-semiconductor eutectic temperature has long been known, the fundamental processes that govern this behavior are poorly understood. Here, we show that hydrogen atoms adsorbed on the Ge nanowire sidewall enable AuGe catalyst supercooling and control Au transport. Our experimental approach combines in situ infrared spectroscopy to directly and quantitatively determine hydrogen atom coverage with a "regrowth" step that allows catalyst phase to be determined with ex situ electron microscopy. Maintenance of a supercooled catalyst with only hydrogen radical delivery confirms the centrality of sidewall chemistry. This work underscores the importance of the nanowire sidewall and its chemistry on catalyst state, identifies new methods to regulate catalyst composition, and provides synthetic strategies for sub-eutectic growth in other nanowire systems. We leverage this newfound understanding of nanowire growth chemistry to fabricate large-area arrays of high quality axial Si/Ge heterostructures for the first time.

12:00pm **SS2+AS+HC+NS-TuM13 Ultrafine Sodium Titanate Nanowires with Extraordinary Strontium Ion-Exchange Property***, **Koji Nakayama**,* Tohoku University, Japan

The removal of radioactive substances released to the environment by a nuclear accident is an emergent issue. The water treatment based on the ion exchange process is the most effective decontamination technology, and inorganic ion exchangers, titanates, have been used for the capture of Sr ions owing to their high radiation stability and extreme ion selectivity. However, the reported adsorption capacity and ion exchange efficiency are not satisfied. We show the formation of sodium titanate nanowires with a few nanometers in diameter, having a mogul-shaped surface, forming hierarchically a three-dimensional network skeletal structure, and exhibiting remarkable Sr ion exchange properties [1]. They are produced by unique and simple non-thermal processes through the simultaneous selective leaching of Al and oxidation of Ti in a rapidly solidified Ti-Al alloy ribbon in NaOH solution. The experimental saturated adsorption capacity is tripledand the uptake rate is at least three hundredtimes faster than these of the previous reports. The results demonstrate that the newly created nanowires exhibit a potential application in the decontamination and disposal of nuclear waste.

[1] Y. Ishikawa, S. Tsukimoto, K. S. Nakayama, and N. Asao, Nano Lett. **15**, 2980-2984 (2015).

Nanometer-scale Science and Technology
Room 101D - Session NS-TuA

Nanoscale Imaging and Characterization

Moderators: Mehmet Z. Baykara, Bilkent University, Turkey, Sidney Cohen, Weizmann Institute of Science, Israel, Rainer Timm, Lund University, Sweden

2:20pm **NS-TuA1 Frontiers of Force Microscopy in Nanoscience and Nanotechnology***, Ricardo Garcia***[*]*,* CSIC, Spain **INVITED**

This contribution aims to provide an overview of some recent developments as well as some challenges faced by force microscopy in nanoscience and nanotechnology. Specifically, the focus will be oriented to applications to study materials in air and liquid environments. The presentation is divided in three sections. The first section provides an introduction to the physics and key instrumental aspects of advanced force microscopes. The second section describes some applications to generate high resolution (atomic, molecular or nanoscale) maps of soft matter interfaces (polymer and biomolecules). Those maps combined topography and nanomechanical properties. A method to generate three dimensional and atomically-resolved mapsof solid-liquid interfaces will be presented. The third section, illustrates how the nanoscale control afforded by scanning probe microscopes has enabled the development of scanning probe-based patterning methods.

References:

E.T. Herruzo, A.P. Perrino and R. Garcia, *Nature Commun.* **5**, 3126 (2014)

R. Garcia and E. T. Herruzo, *Nature Nanotechnol*. **7**, 217-226 (2012).

R.Garcia, A.W. Knoll, E. Riedo, Nature Nanotechnology 9, 577-587 (2014)

3:00pm **NS-TuA3 Elemental and Magnetic Fingerprinting of Materials at the Nanoscale by Synchrotron X-ray Scanning Tunneling Microscopy***, **Volker Rose**,* Argonne National Laboratory **INVITED**

Recently, substantial progress was made on Argonne's Synchrotron X-ray Scanning Tunneling Microscopy (SX-STM) project. In particular, we demonstrated the power of SX-STM for elemental characterization and topography of individual Ni nano-islands on Cu(111) at 2 nm lateral resolution with single atom height sensitivity [1], tested a new probe tip concept based on carbon nanotubes [2], and demonstrated soft x-ray imaging of nanoscale magnetic domains of an iron thin-film by x-ray magnetic circular dichroism (XMCD) contrast [3]. Further substantial advances are expected using the new low temperature (LT) SX-STM system, which has been developed over the last 3 years and is currently under commissioning.

To fully exploit the special capabilities of the new LT x-ray microscope, XTIP, a dedicated beamline for SX-STM is under construction at the Advanced Photon Source. 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 400-1600 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.

This work was funded by the Office of Science Early Career Research Program through the Division of Scientific User Facilities, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant SC70705. Use of the Advanced Photon Source and the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract DE-AC02-06CH11357.

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4:20pm **NS-TuA7 Quantitative Nanomechanics of Soft Materials with AFM: Old and New Methods***, **Igor Sokolov**,* Tufts University **INVITED**

Quantitative study of mechanical properties of soft materials at the nanoscale, such as the Young's modulus, storage and loss moduli, etc. becomes important in the study of nanocomposites materials, polymers, biological tissues, and cells. Nanoindentation techniques are not capable to attain nanoscale resolution for such materials; whereas atomic force microscopy (AFM) techniques do allow quantitative measurements of soft materials at the nanoscale. Although being attractive and simple, direct extrapolation of macroscopic models to the nanoscale is frequently incorrect. In this talk I will describe the AFM methods suitable for measurements of both static and dynamic moduli of soft materials. I will discuss both well-known modes of operation, such as the force-volume and nonresonant modes (e.g, PeakForce QNM) as well as new modes we recently developed (FT-NanoDMA or imaging nanoindentation and Ringing modes). Comparison of all these modes (including the nanoindentation technique) will be given. Studies of elastic moduli of polymers and cells will be exampled.

5:00pm **NS-TuA9 AFM Based Nanoscale Structure-Property Characterization of Nanoporous Organo-Silicates***, **Qichi Hu**, K. Kjoller,* Anasys Instruments*; G. Stan,* NIST/Material Measurement Laboratory*; S.W. King,* Intel Corporation

The continued advancement of nanostructured materials and exploitation of nanoscale size effects will ultimately require understanding material structure-property relationships at nanometer length scales. Despite a plethora of metrologies capable of characterizing thermal, mechanical, electrical, and optical properties at the nanoscale, combined nanoscale chemical structure-property characterization has only recently become possible with the development of atomic force microscope based IR spectroscopy (ARM-IR). In this regard, we have combined AFM-IR chemical structure and contact resonance AFM (CR-AFM) mechanical property measurements in the investigation of 20 – 500 nm wide fin structures fabricated in a nanoporous organosilicate material. By combining these techniques, we have observed nanoscale modifications in the chemical structure and mechanical properties of the nanoporous fins that correlate with one another, the feature size, and fabrication process. This demonstration should lead the way for nanoscale chemical structure-property characterization of other materials systems where such relationships are deemed essential.

5:40pm **NS-TuA11 Scanning Microwave Microscopy Imaging in Liquids through Ultra-Thin Membranes***, **Alexander Tselev**,* Oak Ridge National Laboratory*; J. Velmurugan,* National Institute of Standards and Technology (NIST), University of Maryland (UMD)*; A. Kolmakov,* NIST/CNST

The growing need in operando imaging of submicron objects immersed in liquids relevant to biomedical or energy applications resulted in a significant effort invested into in situ TEM and SEM. In these techniques, objects of interest are incased inside a chamber equipped with ultra-thin electron-transparent but molecularly-impermeable membrane(s) enabling electron or X-ray probing of the chamber interior. However, local radiation damage and radiolysis induced by high-energy electron or X-ray beams often lead to sample deterioration or adversely affect nanoscale chemical processes. Here, we report a novel concept of in situ near-field scanning microwave microscopy of reactive and biological samples in liquids. Microwaves of a few gigahertz frequencies offer photons of energies ~10 μeV, which ensures non-destructive imaging free from radiolysis and radiation damage associated with use of high-energy electron and X-ray beams. In our approach, the nanoscale objects of interest are separated from ambient by a-few-nanometer-thick dielectric membranes transparent for microwave near-fields. The imaging is performed with microwave near-fields formed at a scanning probe of an atomic force microscope in contact with the ultra-thin membrane. In the proposed approach, a liquid and/or a reactive environment of the object of interest are completely isolated from the probe and the rest of the microscope. We performed a comparative, side-by-side study of imaging capabilities of microwave microscopy and SEM in liquids using the same set of biological and inorganic samples. Sensitivity, spatial resolution, probing depth, and probe-induced effects were evaluated and compared. In particular, we demonstrate in situ real-time imaging of growth of metal dendrites at electrode-liquid electrolyte interface during an electrochemical reaction. The demonstrated spatial resolution of the near-field microwave imaging was ca. 250 nm. The resolution can be improved by optimization of probe and membrane geometry, as well as of the membrane material. Under optimal conditions, a resolution of ca. 50 nm can be achieved for metallic objects with commercially available probes. Such resolution is comparable to that demonstrated by in situ SEM in liquids.

The research was supported in part through Scientific User Facilities Division (ORNL), BES, US DOE, US Civilian Research and Development Foundation, and NIST-CNST/UMD-IREAP Cooperative Agreement.

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[*] **NSTD Recognition Award**

6:00pm **NS-TuA12 SnS Nanoplates***, **Nancy Trejo**, A. Hunter, C. Wrasman, S. Ganguly,* University of Minnesota*; J. Dwyer,* St. Catherine University*; E.S. Aydil,* University of Minnesota

Two dimensional (2D) layered materials such as graphene, metal dichalcogenides and black phosphorus are of increasing interest because of their unique electronic properties. Tin monosulfide (SnS) has the same crystal structure as black phosphorus. SnS may have potential applications in photovoltaics, photocatalysis, thermoelectrics, and batteries. We have synthesized 3-60 nm thick and up to approximately 10 micron wide SnS nanoplates via decomposition of tin(IV) diethyldithiocarbamate upon hot injection into oleylamine (300-340 °C). The reaction products are characterized using a combination of electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction (XRD), atomic force microscopy and Raman spectroscopy. All characterization techniques confirm that the final reaction product is orthorhombic SnS (*e.g.,* after 60 minutes at 340 °C). At low temperatures (300 °C) and short synthesis times (1 minute) we also observe the presence of SnS_2 which suggests that decomposition of tin(IV) diethyldithiocarbamate first produces SnS_2. Tin disulfide is subsequently reduced, likely by oleylamine, to SnS. Orthorhombic SnS grows preferentially as plates, with [010] direction normal to the plate surfaces. In fact, when plates are large (>1 micron) XRD from films cast from colloidal dispersions in toluene show predominantly the (040) diffraction. The SnS nanoplate sizes could be altered by controlling the temperature, oleylamine concentration, and reaction time. Nanoplate dispersions in toluene exhibit an optical absorption feature in the visible range of the electromagnetic spectrum, which we surmise to be of plasmonic origin. The nanoplate dispersions in toluene also respond to electric fields.

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+AS+MI+NS+SS-TuA

Probing Spin-Dependent Phenomena

Moderators: Phillip First, Georgia Institute of Technology, Shivani Rajput, Oak Ridge National Laboratory

2:20pm **SP+AS+MI+NS+SS-TuA1 Spin Sensing and Magnetic Design at the Single Atom Level***, **Alexander Khajetoorians**,* Radboud University, The Netherlands **INVITED**

Unraveling many of the current dilemmas in nanoscience hinges on the advancement of techniques which can probe the spin degrees of freedom with high spatial, energy, and ultimately high temporal resolution. With the development of sub-Kelvin high-magnetic field STM, two complementary methods, namely spin-polarized scanning tunneling spectroscopy (SP-STS) [1] and inelastic STS (ISTS) [2-3], can address single spins at the atomic scale with unprecedented precession. While SP-STS reads out the projection of the impurity magnetization, ISTS detects the excitations of this magnetization as a function of an external magnetic field. They are thus the analogs of magnetometry and spin resonance measurements pushed to the single atom limit. We have recently demonstrated that it is possible to reliably combine single atom magnetometry with an atom-by-atom bottom-up fabrication to realize complex atomic-scale magnets with tailored properties [4-6] on metallic surfaces [1,7]. I will discuss the current state of the art of this growing field as it pertains to single spin information storage, and how the functionality of coupled magnetic adatoms can be tailored on surfaces by substrate mediated interactions. I will discuss our recent efforts toward realizing tailored chiral magnets [8] and present an outlook on future perspectives toward probing quantum matter at ultra-low temperatures.

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3:00pm **SP+AS+MI+NS+SS-TuA3 Electron Spin Resonance of Single Atom and Engineered Spin Structures***, **Taeyoung Choi**, W. Paul, C.P. Lutz, A.J. Heinrich,* IBM Almaden Research Center **INVITED**

The scanning tunneling microscope (STM) has been one of the most versatile tools for atomic-scale imaging, manipulation, and tunneling spectroscopy. Inelastic spin excitation and spin-polarized tunneling have been employed to study spin physics of individual atoms and engineered structures, demonstrating nanoscale memory bits [1] and logic gates [2]. However, the energy resolution of the STM is mainly limited by a temperature of a system surrounding the atomic spins (>100 μeV).

Here, we successfully combine electron spin resonance (ESR) and STM, coherently driving spin resonance of individual iron (Fe) atoms on surfaces (MgO/Ag(100)) [3]. A radio-frequency electric field (~20 GHz), applied at the tunneling junction, modulates the spin state of the Fe atoms. The spin resonance signal is detected by a spin-polarized tunneling current. The ESR signals from individual Fe atoms differ by a few GHz (~10μeV) while the ESR linewidth is in the range of only a few MHz (~10neV). Such a high energy resolution enables us to distinguish spin distributions down to single-atom level and to investigate weak magnetic interactions.

When we placed two Fe atoms close together with controlled atom manipulation, we found that the ESR signal from each Fe atom splits into doublet, of which separation depends on the distance between two atoms. Our measurements show $r^{-3.024\pm0.026}$ distance-dependent splitting, in excellent agreement of magnetic dipole-dipole interaction. We utilized this precisely measured dipolar interaction to determine the location and magnetic moment of unknown spin centers with sub-angstrom and one hundredth of Bohr magneton precision [4].

Coherent quantum control of individual atoms on surfaces combined with atom manipulation may promise the STM as a new and unique platform for a quantum sensor, investigating spin-labeled molecular structures and a quantum information processor, modeling quantum magnetism.

We gratefully acknowledge financial support from the IBM and Office of Naval Research.

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4:40pm **SP+AS+MI+NS+SS-TuA8 Controlling Kondo Effect of Magnetic Molecules on Au(111) by Small Molecule Binding***, **MinHui Chang**, S.J. Kahng,* Korea University, Republic of Korea*; Y.H. Chang,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea*; H.W. Kim, S.H. Lee,* Korea University, Republic of Korea*; Y.-H. Kim,* KAIST, Republic of Korea

Controlling and sensing spin states of magnetic molecules at the single molecule level is essential for spintronic molecular device applications. Here, we demonstrate that spin interactions of Co-porphyrin on Au(111) can be controlled by adsorption and desorption of small molecules, and be sensed using scanning tunneling microscopy and spectroscopy (STM and STS). Bare Co-porphyrin showed a clear zero-bias peak, a signature of Kondo effect in STS, whereas Co-porphyrin adsorbed small molecules showed modified zero-bias peaks, with reduced full width half maximum or Kondo temperature. Our density functional theory calculation results explain it with spatial redistribution of unpaired spins in d_z2 Orbitals. Our study opens up ways to tune molecular spin interactions by means of chemical binding.

5:00pm **SP+AS+MI+NS+SS-TuA9 Spin-polarized Scanning Tunneling Microscopy on Surfaces Prepared by Molecular Beam Epitaxy***, **Arthur Smith**,* Ohio University Nanoscale and Quantum Phenomena Institute **INVITED**

Spin-polarized scanning tunneling microscopy (SP-STM) has proven to be a powerful *in-situ* technique for obtaining detailed information about spin structures at surfaces down to atomic scale.[1] It has been applied extensively to investigate pristine ferromagnetic and antiferromagnetic (aFM) transition metal surfaces, with many great results in the case of model systems such as nano-sized magnetic islands and single magnetic monolayers.[2] This has led to fascinating discoveries of nanoscale magnetic domains, domain walls, spin spirals, spin skyrmions, and much more.[3,4] Although not simple in practice, SP-STM can in principle also yield unprecedented spin characterization on a broad spectrum of material surfaces, including practical, real world systems. For example, it could be applied to investigate surfaces of intermetallic compounds, superconductors, complex magnetic oxides, and magnetic semiconductors.

We are applying SP-STM to study various magnetic systems grown *in-situ* by molecular beam epitaxy, including transition metal nitrides,[5] magnetic-doped nitride semiconductors, and several bi-metallic magnetic systems. I will present our recent work using STM and SP-STM, beginning with a discussion of manganese nitrides, including our work on aFM θ-phase MnN and ferrimagnetic ε-phase Mn_4N. The θ-phase films are very complex due to the expectation of canted spins within each atomic layer with four unique canting angles, while the ε-phase films contain two types of spins (Mn^I and Mn^{II}) with equally complex spin arrangements.

A second material we are working on is the chromium nitride system in which we investigate its electronic and spin properties in a low-temperature SP-STM system. Spectroscopy results to date suggest a *d*-wave resonance on the surface and a Kondo signature for nanoscale iron islands grown on atomically-smooth CrN surfaces.

I will also present results for Mn δ-doped semiconducting gallium nitride surfaces in which we find atomic layer ferromagnetism within a unique and stable √3 x √3 - R30° MnGaN surface reconstruction. Spectroscopy clearly reveals spin-polarized and spin-split Mn states, as predicted by first principles theory calculations. SP-STM measurements map out ferromagnetic domains at *room temperature*, and the additional presence of magnetic rim states seen at the edges of ferromagnetic islands, as well as magnetic hysteresis, give further interest to this intriguing system.

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5:40pm **SP+AS+MI+NS+SS-TuA11 The Use of Scanning Probe Techniques to Study the Behaviour of Second Phase Particles in Beryllium and Their Role in Localised Corrosion***, **Christopher Mallinson**, J.F. Watts,* University of Surrey, UK

Scanning Kelvin probe force microscopy (SKPFM) has been employed to examine the galvanic activity of a wide range of second phase particles in S-65 beryllium that are believed to have a role in the localised corrosion of the metal. SKPFM and AFM analysis has been combined with additional surface and bulk analysis techniques of scanning electron microscopy, energy dispersive x-ray spectroscopy and Auger electron spectroscopy to provide a detailed overview of the link between the bulk and surface composition of particles and their Volta potential or surface contact potential.

Initial results appear to show that all second phase particles are more noble than the beryllium matrix with the greatest potential difference observed for $AlFeBe_4$ and alumina or carbide like particles. The more negative Volta potential indicates that the particles should act as local cathodes when the metal is exposed to an aqueous environment.

The initial investigation, which is being performed in-air, will be expanded to determine the effect of increasingly higher humidity environments on the behaviour of the particles. It is hoped that this will provide a greater understanding about the onset of pitting corrosion in beryllium.

6:00pm **SP+AS+MI+NS+SS-TuA12 Many-body Interaction induced Spin-split States of Single Vacancy in Graphite***, **Wonhee Ko**,* Samsung Advanced Institute of Technology, Republic of Korea*; H.W. Kim, Y. Cho,* Samsung Advanced Institute of Technology*; Y. Kuk,* Seoul National University, Korea, Republic of Korea*; S.W. Hwang,* Samsung Advanced Institute of Technology

Although carbon atoms have no magnetic states, it has been known that defects in graphene or graphite can have magnetic states induced by many-body interaction. By utilizing ultra-low-temperature scanning tunneling microscopy, we observed the spin-split states of single vacancy in graphite, which is a hallmark of magnetic states. Evolution of the spin splitting in the magnetic field did not follow the Zeeman effect of single electron states, and can be explained only when we consider electron-electron interaction. Quantitative analysis showed that the strength of the electron-electron interaction is in the range of 1~3 meV. Our observation implies that the simplest defect in graphite like single vacancy can behave as magnetic, which would be an important ingredient for development of carbon-based spintronic devices.

Nanometer-scale Science and Technology
Room Hall D - Session NS-TuP
Nanometer-scale Science & Technology Poster Session

NS-TuP1 tPA Loaded Fe_3O_4 Nanorods to Enhance and Target Stroke Treatment*, Weijie Huang,* University of Georgia*; J.N. Hu, S.W. Huang, K.L. Jin,* University of North Texas*; Y.P. Zhao,* University of Georgia

Stroke remains the 4th leading cause of death in United States and the No. 1 cause of adult disability among the world. Current stroke treatment with tissue plasminogen activator (tPA) therapy faces a lot of challenges due to its side effect. For example, the administration time window of tPA to lyse clots is within the first 3 hours after the initial onset of stroke since the risk of tPA-related hemorrhage is significantly increased after that. Besides this, the traditional tPA therapy also fails to lyse the clot and recanalize the middle cerebral artery in about half cases.

We propose an active drug loaded Fe_3O_4 nanorod strategy to improve the stroke treatment therapy. Fe_3O_4 nanorods were fabricated by oblique angle deposition technique and loaded with tPA using glutaraldehyde as the cross-linker. *In-vitro* study showed that the tPA loaded nanorods could achieve a mass loading ratio (drug mass over rod mass) of 6% and a release time of 30 min. Once the nanorods were immersed in liquid and stimulated by an external rotating magnetic field, about 11% of loaded tPA was released and the thrombolysis efficiency was increased by about 40%. Such an enhancement is due to the increased tPA local concentration and the enhanced mass transport in the fluid, which could help more tPA be delivered into the clot. Such a strategy has been demonstrated using *in vitro* blood clot experiments. We believe that this strategy could improve thrombolysis and recanalization rates, reduce the risk of tPA-mediated hemorrhage, and maybe applied for other disease treatment.

NS-TuP2 Gelatin Nanoparticle Encapsulation of Anti-Parasitic Compound and Characterization for Treatment of Leishmaniasis Disease*, Carlos Serna,* *A. Ornleas, E. Iniguez, K. Michael, R. Maldonado, T. Boland,* The University of Texas at El Paso

Leishmania major is azoonotic flagellate protozoan transmitted to humans and other mammals through phlebotomine female sand flies. *L. major* is mainly responsible for causing cutaneous leishmaniasis (CL) in endemic areas of the Old World, with about 1 million new infections each year [1]. The Mannich base compound *1-acetyl-3,5-dibenzylidene-4-piperidone(**2**)* has been found to have effective anti-parasitic properties, but lacks solubility making it difficult to deliver using standard methods. In this study, we synthesized gelatin nanoparticles (GNP) as carriers for the treatment molecule and demonstrate an effective method of delivering anti-parasitic treatment enhancing drug delivery and reducing toxicity in treatment.

Materials and Methods: *1-acetyl-3,5-dibenzylidene-4-piperidone(**2**)* was synthesized by dissolving *3,5-dibenzylidene-4-piperidone(**1**)*in a mixture of 10% acetic anhydride and 5% diisopropylethylamine in dichloromethane while stirring at room temperature. The Ofokansi et al. [2] two-step desolvation method was applied to produce GNP. To maximize the encapsulation yield of the compound, the preparation method was further modified by limiting the drop-wise cross-linking agent (glutaraldehyde) rate to 30 min and replacing DI water with phosphate buffer saline (PBS) for higher pH stability. Unloaded GNP sizes were determined using a particle size analyzer (Nanosight) in order to test for GNP swelling in varying pH levels. UV visible spectroscopy was used to identify the release rate and total concentration of the compound encapsulated. A viability and cytotoxicity assay was conducted in the testing of loaded and unloaded GNP.

Results and Discussion: The mode values of size distributions using PBS pH 5, 7,and 9 in the production of GNP were found to be 73 nm, 91 nm, and 121 nm respectively. Using UV visible spectroscopy, the concentration of compoundencapsulated by the GNP was found to be 4.01 µg/mL released over a time frame of 96 h in 2.4 g of GNP. A viability assay showed an EC50 value of 2.26 µM for *1-acetyl-3,5-dibenzylidene-4-piperidone(**2**)* in *L. major*; cytotoxicity for the murine intraperitoneal macrophages showed an IC50 value of 6.35 µM.

Conclusions: GNP characterization showed an increase in size with respect to increasing pH in PBS used in the production process; the swelling initiated by exposing GNP produced at pH 5 to a PBS solution of pH 8 showed a release rate of 1 µg/mL per day for 4 days. Viability assays showed the GNP to be effective against *L. major* when encapsulated and non lethal when lacking a molecule payload.

References:

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NS-TuP4 Templated Annealing of Gold Nanowires formed by Directed Assembly on DNA Origami*, Tyler Westover,* *M. Stoddard, B. Uptrey, R.F. Davis, J. Harb, A. Woolley,* Brigham Young University

The formation of gold nanowires using bottom up nanofabrication has resulted in wires of small dimension or high conductivity, but not both. We form nanowires on DNA origami through directed assembly of nanoparticles, electrochemical plating, or a combination of the two. These metal deposition processes result in non-ideal microstructure and correspondingly low conductivities. To remedy this we have sought to reduce the grain boundary density and surface roughness through annealing. However annealing causes the wires to coalesce into beads. We will present results on using polymer layers to maintain overall wire morphology during low temp (200° C) annealing.

NS-TuP5 Zinc Oxide Nanoprobe Spectroscopy for Sensing Trace Levels of Molecular Species in Solution*, Andrew Cook,* Vanderbilt University*; C.S. Carson,* Fisk University*; J. DeCoste,* Edgewood Chemical Biological Center*; T.D. Giorgio,* Vanderbilt University*; R. Mu,* Fisk University

Surface-enhanced Raman spectroscopy (SERS) has great potential to revolutionize clinical diagnostics, yet is limited by an extreme intensity drop-off with distance from the sensing surface. For this reason, much research into SERS-based biosensing relies on chemical or physical adsorption of analytes to the active surface, which limits the types of analytes that can be detected, as well as detection sensitivity. Using the 3-dimensional closely packed architecture of zinc oxide nanowires decorated with silver nanoparticles, the enhancement drop-off can be effectively mitigated, allowing for adsorption-free biosensing. This greatly improves the viability of Raman spectroscopy as a biosensing technique. We demonstrate a significant SERS enhancement from silver nanoparticle-decorated zinc oxide nanoprobes to the Raman spectrum of crystal violet molecules in water, as a model system. More importantly, we demonstrate the detected SERS signal is from molecules un-adsorbed to the sensing surfaces via time-dependent Raman analysis. We also demonstrate growth of high quality zinc oxide nanowires and deposition of silver nanoparticles on the nanowire sides as a surface-enhanced sensing platform.

NS-TuP7 Effect of Deposition Temperature on the Formation of the $SiO_2/ZnO/SiO_2$ Heterostructure Deposited by Reactive RF Sputtering*, *R. Escobedo-Alcaraz, C. Atzin-Mondragon,* Cinvestav-IPN, Mexico*; A. Hernandez-Hernandez,* Escuela Superior de Apan, Mexico*; A. Garcia-Sotelo,* ***MiguelAngel Melendez-Lira,*** Cinvestav-IPN, Mexico

The roughness associated with the sputtering deposition process has been employed to explore the possibility to produce ZnO nanoparticles embedded within a silicon oxide matrix on soda-lime glass and p-silicon substrates. Silicon dioxide and metallic Zn films were deposited employing silicon and zinc targets. An oxygen rich working plasma was employed. Oxygen content of the working plasma was modulated through argon partial pressure. A sequential deposition of $SiO_2/Zn/SiO_2$ films was employed ; SiO_2 layer was produced at 400 °C while deposition temperature of Zn layer was changed between 100 and 500 °C. Results of the chemical, structural and electronic properties are presesented. The Results indicated the successful production of ZnO with properties depending on deposition temperature. X-ray diffraction characterization do not shown the presence of metallic zinc. Secondary ion mass spectroscopy shown an interdifussion of zinc toward the SiO_2 matrix. TEM micrographs indicated the presence of ZnO nanoparticles. XPS corroborates the ZnO formation under specific growth parameters. Photoluminescence emission at room temperature for samples grown on silicon substrates was not observed. Electrical transport properties are discussed on terms of deposition parameters.

*: Partially funded by CONACyT-Mexico

NS-TuP8 Design of High Performance Compact Plasmonic Optical Devices Based on Low Loss Silicon Hybrid Dielectric Loaded Plasmonic Waveguides*, **Cheng-Hung Hsieh**, C.M. Kuo,* National Tsing Hua University*; M.J. Huang,* Naitoal Tsing Hua University*; R.J. Sun,* National Tsing Hua University*; K.C. Leou,* National Tsing Hua University, Taiwan, Republic of China

Here we present the design of several plasmonic optical devices which have gained a great deal of attention recently for potential application in nano photonic circuits. A unique ultra low loss surface plasmon polariton (SPP) waveguide, top metal silicon (Si) hybrid dielectric-loaded plasmonic waveguide (TM-SiHDLW), was first designed. The waveguide adopted a top metal stripe structure for easier process integration with conventional micro fabrications and a thick (200 nm) metal stripe was found to yield optimal performance due to reduced Ohmic loss in conductor around the stripe edge/corner. Moreover, a relatively thick (150 nm) dielectric spacer between the Si ridge and the metal stripe was employed to achieve both long propagation length and good field confinement. Results from numerical simulation show that a long propagation length of 350 μm and a small mode area of 0.03 m^2 are obtained. The TM-SiHDLW structure was also adopted for design of several compact high performance plasmonic optical devices, including a directional coupler, a disk resonator and an switch. The directional coupler adopted a coupled waveguide structure. A coupling length as low as 2.95 μm, only ~ 0.85% of the propagation length, was obtained. The second device is a disk resonator operating at the low loss TE mode. Simulation results demonstrate that a quality factor as high as 2000 can be achieved at a size much smaller than that of a conventional ring resonator. Another plasmonic optical device we have explored was an electro-optical (E-O) switch where an organic E-O material was chosen for low switching voltage along with having a better compatibility with conventional microfabrication processes. The switch we proposed employed a coupled waveguide structure configured in a way that the optical wave can be switched between to two waveguides, depending on the voltage applied on the switch electrodes. All these SPP waveguides and devices were designed to operate at the standard 1550 nm wavelength.

* Work supported by the Ministry of Science and Technology of ROC. The authors also thank the “National Center for High-Performance Computing” of ROC for providing simulation code.

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NS-TuP9 Carbon Nanotube Based Digital X-ray Tube for a Very Short X-ray Pulse with High Dose Rates*, **Jun-Tae Kang**, J.W. Jeong, J.W. Kim, Y.C. Choi, S.H. Kim, H. Jeon, S. Park, M.S. Shin, J.H. Yeon, E. Go, J.W. Lee, Y.H. Song,* Electronics and Telecommunications Research Institute (ETRI), Republic of Korea

Carbon nanotube (CNT) field emitters are being considered as a promising electron source of x-ray tube, which is expected to overcome the limitations of conventional thermionic tubes. The thermionic x-ray tube has been fabricated using a hot cathode, causing analog behaviors like slow response time. On the other hand, the field-emission x-ray tube with CNT emitters can be digitally addressed, which makes it possible to give a very short exposure time. The high x-ray dose rate in a very short exposure time is very important for achieving clear x-ray images.

We have successfully fabricated a digital x-ray tube with CNT field emitters for medical applications. The x-ray tube sealed in a vacuum level of below 5×10^{-6} Torr consists of a CNT field emission gun and a rotating anode made of W/Re target on a Mo block. The field emission current over 100 mA is attained by the gate bias of several kV and is fast modulated through an active-current control at the cathode node, showing a very short x-ray pulse under submicron seconds at a high dose rate. The developed x-ray tube is expected to be used in the advanced diagnostic imaging system with a very short exposure time and high x-ray dose.

Electronic Materials and Photonics
Room 102A - Session EM+NS-WeM

Nanoparticles for Electronics and Photonics

Moderators: Joseph Tischler, U.S. Naval Research Laboratory, Jessica Hilton, Mantis Deposition

8:00am **EM+NS-WeM1 Nanostructures on Surfaces: From Cluster Deposition to Low Energy Ion Bombardment**, ***Luke Hanley***, *K. Steeves Lloyd, M.W. Majeski, I.L. Bolotin,* University of Illinois at Chicago*; M. Schmeling,* Loyola University Chicago*; I.V. Veryovkin,* University of Illinois at Chicago **INVITED**

Two strategies are described for the preparation of unique nanostructures on surfaces or within thin films: cluster beam deposition and low energy ion beam irradiation. In cluster beam deposition, copper sulfide nanoparticles were prepared by magnetron sputtering under a flow of argon and hydrogen sulfide, then codeposited with evaporated pentacene to form a composite thin film (M.W. Majeski, *et al*., ACS Appl. Mater. Interf., 2014, http://dx.doi.org/10.1021/am5028428). This all-gaseous method can prepare a variety of semiconductor nanoparticles without the surface ligand capping and oxidation effects often observed for colloidally prepared nanoparticles that can inhibit charge transfer or cause self-doping. X-ray photoelectron spectroscopy, transmission electron microscopy, and high-angle annular dark-field scanning transmission electron microscopy were used to determine that 2.3 ± 0.4 nm $Cu_{2-x}S$ nanoparticles with copper in the +1 oxidation state were deposited into pentacene films. In low energy ion beam irradiation, nanocone and nanoripple arrays were prepared on Si surfaces by grazing incidence irradiation with 1 keV Ar^+ ion beams that simultaneously sputtered away surface atoms and sputter-deposited metal impurity atoms from adjacent targets (K. Steeves Lloyd, *et al*. Surf. Sci., 2016, http://dx.doi.org/10.1016/j.susc.2016.03.016). Scanning electron microscopy and atomic force microscopy observed that when Si, Cu, or stainless steel was employed as a co-sputtering target, only stainless steel was found to assist the growth of dense arrays of nanocones. The structural characterization of samples further correlated the role of incident ion fluences on the formation of nanoripples vs. nanocones. Characterization of sample chemical composition by total reflection X-ray fluorescence and X-ray photoelectron spectroscopy revealed that the concentration of metal impurities originating from stainless steel (Fe, Cr and Ni) was relatively high in the regions with high density of nanocones and much lower in the region of nanoripples. Overall, these two strategies open up multiple possibilities for the preparation of complex nanostructures on surfaces and in thin films that are compatible with more common lithographic strategies.

8:40am **EM+NS-WeM3 Designer Nanocrystal Electronic and Optoelectronic Materials through Controlled Coupling and Doping**, ***Cherie Kagan,*** University of Pennsylvania **INVITED**

Semiconductor nanocrystals (NCs) are prized for their size- and shape-dependent electronic and optical properties and as building blocks in the assembly of NC solids. However, the long, insulating ligands commonly employed in the synthesis of colloidal NCs inhibit strong interparticle coupling and charge transport once NCs are assembled into the solids state as NC arrays. In this talk, I will describe methods to introduce atoms, ions, and more compact molecules at the NC surface that allows us to increase interparticle coupling and dope NC solids. NC coupling and doping provide control over the density of states, the carrier statistics and the Fermi energy. I will also describe the importance of engineering device interfaces to study the fundamental physics of NC solid transport and to design device architectures for applications. Examples of strong coupling and doping in II-VI and IV-VI semiconductor NC solids will be given that yield high-mobility, high-conductivity NC solids. Temperature--dependent transport measurements of these materials are consistent with a transition from localized to extended-state charge transport. These high mobility n- and p-type materials are used as the semiconductors to construct large-area, flexible, field-effect transistors and integrated circuits and for solar photovoltaics.

9:20am **EM+NS-WeM5 Au Nanoparticle Modified Indium Tin Oxide Ultramicroelectrode for Single Particle Spectro-electrochemistry Study and Ultrasensitive Electrochemistry Sensing**, ***Yanxiao Ma,*** The University of Alabama*; S. Pan,* The Univeristy of Alabama

Plasmonic active metal NPs are broadly used in electrochemical and optical sensing of molecular recognition events. However, it is extremely challenging to resolve chemical and physical transformation at single NP level using conventional optical and electrochemical methods for resolving their local structure-function relationship. We are developing an optical and electrochemical technique to resolve electrocatalytic property of single NPs. Combined methods of photolithography and electrodeposition are used for fabricating Au NP modified indium tin oxide ultramicroelectrode (ITO UME). Dark field scattering (DFS) microscopy and scanning electron microscopy (SEM) were used to characterize NPs on the surface of ITO UME. The electrochemistry voltammetric study shows that Au and Pt NPs are ideal catalytic materials for hydrazine oxidation reaction. Dark field spectroelectrochemical study of hydrazine oxidation at planer ITO and ITO UME confirmed the formation of nanobubbles on NPs surface. Relationship between DFS light intensity and hydrazine oxidation current profile was obtained.

9:40am **EM+NS-WeM6 Band Gap-Control of Spray Pyrolysis Synthesized CZTS Nanoparticles**, ***Stephen Exarhos***, *E. Palmes, A. Alvarez-Barragan, L. Mangolini,* University of California, Riverside

An innovative and scalable synthesis approach to the formation of phase-pure Cu_2ZnSnS_4 (CZTS) nanoparticles has been developed using aerosol spray pyrolysis. CZTS material is an inherent direct-band gap *p*-type semiconductor with a band gap of ~1.5 eV and absorption coefficient of $>10^4\ cm^{-1}$, making it suitable for solar absorption applications. As an earth-abundant absorber material, it has been well-studied for application in thin film photovoltaics [1]. Little experimental work has been done to test the viability of the material as a photocatalyst, though the material shows low activity in driving water splitting or pollutant degradation unless synthesized in a noble metal heterostructure [2]. By its nature, CZTS is a very adaptable material system. It is relatively straightforward to alloy into the material primarily as a method of band gap control. By optimizing the band gap and band alignment of alloyed CZTS-like nanoparticles, we intend to improve the catalytic quality of CZTS-based heterostructures. We have previously shown that aerosol spray pyrolysis is an effective inexpensive and scalable technique for the synthesis of CZTS [3]. By processing a solution with copper-, tin-, and zinc-diethyldithiocarbamate precursors dissolved in a toluene solvent, we can form phase-pure, surface-ligand-free, kesterite CZTS nanoparticles with a size distribution average of ~ 20 nm. Using the same process, by adding hydrogen-terminated silicon nanoparticles — synthesized in-house by a non-thermal plasma process — to the precursor solution, we can alloy silicon into the material (making CZTSiS), and in turn increase the band gap of the material from the 1.5 eV for pure CZTS. We also have the ability to decrease the band gap by alloying different transition metals in place of zinc in the crystal lattice. We present preliminary studies characterizing CZTS and CZTSiS nanoparticles for potential use as a photocatalytic heterostructure material.

[1] Liu, Xiaolei, Yu Feng, Hongtao Cui, Fangyang Liu, Xiaojing Hao, Gavin Conibeer, David B. Mitzi, and Martin Green. Progress in Photovoltaics: Research and Applications, January 1, 2016.

[2] Yu, Xuelian, Alexey Shavel, Xiaoqiang An, Zhishan Luo, Maria Ibáñez, and Andreu Cabot. Journal of the American Chemical Society 136, no. 26 (July 2, 2014): 9236–39.

[3] Exarhos, Stephen. eScholarship, January 1, 2015. http://escholarship.org/uc/item/1pw1t81k.

11:00am **EM+NS-WeM10 Designer Nanomaterials by Magnetron Sputtering and Ion Soft Landing**, ***Grant Johnson***, *V. Prabhakaran,* Pacific Northwest National Laboratory*; T. Moser,* Michigan Technological University*; M.H. Engelhard, N. Browning, J. Laskin,* Pacific Northwest National Laboratory

Clusters and nanoparticles comprised of controlled amounts of different atoms are of interest for applications in optics, magnetics, catalysis, sensors, and biotheraputics. Alloy nanoparticles, in particular, may possess enhanced properties compared to single-metal species due to the additional interplay between their different elemental components. By reducing the quantity of precious metals in alloys by substitution with cheaper base metals, it is possible to achieve equivalent or superior performance to noble metal nanoparticles at reduced material cost. In addition, alloying of elements that are immiscible in the bulk is possible at the nanoscale because the enthalpy of mixing decreases and becomes negative at small particle sizes. As a result, a broad array of alloy species may be generated in the form of clusters and nanoparticles. Magnetron sputtering of multiple targets in the same region of gas aggregation is demonstrated to produce ionic alloy clusters and nanoparticles with defined composition and morphology that are not obtainable through solution synthesis. Introduction of reactive gases into the sputtering and aggregation region is shown to result in the formation of complex morphologies. A suite of characterization techniques including atomic force microscopy, scanning and transmission electron microscopy, and x-ray photoelectron spectroscopy is utilized to determine how the size, shape, and elemental composition of soft landed particles may be tuned through variations in source parameters. The electrochemical activity of the soft landed nanomaterials toward the oxygen reduction reaction, a critical process occurring in proton exchange membrane fuel cells, is evaluated ex-situ using cyclic voltammetry in solution and in-situ using an ionic liquid membrane in vacuum.

11:20am **EM+NS-WeM11 A Facile Electrodeposition Method for Vertically Standing Plasmonic Nanorods for Surface Enhanced Photoelectrochemical Catalysis*, Jue Wang*, *S. Pan,* The University of Alabama**

A facile template-free electrodeposition technique is developed for large-scale fabrication of vertically standing plasmonically active silver nanorods (NRs). The diameter, length, and surface coverage of Ag NRs are dependent on the electrodeposition time. The growth mechanism of the vertically standing Ag NRs is investigated by tracking their morphology evolution as a function of deposition time. Because of their large specific surface area, oriented alignment, broad range light scattering, and light absorption tunability, these NRs are ideal substrates for thin layer photocatalysts for enhancing light absorption and charge collection. The Preliminary tests on plasmon-induced photocurrent of bare Ag NRs, Ag NR converted to Ag_2S NRs, and coated with CdS nanoparticles (NPs) are presented to demonstrate surface enhancement characteristics. This simple NR fabrication method can be extended to other conductive substrates and other materials for obtaining vertically standing NR structures.

11:40am **EM+NS-WeM12 Influence of Surface Reaction on the Infrared Localized Surface Plasmon Resonance of Indium Tin Oxide Nanocrystals*, Weize Hu*, *M.A. Filler,* Georgia Institute of Technology**

Heavily doped oxide nanocrystals exhibit a tunable plasmonic response in the infrared, a capability that is promising for future photonic, spectroscopic, and energy harvesting/transport technologies. Nanocrystal carrier density, and thus spectral response, is adjustable via chemical reaction; however, the fundamental processes governing this behavior are poorly understood. Here, we study the oxidation and reduction of indium tin oxide (ITO) nanocrystals with O_2 and H_2, respectively, with in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). We show that the main absorption feature redshifts upon oxidation more than 1000 cm^{-1} and blueshifts to its original position upon reduction. The same magnitude spectral shift is observed over many cycles of oxidation and reduction. A kinetic model, which includes surface reaction and bulk diffusion, allows us to quantitatively rationalize the process, revealing that surface reaction is rate limiting under the conditions studied. Our experiments provide a deeper understanding of the connection between surface reaction and carrier density in oxide nanocrystals, and open the door to a priori control of plasmonic response.

12:00pm **EM+NS-WeM13 Electrochemical Synthesis of Nanostructured Cu and Cu_xO Electrodes for the Reduction of CO_2 to Usable Fuels*, Nelly Kaneza*, *S. Pan,* The University of Alabama**

In effort to controlling carbon dioxide (CO_2) levels in the atmosphere, the conversion of CO_2 into useful products, although very challenging, has emerged as a very attractive area of research. In this work, a series of Cu based nanostructures are synthesized and characterized to demonstrate a low cost approach to reduce CO_2 electrochemically to specific fuel products at low overpotential. The synthesized Cu and Cu_xO nanostructures are characterized with X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) and their performance evaluated in terms of their activity, selectivity and stability using cyclic voltammetry (CV), gas chromatography (GC) equipped with a mass spectrometry (MS).

Thin Film
Room 105A - Session TF+MI+NS-WeM

ALD and Nanostructures

Moderators: Sean King, Intel Corporation, Mariadriana Creatore, Eindhoven University of Technology, Netherlands

8:00am **TF+MI+NS-WeM1 Scalable Manufacturing of Nanostructured Materials by Gas-Phase Deposition Techniques*, Ruud van Ommen,*** Delft University of Technology, Netherlands **INVITED**

Core-shell nanoparticles and other nanostructured particles have high potential in applications such as catalysis, energy storage and pharma. However, a hurdle in their utilisation is that typically large amounts of such materials are required. Current liquid-phase and gas-phase synthesis methods often lack the high precision required or do not lend themselves to large-scale production. Gas-phase coating can be used to provide the surface of a particle with either a thin continuous coating or a decoration of nanoclusters. Coating techniques that can be used are chemical vapour deposition (CVD) [1], atomic layer deposition (ALD) [2], and molecular layer deposition (MLD) [3].

When carried out in a so-called fluidized bed, gas-phase coating is an attractive way of producing nanostructured particles with excellent scale-up potential. In such a system, the particles are suspended in an upward gas flow. We can do this both for nanoparticles and micron-sized particles. Nanoparticles – contrary to what is typically observed for larger particles – are fluidized as very dilute agglomerates with distinctive fluidization characteristics. I will discuss the challenges related to coating of nanoparticles using CVD, ALD, and MLD with such a system. Moreover, I will give a number of examples of the applications of nanostructured particles produced in this way.

[1] Valdesueiro, D., Meesters, G., Kreutzer, M., and van Ommen, J.R., 'Gas-phase deposition of ultrathin aluminium oxide films on nanoparticles at ambient conditions', Materials 8: 1249-1263 (2015).

[2] Goulas, A. and van Ommen, J.R., 'Atomic layer deposition of platinum clusters on titania nanoparticles at atmospheric pressure', Journal of Materials Chemistry A 1(15): p. 4647-4650 (2013).

[3] Vasudevan, S.A., Xu, Y., Karwal, S., van Ostaay, H.G.M.E., Meesters, G.M.H., Talebi, M., Sudhölter, E.J.R., and van Ommen, J.R., 'Controlled release from protein particles encapsulated by molecular layer deposition', Chemical Communications 51: 12540-12543 (2015).

8:40am **TF+MI+NS-WeM3 Surface Passivation of InP Nanowires by Atomic Layer Deposition*, Lachlan Black*, *Y. Cui, A. Cavalli, M.A. Verheijen, E.P.A.M. Bakkers, W.M.M. Kessels,*** Eindhoven University of Technology, Netherlands

III/V semiconductor nanowires offer a variety of novel properties that make them of interest for electronic and optoelectronic device applications, including enhanced light trapping/concentration, reduced material use, and relaxation of lattice-matching constraints, which enables novel heterostructures and growth on inexpensive substrates. However, the greatly increased surface-to-volume ratio of nanowires compared to planar devices significantly increases the importance of surface recombination and hence of effective passivation of the nanowire surface.

In this work, we focus on nanowires of InP, a material of particular interest for optoelectronic devices. In contrast to the situation for GaAs, the bare or natively oxidised surface of InP presents relatively few electronically active defect states to facilitate surface recombination. However, in order to form InP device structures it is necessary to deposit an insulating dielectric layer on part of the InP surface, and this tends to result in significant depassivation of the surface, to the extent that the performance of InP devices is commonly limited by surface recombination.

Atomic layer deposition (ALD), as a relatively “soft” deposition technique capable of forming well-controlled, high-quality dielectric layers, would seem to offer the best chance of successfully passivating InP nanowire surfaces. ALD can be performed at low substrate temperatures, which is important to avoid phosphorus out-diffusion and resulting damage of the InP surface, while its excellent conformality allows for uniform deposition on nanowire surfaces. Nevertheless, previous attempts to passivate InP surfaces by ALD have encountered similar difficulties to other techniques in achieving low surface recombination for deposited dielectric layers of appreciable thickness.

In this work, we demonstrate successful dielectric passivation of InP planar and nanowire surfaces in the presence of a relatively thick (>10 nm) ALD Al_2O_3 layer deposited from trimethylaluminium (TMA), through the use of a thin phosphate interlayer deposited at low temperature in the same system from trimethyl phosphate (TMP), in both cases using an O_2 plasma oxidant. Time-resolved photoluminescence measurements show that carrier lifetimes are increased relative to the native surface for both planar and nanowire InP samples (e.g. from 1.6 to 2.4 ns for one nanowire sample), in contrast to a strong depassivation observed following ALD of Al_2O_3 and other dielectrics on the bare InP surfaces. X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) are used to elucidate the composition and structure of the deposited phosphate layers.

9:00am **TF+MI+NS-WeM4 Selectivity and Nucleation Effects in Atomic Layer Deposition of Copper for Plasmonic Nanostructures***, **Jie Qi**, B.G. Willis,* University of Connecticut

Plasmonic nanostructures made of conducting metals such as copper, silver, and gold have been intensively investigated due to their capability for enabling optics beyond the diffraction limit and making it possible to manipulate visible and near-IR radiation at the nanometer scale. The interaction between metallic nanostructures and incident light induces large enhancements of the local electromagnetic fields via the excitation of localized surface plasmon resonances (LSPRs). These confined and enhanced fields have many exciting applications in optical detection, cancer therapeutics, biological and chemical sensors, spectroscopy, catalysis, and photovoltaics. A key feature of nanoscale plasmonic materials is a strong dependence of the plasmon resonance on size, shape, composition, and surroundings of the nanostructures. Selective area atomic layer deposition (SA-ALD) offers a promising nanofabrication technique to further tune the properties of plasmonic nanostructures with composition and thickness control at an atomic level. Successful application of SA-ALD requires good control of nucleation and surface morphology evolution, as well as good selectivity. Unfortunately, there are very few studies that report selectivity and/or nucleation characteristics, and their dependence on growth conditions.

In this work, we investigate the growth characteristics of Cu SA-ALD for tuning plasmonic nanostructures. Pd nanostructures are fabricated by electron-beam lithography and used as template layers. Samples are analyzed by AFM, high-resolution SEM, and image processing to investigate nuclei size and density, and morphology evolution. It has been found that nucleation is greatly affected by deposition temperature and co-reactant H_2 partial pressure. Poor nucleation leads to a rough surface with randomly distributed nanoparticles, while good nucleation leads to smooth, conformal growth over the entire feature. Sample surface pretreatments are found to be more critical for initiating growth on nanostructures compared to planar films, which might be related to residual impurities from photoresist layers or other contaminants from nanofabrication processing. Several preparation cleaning methods have been investigated for their effects on Cu film nucleation and growth selectivity including: UV-Ozone, O_2 plasma, annealing in H_2, annealing in He, boiling in water, and dipping in dilute HF.

9:20am **TF+MI+NS-WeM5 Metal Oxide Aerogel Patterning by CO_2 Laser Etching of ALD-coated Carbon Nanotube Macro-Structures***, C. Aksu, P.D. Bradford, **Jesse Jur**,* North Carolina State University

Patterning techniques of metal oxide foam architectures embedded within an ALD-coated carbon nanotube interconnected matrix are defined. Three dimensionally interconnected networks of carbon nanotube are produced from spinnable vertically aligned CNT arrays in which CNTs make. Atomic layer deposition is used to functionalize the surface of the CNTs in the array. Prior work has demonstrated that the CNT networks can be sacrificially removed to form aerogel architectures of the ALD material. In this study, we present a simple and scalable method to fabricate macro-sized structures of ALD alumina foams embedded in the carbon nanotube foam architecture via a CO2 continuous wave laser etching. Specifically, we have demonstrated the ability to ALD modify the CNT in large macro-structures (>1 cm2) and subsequently remove the CNT from specified areas, leading to the complex hybrid alumina-CNT periodic structures. The effects of ALD coating thickness are inspected by in-situ heating transmission electron microscopy methods and by high resolution scanning electron microscopy. Factors relating to manufacturability (i.e. etching speed and power) and dimension stability (i.e. laser etch size) are defined to identify scale-up opportunities.

9:40am **TF+MI+NS-WeM6 Tungsten ALD in Porous Carbon Nanotube Forests***, K. Hinton, N. Hollingworth, D.D. Allred, **Richard Vanfleet**,* Brigham Young University

We have deposited tungsten on carbon nanotube (CNT) forests by CVD (WF_6 & H_2) and ALD -the silane reduction of WF_6. Resulting structures are studied by scanning electron and transmission electron microscopy. We observed that the CNT forest provides a scaffolding for the nucleation and growth of the tungsten. Such structures may be a useful avenue for metal MEMS that does not require extensive etching. The present study may provide insight into the mechanisms of ALD in highly porous structures. In conventional ALD on surfaces which are largely planar, the amount of reactants needed to completely cover the surface does not change much from step-to-step. In contrast the surfaces of carbon nanotube forests consist of cylindrical tubes largely oriented perpendicular to the sample surface. Thus, the surface area increases with deposition. This is in addition to the changes in surface area associated with incubating early stage nucleation sites. When beginning with adequate tungsten or silane one might expect to move to starvation mode as the number of cycles increases if the amount of each reactant is kept constant. We see evidence for tungsten starvation in our research results. For low number of cycles the CNT fibers have a spatially uniform nucleation of tungsten. For low amounts of WF_6 or low "soak" times, as cycles increase, growth on the top surface and sidewalls of the carbon nanotube forest outpaces growth within the structure. Post deposition cross-sections show distinct bands witnessing the starvation of tungsten growth in the interior as more of the tungsten is deposited on regions that have direct access to the WF_6 gas. EDX analysis across such a cross-section shows distinct plateaus in the amount of tungsten present corresponding to the bands.

11:00am **TF+MI+NS-WeM10 Rational Design of Hyperbranched ZnO Nanowire Systems for Superomniphobic Surfaces Enabled by ALD***, **Ashley Bielinski**, M. Boban,* University of Michigan, Ann Arbor*; Y. He,* Pacific Northwest National Laboratory*; E. Kazyak,* University of Michigan, Ann Arbor*; C. Wang,* Pacific Northwest National Laboratory*; A. Tuteja, N.P. Dasgupta,* University of Michigan, Ann Arbor

Semiconductor nanowires (NWs) are powerful 1D building blocks for a range of technologies including electronics and optics, sensors, mechanical resonators, and energy conversion [1]. NW arrays are synthesized with careful control of morphology and composition using both top-down and bottom-up approaches. However, the hierarchical assembly of these NWs into heterogeneous systems remains challenging, largely due to lack of deterministic control of feature size, shape and position in 3D assemblies. Here we demonstrate that Atomic Layer Deposition (ALD) is a powerful tool for modifying interfaces to control the fabrication of ordered hyperbranched NW systems. Hierarchical branched NWs bridge the nano and micro length scales, while providing an exponential increase in surface area. Examples have been synthesized for a variety of applications, but the ability to tune the morphology along a spectrum in order to optimize the structure requires development.

Nanoscale patterning techniques for NW placement, while slow and costly on planar substrates, often become impossible on high aspect ratio structures. Solution-based techniques offer scalability and lower cost, but the results are often disordered and difficult to tune. Our approach uses ALD to catalyze the nucleation of NWs on the substrate during hydrothermal growth. ALD is essential for this approach because it deposits conformal films on ultra-high aspect ratio substrates, with atomic-scale control of film composition and structure. We've demonstrated that by varying the thickness of ALD ZnO films, their crystallographic orientation, roughness, and surface stress can be controlled [2]. These catalyst seed layers allow us to tune the NW array morphology, including density and orientation, over a range of substrate materials and geometries.

We further show that ALD can overcome challenges that arise when transitioning from simple NW arrays to complex branched structures [3]. First, amorphous ALD TiO_2 over-layers are used to reduce nanowire density creating space for subsequent levels of hierarchy. Next, ALD interlayers are used to block the crystallinity of the previous level of ZnO NWs to allow for non-epitaxial deposition of the subsequent ALD seed layer, forming core-shell NWs. These new techniques were used to grow hierarchical branched NW arrays, which were shown to be superomniphobic (repellent to high and low surface tension liquids) with tunable contact angles for different liquids using ALD to control the array properties.

[1] Dasgupta, N. P.; et al. *Adv. Mater.***2014**, *26* (14), 2137–2184.

[2] Bielinski, A. R.; et al. *Chem. Mater.***2015**, *27* (13), 4799–4807.

[3] Bielinski, A. R.; et al. *Submitted***2016**

11:20am **TF+MI+NS-WeM11 Bio-Templated *Morpho* Butterfly Wings by ALD for Photocatalysis***, **Robin E. Rodriguez**, D. Das, S.P. Agarwal,* University of Michigan, Ann Arbor*; W. Shang, T. Deng,* Shanghai Jiao Tong University, China*; N.P. Dasgupta,* University of Michigan, Ann Arbor

Hierarchical nanostructures found in biology have unique properties that inspire bio-mimetic engineering. These natural nanostructures present design principles of bottom-up nanomanufacturing for materials with tunable properties. For example, structural coloration is a phenomenon observed in a wide range of natural materials that take advantage of nanoscale hierarchical structures to tune their reflection and absorption properties through periodic diffraction and photonic resonances. Here we demonstrate *bio-templating* via Atomic Layer Deposition (ALD) as an approach to manufacture atomically-precise synthetic materials that manipulate the natural structural coloration found in *Morpho* butterfly wings for enhanced photocatalytic activity.

Until recently, conventional approaches to bio-templated nanomaterial synthesis have been limited in their ability to create highly conformal 3-D interfaces between temperature- and chemically-sensitive bio materials and functional thin films. ALD is uniquely suited for scalable and conformal bio-templating, which allows us to use the nanoscale structural complexity that nature provides to tune the interfacial properties of natural systems by coating them with functional materials. By varying the geometric and optical properties of the surface, ALD is able to tune structural coloration to manipulate the light absorbing and photocatalytic properties of natural materials with nanostructured surfaces.

Morpho butterflies are particularly interesting examples of structural coloration, which occurs due to hierarchical nanostructures on their wing surfaces. The combination of strong photonic resonances and high surface area in these wings represent an ideal template for photocatalysis. To demonstrate this, proof-of-concept tests were performed on *Morpho* wings coated by ALD of TiO_2 and ZnO. Electron microscopy images showed conformal coating of the wing geometries at the nanoscale. The structural coloration of the butterfly wings could be tuned using this approach, which was modeled using finite-difference time-domain simulations of the modified wing geometry. The viability of this approach was further demonstrated in the photocatalytic degradation of methylele blue dyes in water, which led to an increase in photocatalytic activity relative to planar thin film samples. The ALD deposited materials show superior photocatalytic activity which was attributed to enhanced light absorption and increased surface area from the butterfly’s hierarchical structures.

2D Materials Focus Topic

Room 103B - Session 2D+NS-WeA

Nanostructures including Heterostructures made of 2D Materials

Moderators: Charlie Johnson, University of Pennsylvania, Arkady Krasheninnikov, Helmholtz Zentrum Dresden-Rossendorf, Germany

2:20pm **2D+NS-WeA1 Single- and Few-Layer WTe_2 Nanosheets: New Raman Fingerprints, Nanomechanical Resonances, and Environmental Instability Studies***, **Fan Ye**, J. Lee,* Case Western Reserve University*; J. Hu, Z.-Q. Mao, J. Wei,* Tulane University*; P.X.-L. Feng,* Case Western Reserve University

Among recently emerging two-dimensional (2D) materials, 1T'-phase semi-metallic tungsten ditelluride (WTe_2) [4] possesses unique properties – large, non-saturating magnetoresistance [1] that originates from perfect balance between electrons and holes populations [2], a metallic to insulating transition under low temperature with varying number of layers [3] and superconductivity under high pressure [5]. These properties are not easily accessible in other 2D materials, thus making WTe_2 highly attractive for further investigations on their basic properties, especially in the single layer (1L) to few-layer regime.

In this work, we have systematically investigated new Raman signatures, nanomechanical properties [6], and environmental instability of single- and few-layer WTe_2. In Raman study, we have observed up to 12 peaks in few-layer WTe_2. We find clear softening, stiffening and invariant behaviors in the measured 12 Raman modes as thickness decreases from 8L to 1L. These Raman fingerprints could be an effective 'thickness indicator' for identifying layer number in atomically thin WTe_2. We have also investigated mechanical properties of few-layer suspended WTe_2 by measuring their resonances, and further determined its Young's modulus to be E_Y~80GPa. In addition, by employing surface sensitive material characterization tools such as Raman spectroscopy, XPS, and AES, we carefully study the degradation behavior of single- and few-layer WTe_2 in ambient conditions [7]. We find that oxidation is the main driving force of WTe_2 degradation and it is a self-limiting process. In particular, 1L WTe_2 quickly oxidize in ~13mins, while 2L and 3L WTe_2 exhibit relatively slower, saturating and self-limiting degradation process over two weeks.

This work paves the way for future investigations and utilization of the multiple new Raman fingerprints of few-layer WTe2, and for exploring mechanical control of WTe2 atomic layers.

[1] X. L. Fan, *et al J. Mater. Chem. A* .**2**, 20545–20551 (2014).

[2] M. N. Ali, *et al.*, *Nature***514**, 205-208 (2014).

[3] P. L. Cai, *et al.*, *Phys. Rev. Lett.* **115,** 057202 (2015).

[4] L. Wang, *et al.*, *Nat. Comm.***6**, 8892 (2015).

[5] X.C. Pan, *et al.*, *Nat. Comm.***6**, 7805 (2015).

[6] J. Lee *et al., Nanoscale*. **8**, 7854–7860 (2016).

[7] F. Ye *et al.*, *In Submission* (2016).

3:00pm **2D+NS-WeA3 Laser-based Synthesis and Processing of Two-dimensional Monolayers and Heterostructures***, **Masoud Mahjouri-Samani**, C. M. Rouleau, A.A. Puretzky, D.B. Geohegan,* Oak Ridge National Laboratory **INVITED**

Two-dimensional (2D) materials, such as metal chalcogenides, graphene, and oxides, have emerged as an exciting class of materials with extraordinary physical, chemical, electrical, and optical properties. These classes of 2D materials have the potential to enable numerous new technological applications ranging from electronics to photonics. However, realization of this potential requires (i) novel synthesis approaches for growth of high-quality 2D materials, (ii) controllable chemical and structural modification of the crystals, and (iii) a fundamental understanding of their structural properties and device characteristics.

In this talk, I will demonstrate the use of non-equilibrium laser-based approaches to form and deliver atoms, clusters, or stoichiometric nanoparticles with tunable kinetic energies for the synthesis and processing of 2D layered semiconductors. Utilizing stoichiometric nanoparticles as feedstock, we have shown the growth of either small domain nanosheet networks (~ 20 nm) or large crystalline domains (~100 µm) of GaSe, $MoSe_2$, and WSe_2 with controlled orientation, number of layers, crystallite size, and growth location. We have also shown that atomic precursors with tunable kinetic energies can be used for doping, alloying, and conversion of 2D monolayers. I will show the structural, optical, and electrical properties of monolayer crystals modified by defect formation, healing, doping, and conversion processes. I will then highlight our newly developed method that enables the formation of patterned arrays of lateral heterojunctions between two different 2D semiconductors necessary for ultrathin electronics. These non-equilibrium approaches provide unique synthesis and processing opportunities that are not easily accessible through conventional methods.

4:20pm **2D+NS-WeA7 Pulsed Laser Deposition of Single Layer, Hexagonal Boron Nitride on Fiber-oriented Ag(111)/$SrTiO_3$(001)***, **Jeff Terry**, D. Velazquez, R. Seibert, L. Spentzouris,* Illinois Institute of Technology

We have grown thin films of hexagonal boron nitride (h-BN) of thickness 1-10 ML on fiber-oriented Ag buffer films on $SrTiO_3$(001) by pulsed laser deposition. We used Ag buffer films of 40nm thickness to substitute for expensive single crystal metallic substrates. Reflection high-energy electron diffraction (RHEED) was used to monitor the surface structure of the Ag films and to observe the formation of the characteristic h-BN diffraction pattern. Attenuated total reflectance spectroscopy showed the characteristic h-BN peaks at 780 cm^{-1} and 1367.4 cm^{-1}. Ex-situ photoelectron spectroscopy showed that the surface of the h-BN films was stoichiometric. Scanning electron microscopy showed that the h-BN films grew as large, sub-millimeter sheets with nano- and micro-sheets scattered on the surface. The h-BN sheets was easily exfoliated by the micromechanical adhesive tape method. The use of thin film Ag allowed us to adjust the surface morphology of the thin film prior to h-BN growth.

4:40pm **2D+NS-WeA8 Fracture Toughness Measurements of Graphene Oxide***, **Tobin Filleter**, C. Cao,* University of Toronto, Canada*; J.Y. Howe,* Hitachi High Technologies Canada Inc., Canada*; D. Perovic,* University of Toronto, Canada*; Y. Sun,* Univeristy of Toronto, Canada

Graphene Oxide (GO) is a functionalized form of graphene that we have recently shown to possess high tensile strength [1-2]. These studies on the strength of GO have revealed a size dependent mechanical behavior in which the strength is found to increase with decreasing thickness, a behavior which is controlled by a transition in the fracture mechanism [2]. In real engineering applications in which materials exhibit pre-existing flaws, the fracture toughness of a material is also a critical property in predicting the failure of the material. Here we present studies of GO with preexisting defects that enable the first measurements of the fracture toughness of GO nanosheets. Application of traditional experimental techniques used to measure the fracture toughness (and monitor the fracture behavior) of bulk materials is not feasible for the measurement of ultra-thin films such as GO. In this work, we apply a micro-electro-mechanical system (MEMS) based *in situ* transmission electron microscope (TEM) method to measure the fracture toughness of GO and directly characterize its fracture behavior through high resolution TEM imaging. GO nanosheets suspended on monolithic MEMS devices *in situ* TEM were first controllably etched by high-energy electrons to create well defined holes in the GO nanosheets used for fracture toughness measurements. After a defect was created, *in situ* TEM tensile tests allowed both measurement of the stress at the onset of fracture, as well as direct monitoring of the fracture response via TEM imaging.

[1] C. Cao, M. Daly, C. V. Singh, Y. Sun, and T. Filleter, "High strength measurement of monolayer graphene oxide", Carbon, vol. 81 (2015) p.g. 497-504

[2] C. Cao, M. Daly, B. Chen, J. Howe, C. V. Singh, T. Filleter, and Y. Sun, "Stengthening in graphene oxide nanosheets: bridging the gap between interplanar and intraplanar fracture", Nano Letters, vol. 15 (2016) p.g. 6528-6534

5:00pm **2D+NS-WeA9 Strain, Solitons, and Bimorphs with 2D Materials***, **Paul McEuen**,* Cornell University **INVITED**

Two-dimensional sheets combine many remarkable properties in a single, atomically thin package. For example, a graphene sheet can be made into a high-performance transistor, but it is also the ultimate realization of a thin mechanical sheet. In this talk, I will discuss some of the fascinating properties of heterostructures of these materials, touching on everything from creating the world's thinnest bimorph to the electronic and mechanical properties of interlayer strain solitons.

5:40pm **2D+NS-WeA11 Strain-Engineered Graphene Grown on Boron Nitride and Hexagonal Boron Nitride Grown on Graphite using High-Temperature Molecular Beam Epitaxy***, **Alex Summerfield**, A. Davies, T.S. Cheng, V.V. Korolkov, Y. Cho, C.J. Mellor, E.F. Smith, C.T. Foxon, A.N. Khlobystov,* University of Nottingham, UK*; K. Watanabe, T. Taniguchi,* National Institute for Materials Science (NIMS), Japan*; L. Eaves, S.V. Novikov, P. Beton,* University of Nottingham, UK

To scale up the production of graphene-hexagonal boron nitride (hBN) heterostructure devices, direct epitaxial growth of these materials will be necessary. As an alternative to commonly used techniques such as the exfoliation of graphene/hBN flakes or growth using chemical vapour deposition we have investigated high-temperature molecular beam epitaxy (HT-MBE) in order to produce high-quality graphene and hBN monolayers.

We show that graphene grown using HT-MBE on hBN surfaces form continuous domains with dimensions of order 20 µm, and exhibits moiré patterns with large periodicities, up to ~30 nm, indicating that the layers are highly strained. Topological defects in the moiré patterns are observed using atomic force microscopy (AFM) and attributed to the relaxation of graphene islands which nucleate at different sites and subsequently coalesce. In addition, cracks are formed leading to strain relaxation, highly anisotropic strain fields, and abrupt boundaries between regions with different moiré periods. These cracks can also be formed by modification of the layers with a local probe resulting in the contraction and physical displacement of graphene layers. The Raman spectra of regions with a large moiré period reveal split and shifted G and 2D peaks confirming the presence of strain.

We also demonstrate the epitaxial growth of high-quality hBN atomic layers on graphite using plasma-assisted HT-MBE. AFM reveals mono- and few-layer island growth, while conductive AFM measurements show that the grown hBN has a resistivity which increases exponentially with layer thickness comparable with exfoliated hBN samples. Furthermore, X-Ray photoelectron spectroscopy, Raman and spectroscopic ellipsometry confirm the formation of sp^2-bonded hBN with a band gap of 5.87 eV. Hexagonal moiré patterns of 15-17 nm are also observed on the hBN surface, suggesting that the grown layers may be strained due to the lattice mismatch with the graphite surface.

Our work demonstrates a new approach to the growth of epitaxial graphene/hBN and provides a route to the production of vertical superlattice structures for use in future devices.

6:00pm **2D+NS-WeA12 Metallic Edges in Atomically Thin WSe$_2$***, **Rafik Addou**, C.M. Smyth,* The University of Texas at Dallas*; Y.-C. Lin,* The Pennsylvania State University*; J. Noh,* The University of Texas at Dallas*; S.M. Eichfeld,* The Pennsylvania State University*; K.J. Cho,* The University of Texas at Dallas*; J.A. Robinson,* The Pennsylvania State University*; R.M. Wallace,* The University of Texas at Dallas

Transition metal dichalcogenides (TMDs) is a unique class of layered two-dimensional (2D) crystals with extensive promising applications. Tuning their electronic properties is vital for engineering new functionalities. Surface oxidation is of particular interest because it is a relatively simple and low-cost method compared with other processes involving complicated steps. By means of scanning tunneling microscopy and spectroscopy (STM and STS), and X-ray photoelectron spectroscopy (XPS), we show here the observation of metallic step edges in atomically thin WSe$_2$ monolayers grown by chemical vapor deposition (CVD) on epitaxial graphene (Gr). STM images show the shape and the structure of WSe$_2$ step edges and STS reveals their metallic nature. Photoemission demonstrates that the formation of metallic sub-stoichiometric tungsten oxide (WO$_x$, x<3) is responsible of high conductivity measured along the WSe$_2$ step edges. DFT Calculations [1,2] revealed that the W$_{18}$O$_{49}$ have a metallic behavior which is in excellent agreement with our photoemission estimated WO$_x$, with 2.61≤x≤2.72. Our findings are in contrary with reported results of air-exposed WSe$_2$ edges with large band gap measured at ~3.1 eV. [3] We explain this discrepancy by considering the differences in WO$_x$ stoichiometry. [1]

This work was supported in part by the Center for Low Energy Systems Technology (LEAST), one of the six SRC STARnet Centers, sponsored by MARCO and DARPA, and by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST, and the US/Ireland R&D Partnership (UNITE) under the NSF award ECCS-1407765.

[1] D. B. Migas *et al. J. Appl. Phys.* **108**, 093714 (2010)

[2] M. Remskar *et al. Adv. Funct. Mater.* **17**, 1974-1978 (2007)

[3] J. H. Park *et al. ACS Nano* ***10***, 4258–4267 (2016)

Electronic Materials and Photonics
Room 102A - Session EM+NS+SP+SS-WeA

Nanoscale Imaging of Metals and Compound Semiconductor based Nanostructures, Surfaces and Interfaces

Moderators: Yohannes Abate, Georgia State University, Andy Antonelli, Nanometrics

2:20pm **EM+NS+SP+SS-WeA1 The Importance of Contact Engineering for 2D Devices***, **Saptarshi Das**,* Pennsylvania State University **INVITED**

Contact resistance is one of the most important factors which could potentially limit the performance of novel electronic and optoelectronic devices based on two-dimensional (2D) materials like graphene, black phosphorus, various transition metal dichalcogenides (TMDs) like MoS$_2$, WSe$_2$ and beyond [1-3]. It is now widely accepted that metal-2D contacts are mostly Schottky barriers type [1-3]. Hence, various contact engineering strategies have been adopted to minimize the Schottky barrier height at the metal-2D interface and thereby reduce the contact resistance. In this talk I will provide a comprehensive overview of different contact engineering schemes metal work function engineering, interface engineering and phase engineering [4-6]. Additionally, I will also talk about the scalability of the contact resistance since an aggressively scaled 2D device will also have aggressively scaled contacts.

1. Das S, Chen H-Y, Penumatcha AV, Appenzeller J: **High performance multilayer MoS2 transistors with scandium contacts**. *Nano letters* 2012, **13**(1):100-105

2. Das S, Appenzeller J: **WSe2 field effect transistors with enhanced ambipolar characteristics**. *Applied Physics Letters* 2013, **103**(10):103501

3. Das S, Demarteau M, Roelofs A: **Ambipolar phosphorene field effect transistor**. *ACS nano* 2014, **8**(11):11730-11738.

4. Das S, Appenzeller J: **Where does the current flow in two-dimensional layered systems?***Nano letters* 2013, **13**(7):3396-3402

5. Das S, Gulotty R, Sumant AV, Roelofs A: **All two-dimensional, flexible, transparent, and thinnest thin film transistor**. *Nano letters* 2014, **14**(5):2861-2866.

6. Kappera R, Voiry D, Yalcin SE, Branch B, Gupta G, Mohite AD, Chhowalla M: **Phase-engineered low-resistance contacts for ultrathin MoS2 transistors**. *Nature materials* 2014, **13**(12):1128-1134.

3:00pm **EM+NS+SP+SS-WeA3 Imaging Stress-Directed Compositional Patterning in Silicon Germanium with µ-Raman Spectroscopy***, **Brian Rummel**, S.M. Han,* University of New Mexico

We have previously demonstrated that a patterned elastic stress field can be used to change the near-surface atomic composition in an epitaxial compound semiconductor film.[1] This compositional patterning laterally manipulates quantum barriers within the film in a press-and-print manner. In this example, an array of silicon pillars is pressed against a relaxed Si$_{0.8}$Ge$_{0.2}$ substrate in a mechanical press, and the entire assembly is heated to high temperatures. This serves to promote a diffusive separation of the germanium into highly localized regions. Here, the difficulty in analyzing these structures is due to the lack of surface detail on the stress-annealed substrate as there is only elastic deformation observed during the fabrication process. To visualize the regions compressively stressed by the pillars and therefore compositionally altered regions, we report the use of µ-Raman spectroscopy to produce a 2D compositional map of a substrate. The substrate is patterned with feature sizes on the order of 1 to 3 microns to remain within the spatial resolution of µ-Raman spectroscopy for the purpose of demonstration. The first-order Raman spectrum for pure silicon and germanium produces peaks at 520.2 and 300.7 cm^{-1}, respectively. The deviations from these relaxed silicon and germanium peaks have been attributed to residual tensile stress in the Ge-depleted regions. Lateral line scans are performed to map the compositions of the stressed and annealed substrate, which provides a clear image of the resulting diffusion process. This imaging also allows the quantum structures to be addressable.

[1] S. Ghosh, D. Kaiser, J. Bonilla, T. Sinno, and S. M. Han, "Stress-Directed Compositional Patterning of SiGe Substrates for Lateral Quantum Barrier Manipulation," *Applied Physic Letters* **107,** 072106-1:5 (2015).

3:20pm **EM+NS+SP+SS-WeA4 Atomic-scale Characterization of III-V Nanowire Heterostructures and Devices***, J. Knutsson, S. McKibbin, M. Hjort, J. Colvin, S. Yngman, A. Troian, O. Persson, A. Mikkelsen,* ***Rainer Timm,*** Lund University, Sweden

III-V semiconductor nanowires (NWs) have a large technological potential within electronics, optoelectronics, and energy harvesting [1]. With their flexibility in creating heterostructures, by radial and axial stacking during epitaxial growth, comes an increasing complexity of device structure. Furthermore, due to their small diameter and their very large surface-to-volume-ratio, the performance of NW devices is strongly determined by surface properties. It is therefore essential to study the structural and electronic properties of NW surfaces down to the atomic level and across interfaces regarding doping, material composition, or crystal phase.

We recently obtained atomically resolved scanning tunneling microscopy (STM) images of various GaAs, InAs, and InP NW surfaces [2,3]. By combining STM imaging with scanning tunneling spectroscopy (STS) measurements, we correlate the surface structure and local electronic properties [3]. Here, we will present examples from InAs NWs with interfaces between different crystal phase. Our low-temperature STM/S results show that even the smallest possible insertion of zincblende phase within a wurtzite segment, a single bilayer stacking fault, shows a clear zincblende signature. We observe transitions in the local density of states with sub-nm lateral resolution. Furthermore, we map the interface band alignment and measure quantum confinement energies of single and double bilayer stacking faults.

Beyond traditional steady-state surface characterization, it is desirable to even investigate nanostructure devices *in-situ*, meaning while they are operating under an applied bias. We are now using simultaneous STM, AFM, and electrical transport measurements for studying individually contacted NWs during device operation [4], complemented by Kelvin probe force microscopy and scanning photoemission microscopy. We will present initial results of such combined *in-situ* studies on axial *pn*-junctions in InP and GaInP NWs, where we also investigate the influence of NW surface modification (e.g. removal of native oxide by atomic hydrogen) on photovoltaic properties.

[1] E. Lind *et al.,* IEEE J. El. Dev. Soc. **3**, 96 (2015); J. Wallentin *et al*., Science **339**, 1057 (2013).

[2] M. Hjort *et al*., ACS Nano **6**, 9679 (2012); J. Knutsson *et al.,* ACS Appl. Mat. & Interf. **7**, 5748 (2015).

[3] M. Hjort *et al*., Nano Lett. **13**, 4492 (2013); M. Hjort *et al.,* ACS Nano **8**, 12346 (2014).

[4] O. Persson *et al.,* Nano Lett. **15**, 3684 (2015); J. L. Webb *et al*., Nano Res. **7**, 877 (2014).

4:20pm **EM+NS+SP+SS-WeA7 Revealing Optical Properties of Reduced-Dimensionality Materials at Relevant Length Scales using Nanospectroscopic Imaging***,* ***P. James Schuck,*** The Molecular Foundry, Berkeley Lab **INVITED**

Reduced-dimensionality materials for photonic and optoelectronic applications including energy conversion, solid-state lighting, sensing, and information technology are undergoing rapid development. The search for novel materials based on reduced-dimensionality is driven by new physics. Understanding and optimizing material properties requires characterization at the relevant length scale, which is often below the diffraction limit. The nano-optical imaging community has now crossed the boundary from insufficient to sufficient resolution, mapping critical optoelectronic properties in these exciting materials at their native length scales. Here, I will describe the recent near-field imaging advances that lay groundwork for generally-applicable nano-optical studies of these low-D materials, and will show recent results on 0, 1, and 2D systems. I will spend time discussing the importance of near-field polarization in probing these materials, and will also highlight recent applications in 2-D semiconductor transition metal dichalcogenides (TMDCs), where we and others have uncovered new optoelectronic regions and spatially-varying features that were hidden in prior optical studies. These findings have broad implications for the development of atomically thin transistors, quantum optical components, photodetectors and light-emitting devices.

5:00pm **EM+NS+SP+SS-WeA9 Polarizability Mapping of Nanolayers Based on Near-Field Edge Fringes***,* ***Viktoriia Babicheva****, V.S. Yakovlev, S. Gamage, M.I. Stockman, Y. Abate,* Georgia State University

Scattering-type scanning near-field optical (s-SNOM) microscopy enable spectroscopic imaging with nanoscale resolution and provide chemical and structural information of surfaces [1]. In this work, we investigate identification of material type using an approach based on analyzing near fields at the sample edge [2]. We develop theoretical approach that includes full-wave numerical simulations and calculations of s-SNOM signal in different demodulation orders. This model allow characterization of structures of any shape and material, as well as different tips, and does not include any fitting parameters. In this way, we defined that metallic edge has bright and dark fringes in near-field characterization, whereas a bright edge of dielectric material has no outside fringe. Similar behavior is observed for anisotropic material with hyperbolic dispersion (boron nitride in mid-IR range): depending on the wavelength, it shows either metallic or dielectric properties.

1. Y. Abate, R.E. Marvel, J.I. Ziegler, S. Gamage, M.H. Javani, M.I. Stockman, and R.F. Haglund "Control of plasmonic nanoantennas by reversible metal-insulator transition" Sci. Rep. 5, 13997 (2015).

2. Y. Abate, S. Gamage, L. Zhen, S.B. Cronin, H. Wang, V. Babicheva, M.H. Javani, M.I. Stockman, “Nanoscopy reveals metallic black phosphorus,” Light: Science & Applications, accepted (2016). http://arxiv.org/abs/1506.05431

5:20pm **EM+NS+SP+SS-WeA10 Wedding Cake Growth Mechanism in One-Dimensional and Two-Dimensional Nanostructure Evolution***,* ***Xin Yin***[*], University of Wisconsin-Madison*; J. Shi,* Rensselaer Polytechnic Institute*; X. Niu,* Northeastern University*; D. Geng,* University of Wisconsin-Madison*; H. Huang,* Northeastern University*; X.D. Wang,* University of Wisconsin-Madison

Morphology is one essential element that gives rise to extraordinary physical, chemical, and mechanical properties in nanomaterials. Precise morphology control of nanomaterials is a notorious task, which heavily relies on fundamental understanding of the governing atomistic mechanisms and kinetics at the nanoscale. Despite numerous studies on the growth and application of nanostructures, current understanding of kinetics that governs the nanocrystal evolution is yet limited.

By programming deposition conditions at time domain, we observed the wedding cake growth mechanism in the formation of 2D ZnO nanostructures. Within a narrow growth window, the surfaces of 2D structures were covered with a unique concentric terrace feature. This mechanism was further validated by comparing the characteristic growth rates to the screw dislocation-driven model. An interesting 1D to 2D morphology transition was also found during the wedding cake growth, when the adatoms overcome the Ehrlich-Schwoebel (ES) barrier along the edge of the top crystal facet triggered by lowering the supersaturation. The evolution of 2D plate structure from 1D pillars represents a dynamic crystal growth behavior transition when the local deposition conditions were tuned in-situ. It lively recorded the wedding cake growth model in nanostructure formation from vapor phase, which was rare to be observed when the deposition conditions were remained constant. The terrace feature on these nanostructures provided a valuable platform for understanding the wedding cake growth kinetics that could be an important mechanism to design and predict the nanocrystal morphology formation from the bottom-up. Analyzing the supersaturation and temperature-related growth behavior provides a new insight into nanostructure growth mechanisms and morphology control.

Wedding cake growth is a layer-by-layer growth model commonly observed in epitaxial growth of metal films, featured by repeated nucleation of new atomic layers on the topmost surface owing to the confinement of the Ehrlich–Schwoebel (ES) barrier. This study expands the application of the wedding cake growth mechanism to the nanostructure growth. It enriches our understanding on the fundamental kinetics of nanostructured crystal growth and provides a transformative strategy to achieve rational design and control of nanoscale geometry.

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[*] **NSTD Student Award Finalist**

5:40pm **EM+NS+SP+SS-WeA11 Detecting the Invisible - The Atomic Structure of Radiation Sensitive Nano-Materials**, ***Christian Kisielowski,*** Molecular Foundry, Lawrence Berkeley National Laboratory; *P. Specht,* University of California Berkeley **INVITED**

As heterogeneous materials scale below 10 nm, a suitable combination of single digit nanocrystals with their rich variety of tunable surfaces and interfaces allows tailoring unprecedented materials with novel structure-function relationships. The design of new catalysts [1], investigations of polymers at atomic resolution [2] or analyses of deviations from a random doping distributions at atomic resolution [3] may serve as examples. This contribution describes research that aims at exploiting the emerging ability to analyze and understand such materials by directly determining their atom arrangement in three-dimensions using aberration-corrected transmission electron microscopy [4]. Attempts to unravel the atomic structure of such nanoscale composites in this manner must explicitly address their pronounced sensitivity to the probing radiation that can unintentionally alter their pristine structure, often beyond recognition. We address this challenge by applying low dose-rate in-line holography [5], which allows operating electron microscopes with dose rates as low as 5-10 e/Å^{2}s that help maintaining structural integrity at atomic resolution to an unexplored end. The approach mimics best practices in biological research but achieves atomic resolution with single atom sensitivity by the acquisition of large image series. We observe a variety of previously unknown atom configurations in surface proximity of CoO$_x$ nanocrystals and coatings that are hidden behind unusually broadened diffraction patterns but become visible in real space images because the phase problem is solved. The observed structures are drastically altered by an exposure of the material to water vapor or other gases, which is investigated at atomic resolution in environmental electron microscopy. It is shown for Rh/W catalysts that electron beam-induced atom dynamics can be entirely suppressed even for atom clusters made from less than 10 atoms. Resultantly, chemical compositions can be determined by contrast measurements alone and functional processes can be triggered and tracked in real time at atomic resolution.[6]

[1] J. A. Haber et al., **Advanced Energy Materials** 5 (2015) 1402307

[2] D. Lolla et al., **Nanoscale** 8 (2016) 120 - 128

[3] P. Specht, C. Kisielowski, On the chemical homogeneity of InxGa1-xN alloys - Electron microscopy at the edge of technical limits, submitted (2016)

[4] F.R. Chen et al., **Nature Commun**. 7:10603 doi: 10.1038/ ncomms10603 (2016)

[5] C. Kisielowski, **Advanced Materials** 27 (2015) 5838-5844

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

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 103A - Session HC+NS+SS-WeA

Nanoscale Surface Structures in Heterogeneously Catalyzed Reactions

Moderator: Arthur Utz, Tufts University

2:20pm **HC+NS+SS-WeA1 Ceria Nanoclusters on Graphene/Ru(0001): A New Model Catalyst System**, *Z. Novotny,* Pacific Northwest National Laboratory; *F.P. Netzer,* Karl-Franzens University, Austria; ***Zdenek Dohnalek,*** Pacific Northwest National Laboratory **INVITED**

Cerium oxide is an important catalytic material known for its ability to store and release oxygen, and as such, it has been used in a range of applications, both as an active catalyst and as a catalyst support. Using scanning tunneling microscopy and Auger electron spectroscopy, we investigated the growth of ceria nanoclusters and their oxygen storage/release properties on single-layer graphene (Gr) on Ru(0001) with a view towards fabricating a stable system for model catalysis studies. The ceria nanoclusters are of the CeO$_2$(111)-type and are anchored at the intrinsic defects of the Gr surface and display a remarkable stability against reduction in ultrahigh vacuum up to 900 K, but some sintering of clusters is observed for temperatures > 450 K. The evolution of the cluster size distribution suggests that the sintering proceeds via a Smoluchowski ripening mechanism, i.e. diffusion and aggregation of entire clusters. To follow the cluster redox properties we examined their oxygen storage and release in an oxygen atmosphere (<10^{-6} Torr) at elevated temperature (550 – 700 K). Under oxidizing conditions, oxygen intercalation under the Gr layer is observed. Time dependent studies demonstrate that the intercalation starts in the vicinity of the CeO$_x$ clusters and extends until a completely intercalated layer is observed. Atomically resolved images further show that oxygen forms a p(2×1) structure underneath the Gr monolayer. Temperature dependent studies yield an apparent kinetic barrier for the intercalation of 1.2 eV. At higher temperatures, the intercalation is followed by a slower etching of the intercalated Gr (apparent barrier of 1.6 eV). Vacuum annealing of the intercalated Gr leads to the formation of carbon monoxide and causing etching of the Gr film thus revealing that the spillover of oxygen is not reversible. These studies demonstrate that the easily reducible CeO$_x$ clusters act as intercalation gateways capable of efficiently delivering oxygen underneath the Gr layer.

3:00pm **HC+NS+SS-WeA3 Lowering the Barrier to C-H Activation using Pt/Cu Single Atom Alloys**, ***Matthew Marcinkowski,*** *M. El Soda, F.R. Lucci, E.C.H. Sykes,* Tufts University

Due to the increased in shale gas production in recent years the availability of light alkanes such as ethane and propane has increased significantly. Although these chemicals are typically considered inert, the ability to cleave C-H bonds in alkanes would allow for production of alkenes, which are important precursors to polymers. In this work, we use a surface science approach to model C-H activation on a Cu(111) surface using methyl iodide. Methyl iodide is known to decompose to produce methyl groups and iodine atoms on Cu(111) below 200 K. The methyl groups are then stable on the surface up until 450 K, at which temperature they decompose to form a number of products including methane, ethylene, ethane, and propylene. The rate limiting step to forming these products is the activation of one of the C-H bonds in the methyl group to produce surface bound hydrogen and methylene. Pt(111) is also able to activate the C-I bond in methyl iodide, but methyl groups on this surface only produce methane, hydrogen, and surface bound methylene groups at 290 K. While the barrier to C-H activation is lowered on Pt compared to Cu, the Pt surface is unable to perform carbon coupling reactions. Inspired by these previous results, we fabricated surfaces consisting of 1% Pt in the Cu(111) surface. At this concentration, Pt exists as single, isolated atoms substituted into the Cu(111) lattice. These *single atom alloys* exhibit synergistic chemistry and yield the desirable properties of each of the two pure metal surfaces. They are able to produce carbon coupling products like pure Cu, but are able to activate the C-H bond necessary to begin these reactions at 340; 110 K cooler than on Cu(111). Increasing the concentration of Pt further decreases the temperature necessary to activate C-H bonds, but also decreases the amount of carbon coupling products formed as the surface becomes more similar to Pt(111). Single atom alloys therefore provide an ideal model catalyst for the decomposition of methyl iodide, allowing for more facile activation of the C-H bond than pure Cu while also producing the desired coupling products, which Pt(111) is unable to do.

3:20pm **HC+NS+SS-WeA4 Formation, Migration and Reactivity of Au-CO Complexes on Gold-Surfaces**, ***Jun Wang,*** Oak Ridge National Laboratory; *M. McEntee, W. Tang, M. Neurock,* University of Virginia; *A.P. Baddorf, P. Maksymovych,* Oak Ridge National Laboratory; *J.T. Yates, Jr.,* University of Virginia

We report experimental as well as theoretical evidence that suggests formation of Au-CO complexes upon the exposure of CO to active sites (step edges and threading dislocations) on a Au(111) surface. Room-temperature scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy, transmission infrared spectroscopy, and density functional theory calculations point were combined to investigate morphological changes of the Au(111) surface with an intentionally created array of etch-pits. Room-temperature STM of the Au(111) surface at CO pressures in the range from 10^{-8} to 10^{-4} Torr (dosage up to 10^6 langmuir) indicates Au atom extraction from dislocation sites of the herringbone reconstruction, mobile Au–CO complex formation and diffusion, and Au adatom cluster formation on both elbows and step edges on the Au surface. The formation and mobility of the Au–CO complex result from the reduced Au–Au bonding at elbows and step edges leading to stronger Au–CO bonding and to the formation of a more positively charged CO (CO$^{\delta+}$) on Au. Our studies indicate that the mobile Au–CO complex is involved in the Au nanoparticle formation and reactivity, and that the positive charge on CO increases due to the stronger adsorption of CO at Au sites with lower coordination numbers.

ACKNOWLEDGEMENTS: Part of this research was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility .

Reference: J. Wang, M. McEntee, W. Tang, M. Neurock, A. P. Baddorf, P. Maksymovych, and J. T. Yates, Jr., *J. Am. Chem. Soc.* 138, 1518 (2016)

4:20pm **HC+NS+SS-WeA7 Sulfur-Metal Complexes on Surfaces of Copper, Silver, and Gold***, **Patricia A. Thiel,*** Iowa State University*; H. Walen,* RIKEN Surface and Interface Science Laboratory, Wako, Saitama, Japan*; D.-J. Liu,* Ames Laboratory, Ames, IA*; J. Oh,* RIKEN Surface and Interface Science Laboratory, Wako, Saitama, Japan*; H.J. Yang,* University College London, UK*; Y. Kim,* RIKEN Surface and Interface Science Laboratory, Wako, Saitama, Japan **INVITED**

The nature of sulfur interaction with surfaces of coinage metals (M=Cu, Ag, Au) is relevant to aspects of heterogeneous catalysis, corrosion, and self-assembled monolayers. We have discovered a number of unexpected complexes—independent, molecule-like MxSy species—that form on low-index M surfaces. In a sense, these complexes are iidway between the well-known phenomena of chemisorption and adsorbate-induced reconstruction. Our primary experimental tool is scanning tunneling microscopy (STM) used in ultrahigh vacuum. We tailor our experimental conditions to isolate the complexes, by working at ultra-low sulfur coverage to avoid competition from surface reconstructions. Furthermore, we prepare the surface at 300 K, but image at 5 K, in order to immobilize these small species. Density fucntional theory (DFT) is used to interpret the experimental results. For instance, application of DFT is essential to identify the complexes that form on Cu(111), Ag(111), and Au(100), and this identification is made both on the basis of their physical characteristics in real vs. stiimulated STM images (size, orientation, shape) as well as their calculated stability. On other surfaces, including Au(111), Cu(10o0), and Au(110), MxSy complexes do not form under comparable conditions. This broad database and extensive analysis provides insights into factors that favor complexation in this class of systems.

5:00pm **HC+NS+SS-WeA9 Titania/Gold Inverse Model Catalysts for Acetaldehyde Formation from Ethanol***, **Ashleigh Baber**, D.T. Boyle, W. Andahazy, V. Lam, D. Schlosser, N. Tosti, J. Wilke,* James Madison University

The fundamental investigation of the catalytic chemistry of ethanol at interfaces is important for many fields including the automotive industry due to the use of ethanol as a fuel. The redox chemistry of small alcohols, including methanol and propanol, has been studied on Au(111) supported TiO_2 nanoparticles, yet the active site for the chemistry has not yet been elucidated. Here, the systematic study of ethanol has been investigated on Au(111) and TiO_2/Au(111) via temperature programmed desorption in an effort to gain insight on the interfacial role of the reactivity for ethanol, as a function of titania coverage. Ex situ atomic force microscopy was used to image the gold–supported titania particles, and X-ray photoelectron spectroscopy was used to confirm the presence of titania on the surface. The presence of TiO_2 nanoparticles on Au(111), ~25 nm in diameter, led to the catalytic conversion of ethanol to acetaldehyde at temperatures greater than 400 K. The interaction of ethanol with Au(111)–supported TiO_2 nanoparticles is markedly different than its interaction with the individual counterparts: bulk titania and gold, which both lead to the desorption of molecular ethanol at temperatures lower than 400 K.

5:20pm **HC+NS+SS-WeA10 Shape and Support Interaction of Size Selected Pt Nanoparticles in Presence of H_2***, **Mahdi Ahmadi**, F. Behafarid,* University of Central Florida*; B. Roldan Cuenya,* Ruhr-University Bochum, Germany

Pt nanoparticles (NPs) supported on TiO2 have been widely used as a catalysts in industrial applications.

Strong metal-support interaction (SMSI) is expected to occur for this system under reducing environments

such as vacuum and H2. Since the morphology of NPs depends on their surface energy and their interaction

with the support, investigating the shape of NPs could be an excellent pathway to understand the metal

support interactions. In this study we have investigated the in situ shape evolution of TiO2 supported Pt NP

using grazing incidence small angle X-ray scattering (GISAXS) during annealing in H2 environment. The

size selected Pt NPs with an initial spherical shape were synthesized via inverse micelle encapsulation

method. The sample was step annealed up to 700°C in H2 environment and the onset for NPs faceting was found to be 600°C. Annealing at a higher temperature (700°C) did not cause any further change in NPs

structure. The presence of a sharp scattering ray at 45° with respect to the surface normal indicates the (110)

facet to be the dominant side facet for Pt NPs and the top and interfacial facets to be Pt(100). These features

point out that the shape of Pt NPs supported on TiO2 under hydrogen environments is pyramidal. The

specific shape of Pt NPs are discussed based on the SMSI phenomenon.

5:40pm **HC+NS+SS-WeA11 Single Atom Alloys as a Strategy for Selective Heterogeneous Hydrogenation and Dehydrogenation Reactions***, **Charles Sykes**,* Tufts University **INVITED**

Catalytic hydrogenations are critical steps in many industries including agricultural chemicals, foods and pharmaceuticals. In the petroleum refining, for instance, catalytic hydrogenations are performed to produce light and hydrogen rich products like gasoline. Typical heterogeneous hydrogenation catalysts involve nanoparticles composed of expensive noble metals or alloys based on platinum, palladium, rhodium, and ruthenium. We demonstratedhow single palladium and palladium atoms can convert the otherwise catalytically inert surface of an inexpensive metal into an ultraselective catalyst.(1-3) High-resolution imaging allowed us to characterize the active sites in single atom alloy surfaces, and temperature programmed reaction spectroscopy to probe the chemistry. The mechanism involves facile dissociation of hydrogen at individual palladium atoms followed by spillover onto the copper surface, where ultraselective catalysis occurs by virtue of weak binding. The reaction selectivity is in fact much higher than that measured on palladium alone, illustrating the system's unique synergy.

Our *single atom alloy* approach may in fact prove to be a general strategy for designing novel bi-functional heterogeneous catalysts in which a catalytically active element is atomically dispersed in a more inert matrix. Very recently we demonstrated that this strategy works in the design of real catalysts. Platinum/copper nanoparticles can perform the industrially important butadiene hydrogenation at lower temperature using just 1% platinum.(3) Moreover, some of the best industrial alloy catalysts to date may already be operating via this mechanism, but there is currently no method to directly probe the atomic geometry of a working catalyst. Our scientific approach allows one to parse out the minimal reactive ensembles in an alloy catalyst and provide design rules for selective catalytic nanoparticle. *From another practical application standpoint, the small amounts of precious metal required to produce single atom alloys generates a very attractive alternative to traditional bimetallic catalysts.*

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MEMS and NEMS
Room 102B - Session MN+NS-WeA
Optomechanics, Photonics, and Quantum Nanosystems

Moderators: Leonidas Ocola, Argonne National Laboratory, Robert Ilic, National Institute of Standards and Technology, Center for Nanoscale Science and Technology

2:20pm **MN+NS-WeA1 Transducing between Microwaves and Light using Mechanics***, **Andrew Cleland**,* University of Chicago **INVITED**

In this talk, I will describe my group's progress in developing technology that would serve as a fundamental component of a quantum repeater, a hypothetical device that will be a central component for practical long-range quantum communication. The devices we have developed to date rely on the parametric conversion of signals between microwave and optical frequencies, via a strong optomechanical interaction in a suspended one dimensional photonic/phononic crystal. The device is coupled to a fiber optic line for transmission of classical (ultimately quantum) optical information, and its microwave frequency (few GHz) mechanical mode is strongly coupled to a piezoelectric transducer. This device would ultimately be coupled to a microwave frequency quantum bit, either based on superconducting or semiconducting quantum technology, which would serve to purify and/or entangle quantum information. I will include a brief description of our approach and a description of the current status of development. Worked is supported by grants from AFOSR and NSF.

3:00pm **MN+NS-WeA3 Single Laser Modulated Drive and Detection of a Nano-Optomechanical Cantilever**, ***Vincent Sauer***, *J.N. Bachman, Z. Diao, M.R. Freeman, W.K. Hiebert,* University of Alberta and The National Institute for Nanotechnology, Canada

Nano-optomechanical systems (NOMS) offer many advantages in transducing nanomechanical motion including very high displacement sensitivities and large frequency detection bandwidths due to their optical nature. It follows from this that NOMS are a promising avenue for on-chip nanomechanical mass sensing. To take full advantage of the operational frequency properties that NOMS devices possess it is important to drive the devices optically as well. Here, a single laser modulated drive and detection (SLMDD) system is modeled and demonstrated. The setup operates similarly to a traditional NOMS pump/probe system, but instead of using a separate probe laser with a constant output power, the probe laser is power modulated to coherently drive the nanomechanical resonator using an optical gradient force. Using the SLMDD system the second laser source and its optical filter can be removed from a standard NOMS measurement system reducing the cost and complexity. This results in signal mixing between the modulated optical pump power and the Lorentzian response of the nanomechanical cantilever. The response at 1f gives a fano-like shape, but we are still able to track this characteristic mechanical frequency within a phase-lock loop. This demonstrates that the device could still be used for inertial mass loading experiments which rely on mechanical frequency tracking. Interestingly, the SLMDD system also enables homodyne detection through the DC response. As such, this can circumvent some difficulties of measuring high frequency devices with lower frequency equipment.

3:20pm **MN+NS-WeA4 Optomechanical Limit Cycle Oscillations in Metallic Nanowires**, ***Roberto De Alba,*** *T.S. Abhilash, R.H. Rand, J.M. Parpia,* Cornell University

Guitar strings are possibly the most common example of mechanical systems in which the frequency is temperature dependent. MEMS devices are similarly subject to thermal forces, and can be parametrically controlled by them under the correct conditions. Silicon domes and suspended graphene membranes are two systems that have been shown to self-oscillate when illuminated with intense laser light -- both resulting from optical absorption and associated temperature fluctuations. Here we study these optomechanical effects in metallized silicon-nitride nanowires with 50 nanometer square cross-sections and 40 micrometer length. We observe stable limit-cycle behavior with an amplitude of roughly one-eighth of the impinging laser wavelength, and characterize entrainment of this motion with inertial forcing. Lastly, we attempt to overcome viscous air damping in these nanowires using these optical interactions. In future MEMS designs, self-driven motion using on-chip optical sources could be a viable alternative to external drive electronics or active feedback circuits.

4:20pm **MN+NS-WeA7 Transducer Array with Optomechanical Read-out and Integrated Actuation for Simultaneous High Sensitivity force Detection**, ***Thomas Michels****, Ilmenau University of Technology, Germany; *B.R. Ilic, V. Aksyuk,* National Institute of Standards and Technology; *I.W. Rangelow,* Ilmenau University of Technology, Germany

Research and development of transducers based on cavity optomechanics is a topic of high interest particularly because these transducers enable measurement of mechanical motion down to the fundamental limit of precision imposed by quantum mechanics. We have developed an on-chip cavity optomechanical transducer array that combines high bandwidth and high sensitivity with compactness, robustness, small size, and potential for low cost batch fabrication inherent in MEMS. The parallelization of multiple probes within one transducer array allows the simultaneous measurement of serial forces or mass detection.

Our fully-integrated, fiber-pigtailed transducer array combine high sensitivity (≈ 0.5 fm $Hz^{-1/2}$ to ≈ 10 fm $Hz^{-1/2}$), high bandwidth optomechanical readout and built-in thermal actuation. We use a wafer-scale microfabrication process combining one e-beam patterning, six stepper, and three contact mask aligner lithography steps. These define the silicon nitride (SiN) cantilever, the single-crystal silicon-on-insulator (SOI) microdisk optical cavity with high optical Q (up to $2x10^{6}$), SOI optical waveguides, and the patterned gold layer for bimorph actuation. Back and front side anisotropic potassium hydroxide (KOH) silicon etch allows to overhang the cantilever over the edge of the silicon chip and to define v-grooves for single mode optical fiber attachment. Two sacrificial silicon dioxide layers are removed by an isotropic hydrofluoric acid (HF) etch to free the mechanically movable structures.

The SiN cantilever can be excited by an electrical signal supplied to an integrated thermal actuator. The cantilever is evanescently coupled to a high-Q optical whispering gallery mode of the optical microdisk cavity and the motion is detected by measuring the resonance frequency shift of the optical cavity mode. The actuator can be used to individually address the cantilever and dynamically move them as well as to tune the distance between the cantilever and the optical cavity, to change the sensitivity and range of measurement of the cantilever. One side of the cantilever overhangs the edge of the chip, where it can be easily coupled to a variety of off-chip samples and physical systems of interest. A 10 um long probe is currently designed to have a stiffness of 0.1 N/m to 5 N/m and a resonance frequency of 50 kHz to 2 MHz, while the design can be easily and broadly tailored for specific sensing applications.

4:40pm **MN+NS-WeA8 Magnetic Resonance Spectroscopy with Torsional Optomechanics**, ***Mark Freeman,*** University of Alberta and The National Institute for Nanotechnology, Canada **INVITED**

A broadband magnetic resonance spectrometer based on optomechanical detection will be described. Demonstrations of inductive detection of spin precession in the early 1940s launched magnetic resonance spectroscopy as a general-purpose tool. As an easily miniaturizable complement to this, a resonant AC torque on a mechanical torsion sensor is choreographed from the precessing transverse RF moment via frequency mixing and then recorded through optical interferometry.

Comprehensive electron spin resonance spectra of a single-crystal, mesoscopic yttrium iron garnet disk at room temperature will be presented to illustrate the approach. A key feature of the method is that it is broadband to DC, enabling measurements of the intricate magnetostatics of individual mesoscopic magnetic objects to be performed simultaneously with the spin resonance studies. Progress in enhancing the detection sensitivity with nanocavity optomechanics also will be reported.

Work performed in collaboration with J Losby, F Fani Sani, D Grandmont, Z Diao, M Belov, J Burgess, S Compton, W Hiebert, D Vick, T Firdous (University of Alberta and National Institute for Nanotechnology, Edmonton), M Wu, N Wu, P Barclay (University of Calgary and NINT), and K Mohammad, E Salimi, G Bridges, D Thomson (University of Manitoba, Winnipeg). We are grateful for support from NSERC, NINT, AITF, and CRC.

Tribology Focus Topic
Room 101A - Session TR+AS+NS+SS-WeA

Nanoscale Wear: Applications to Nanometrology and Manufacturing

Moderators: Tevis Jacobs, University of Pittsburgh, Filippo Mangolini, University of Leeds, UK

2:20pm **TR+AS+NS+SS-WeA1 A Multi-Bond Model of Single-Asperity Wear at the Nano-Scale**, *Y. Shao,* Johns Hopkins University; *T.D.B. Jacobs,* University of Pittsburgh; ***Michael L. Falk,*** Johns Hopkins University **INVITED**

Single-asperity wear experiments and simulations have identified different regimes of wear including Eyring- and Archard- like behaviors. A multi-bond dynamics model based on Filippov *et al.* [Phys. Rev. Lett. **92**, 135503 (2004)] captures both qualitatively distinct regimes of single-asperity wear under a unifying theoretical framework. In this model, the interfacial bond formation, wear-less rupture and transfer of atoms are governed by three competing thermally activated processes. The Eyring regime holds under the conditions of low load and low adhesive forces; few bonds form between the asperity and the surface and wear is a rare and rate-dependent event. As the normal stress increases the Eyring-like behavior of wear rate tends to break down. A nearly rate-independent regime holds under high load or high adhesive forces; bonds form readily and the resulting wear is limited by the sliding distance. In a restricted regime of normal load and sliding velocity, the dependence of wear rate on normal load is nearly linear and independent of sliding velocity, as described by the Archard equation. Detailed comparisons to experimental and molecular

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* **NSTD Student Award Finalist**

dynamics simulation investigations have illustrated both Eyring and Archard regimes and an intermediate cross-over between the two.

3:00pm **TR+AS+NS+SS-WeA3 Surface Chemical and Tribological Studies of Solid Lubricants for Space***, **Jeffrey Lince**,* The Aerospace Corporation **INVITED**

Successful operation of satellites and launch vehicles requires using multiple moving mechanical assemblies (MMAs). The correct choice of lubricants and tribocoatings is critical for the operation of spacecraft MMAs. However, the space environment is challenging. Examples include vibration during launch, thermal cycling on orbit, and the need to work effectively for missions up to twenty years in duration without lubricant replenishment. Especially challenging is the need for tribomaterials to withstand the vacuum of space during lengthy missions. As such, they must exhibit low vapor pressures, since evaporation of lubricants can result in loss from and premature failure of devices, as well as contamination of sensitive spacecraft components. Although unique synthetic liquid lubricants are used heavily in spacecraft for a variety of applications, solid lubricants are used with many devices because of their low vapor pressure, lack of migration, relative insensitivity to temperature changes, and low contamination potential. Soft solid lubricants such as molybdenum disulfide (MoS_2) and polytetrafluoroethylene (PTFE) have been used traditionally. More recently, hard low friction coatings such as hydrogenated diamond-like carbon have shown promise for operation in vacuum with existing spacecraft lubricants, or even unlubricated operation in vacuum. In addition, increasing interest in low friction nanoparticles has highlighted their potential utility. Tribomaterials show performance in vacuum that differs from that in air. This issue is important for spacecraft hardware, because it is often prohibitive to test them in a space-like environment, including vacuum, before launch. In addition, degradation during long-term storage can occur, and real-time storage studies correlating surface chemical changes with tribological performance are lacking. In this talk, results will be presented from studies done at The Aerospace Corporation that elucidate the effects of vacuum and temperature extremes on the tribological performance of important spacecraft tribomaterials. Emphasis will be on correlating surface chemical and tribological properties.

4:20pm **TR+AS+NS+SS-WeA7 Molecular Control of Friction***, **Roland Bennewitz**,* INM - Leibniz Institute for New Materials, Germany*; J. Blass, BL. Bozna,* INM - Leibniz Institute for New Materials*; M. Albrecht, G. Wenz,* Saarland University **INVITED**

Molecular films on surfaces can be used to control friction if it is dominated by adhesive shear rather than surface deformation. The underlying molecular mechanisms can be explored by high-resolution friction force microscopy.

We have developed a molecular toolkit for the control of friction and adhesion by supramolecular interactions in aqueous environments. The contacting surfaces are functionalized by cyclodextrin molecules. The interaction is mediated by ditopic connector molecules with hydrophobic end groups which form inclusion complexes with the cyclodextrin molecules on opposing surfaces. Significant friction and adhesion has been measured in atomic force microscopy experiments for connector molecules with adamantane, ferrocene, and azobenzene end groups.

For adamantane connector molecules, adhesion is found to be strongly dependent on the pulling rate due to a transition from subsequent peeling of individual bonds for slow pulling to multivalency effects at fast pulling. In contrast, friction does not depend on the sliding velocity [1].

The use of azobenzene connector molecules allows for switching of adhesion and friction by light stimuli [2]. Switching of friction by electrochemical stimuli for ferrocene connector molecules is less effective due to molecular interactions which are specific to the connector molecules but do not change with the potential [3]. We will discuss differences in rupture and rebinding dynamics for the three connector molecules and their influence on the rate dependence of adhesion and friction.

Cyclodextrin molecules have also been included in stiff polymers whose end groups are attached to tips or surfaces. The polymer-functionalized surfaces exhibit interesting variations of shearing and peeling mechanisms.

1. Blass, J., et al., Dynamic effects in friction and adhesion through cooperative rupture and formation of supramolecular bonds. Nanoscale, 2015. 7(17): p. 7674-7681.

2. Blass, J., et al., Switching adhesion and friction by light using photosensitive guest-host interactions. Chemical Communications, 2015. 51(10): p. 1830-1833.

3. Bozna, B.L., et al., Friction Mediated by Redox-Active Supramolecular Connector Molecules. Langmuir, 2015. 31(39): p. 10708-10716.

5:00pm **TR+AS+NS+SS-WeA9 Plasticity Controlled Friction and Wear in Single-Asperity Contacts***, **Izabela Szlufarska**, L. Zhao, A. Li, C. Tangpatjaroen, D. Grierson,* University of Wisconsin - Madison **INVITED**

One of the critical challenges in designing materials with superior tribological properties is the current lack of understanding of the microstructural evolution that takes place in sliding contacts. Phenomena that contribute to such evolution are grain growth and refinement, evolution of dislocation networks, and interaction of dislocations with interfaces. In this talk I will discuss examples of how we use multi-scale simulations and atomic force microscopy (AFM) experiments to determine the role of microstructural evolution and plastic deformation in friction and wear. Specifically I will discuss: (i) Our developments of a continuum model that couples grain growth, plastic deformation, and mechanics. This model combines for the first time the phase field method, crystal plasticity, and finite element analysis of mechanical contacts, and parameters for this model are determined from atomistic simulations and experiments. The new model is capable of simulating deformation at strain rates comparable to those encountered in AFM experiments. (ii) Results from our molecular-level simulations on the effects of dopants on strength and wear resistance of nanostructured metal alloys. (iii) Discovery from our complementary AFM and nanoindentation experiments that, although a harder material (silicon carbide) is typically more wear resistant than a softer material (silicon), this trend can be reversed with smaller contact sizes. The contact pressure is the same in both sets of experiments, and both are carried out in the regime where a plastic zone is well-developed. We demonstrate that this surprising finding is due to a transition from abrasive to adhesive wear, which for the first time is observed in single-asperity contacts. Our results show that surface chemistry can have a significant effect on sub-surface plastic deformation.

5:40pm **TR+AS+NS+SS-WeA11 Applying Analytical Roughness Models to Real Surfaces: Reconstructing the Power Spectral Density from Surface Topography Measurements***, **Tevis Jacobs**, A. Gujrati, S.R. Khanal,* University of Pittsburgh*; T. Junge, L. Pastewka,* Karlsruhe Institute of Technology (KIT), Germany

Surface topography is a critical factor for optical, mechanical, and tribological properties of materials. Many studies report single scalar roughness parameters that contain information over just a limited range of wavelengths. Analytical models of roughness have shown in recent years that properties such as stiffness, adhesion, and friction depend on the nature of roughness across many length scales. The power spectral density (PSD) is the mathematical instrument that provides a description of surface roughness as a function of scale. A truly quantitative analysis of surface roughness in terms of the PSD is necessary to validate and apply these analytical roughness models. However, this is currently limited by: (A) inconsistencies in the way that the quantitative PSD is computed; (B) bandwidth-limits of conventional surface metrology; and (C) instrumental artifacts at the smallest scales. Here, we demonstrate these limitations – first, by comparing the various forms of the PSD, then by computing the PSDs both for simulated and experimental surfaces.

We show that experimentally-determined PSDs suffer three types of systematic error, each of which will hinder quantitative comparison to models. We demonstrate strategies for detection and mitigation of these artifacts, to ensure accurate and reliable PSDs. A novel web-based application has been created and made available for general use which computes accurate PSDs and assesses the limits of their reliability. This enables the application of analytical roughness models to calculate upper and lower bounds of surface properties.

Finally, we report on the roughness characterization of an ultrananocrystalline diamond (UNCD) surface over the range from Angstroms to centimeters. This range of characterization enables quantitative comparison with rough-surface adhesion models. By elucidating experimental barriers to accurate surface characterization, and by demonstrating solutions to these barriers, this work facilitates the application of analytical roughness models to real-world surfaces – both to predict and tailor surface properties.

6:00pm **TR+AS+NS+SS-WeA12 Universal Ageing Mechanism for Static and Sliding Friction of Metallic Nanoparticles***, M. Feldmann,* ***Dirk Dietzel****, A. Schirmeisen,* Institute of Applied Physics, Justus-Liebig-University Giessen, Germany

On the macroscale, the distinct difference between static and sliding friction can well be explained by the phenomenon of contact ageing, which is typically related to an increase of contact area with time within a multi asperity interface model. On the nanoscale, however, the role of contact ageing is less clear, especially when considering nanoscale asperities of constant size.

Recently, the role of contact ageing for nanoscale friction dynamics was analyzed for antimony nanoparticles sliding on HOPG. The antimony nanoparticles have been prepared by thermal evaporation on HOPG and comprise an ideal model system with atomically flat interfaces of constant size where friction can be described by the concept of structural superlubricity [1]. Friction of the particles was assessed by nanomanipulation techniques and it was found, that sliding friction can be described as a complex process of thermally activated contact ageing and bond breaking [2]. Further measurements have now revealed, that the particle movement follows an irregular stick slip pattern, where the slip events can be considered as recurring contact renewal, while the stick times can be interpreted as the age of the contact. By correlating the stick times with the lateral force values measured for contact breaking, we found that our system can well be described by logarithmic ageing [3], as it might be expected by assuming atom by atom relaxation processes at the interface.

To check whether ageing during sliding motion is fundamentally different from ageing under stationary conditions, we have performed additional “slide hold slide” measurements [4] and found that in both cases ageing can be described by exactly the same logarithmic function. This indicates, that the strength of the contact is determined by the ageing time but independent of the kinetic conditions. This means that static and sliding friction can be described by a universal ageing law where the age of the contact is the crucial parameter.

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Advanced Ion Microscopy Focus Topic
Room 104A - Session HI+NS-ThM

Fundamentals of Ion Beam Microscopy

Moderators: Armin Gölzhäuser, Bielefeld University, Germany, Philip D. Rack, The University of Tennessee Knoxville

8:00am **HI+NS-ThM1 Generation of Hydrogen Beams using Single Atom and Trimer Nanotips***, **Radovan Urban,*** University of Alberta and The National Institute for Nanotechnology, Canada*; K. Nova,* University of Alberta, Canada*; M. Salomons,* National Institute for Nanotechnology, Canada*; R.A. Wolkow,* University of Alberta and The National Institute for Nanotechnology, Canada*; J.L. Pitters,* National Institute for Nanotechnology, Canada

Hydrogen ion beams have been discussed as useful for scanning ion microscopy (SIM) due to their low mass and low sputtering rates. However, hydrogen ion beams are known to occur as mixtures of H^+, H_2^+ and H_3^+ depending on the electric field strength. There is some evidence that various tip orientations contribute differently to the ratios of the ions and also that site-specific regions also affect the gas species but it has not been clearly determined. Understanding the relationship between the field strength dependence, tip shape, and apex termination with specific hydrogen ion creation is therefore critical to prepare pure hydrogen ion beams of a single species. We employed W and Ir to prepare atomically sharp nanotips with various atomic arrangements at the very apex to compare the ratios of H^+, H_2^+ and H_3^+.

The experimental setup included a custom field ion microscope (FIM) operating in ultrahigh vacuum (base pressure $<5x10^{-11}$ Torr). The tip was mounted on a heating loop wire for degassing and could was cooled with a liquid helium flow cryostat. Nanotips were prepared from tungsten single crystal W(111) wire and polycrystalline Ir wire using the field assisted chemical etching method. A magnetic field of ~1T was generated using two permanent magnets mounted between the extractor and the micro-channel plate.

The hydrogen beam composition from a single atom W(111) and Ir nanotips at different applied tip voltages was recorded and analyzed. At low voltages the H_2^+ beam dominates. As the voltage is increased, H_3^+ is also observed until it dominates at larger voltages. In this manner, a particular species can be selected depending on the operating voltage. Furthermore, comparing the hydrogen beam composition between W(111) single atom tip and trimer structure reveal important differences. For trimer nanotip, H_2^+ becomes a significant species and equals the H_3^+ current. However, in the case SAT, H_3^+ becomes the only contribution to ion current at higher voltages resulting in pure H_3^+ beam suitable for imaging.

Relative ratios of H^+, H_2^+ and H_3^+ were studied as a function of tip material (tungsten and iridium), applied voltage, and tip apex structure (single atom and trimer nanotips). We have determined that the tip structure and apex termination for both tungsten and iridium nanotips play important roles in the production of hydrogen ion beams. It has been found that single atom tip at high tip voltages produces nearly pure H_3^+ beam.

8:20am **HI+NS-ThM2 High-brightness Xenon Gas Field Ion Source from a Single-Atom Tip***, **Ing-Shouh Hwang,*** Institute of Physics, Academia Sinica, Taipei, Taiwan, Taiwan, Republic of China*; W.T. Chang, W.C. Lai, P.-C. Li,* Institute of Physics, Academia Sinica, Taipei, Taiwan*; T.Y. Fu,* Department of Physics, National Taiwan Normal University, Taipei, Taiwan*; T.T. Tsong,* Institute of Physics, Academia Sinica, Taipei, Taiwan

Current focused ion beam systems are mainly equipped with liquid metal ion sources (LIMSs). Even though LMISs are very reliable in operation, their relatively large source size and high energy spread limit the current density. In contrast, gas field ion sources**(**GFISs) can reach higher beam currents at smaller beam diameters because of their atomic-scale source size and a small energy spread (<1 eV). Since 2006, Zeiss Orion helium ion microscope (HIM) has demonstrated superior performance with a spatial resolution better than 0.5 nm [1]. To expand the application of GFISs, it is essential to develop GFISs of various ion species, particularly, ions of high mass.

Here we present Xe-GFIS emitted from a noble metal covered W(111) single-atom tip (SAT) [2,3]. This type of SATs are thermally and chemically stable, and high-brightness helium, neon, argon, hydrogen, oxygen, and nitrogen GFISs have been generated [4,5]. The Xe-GFIS also exhibits a very narrow beam with a half opening angle of ~0.5°. The ion current stability is good (instability ~2%). The reduced brightness of Xe-GFIS is measured to be 1.3×10^8 $Am^{-2}sr^{-1}V^{-1}$ at the gas pressure of 10^{-4} torr, 3 orders of magnitude higher than that of Ga-LMIS and several orders of magnitude higher than that of Xe magnetically enhanced inductively coupled plasma ion source ($5.4x10^3$ $Am^{-2}sr^{-1}V^{-1}$) [6]. In principle, the brightness of the Xe-GFIS can be further enhanced at a higher gas pressure or by using an emitter of a larger radius. The operation temperature can be ~200 K, which is much higher than the cryogenic temperature required for HIM. Thus Xe-GFIS-FIB would be easier to implement than HIM and may become a powerful tool for nanoscale milling and secondary ion mass spectroscopy.

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8:40am **HI+NS-ThM3 New Ion Source for Nanofabrication and Microscopy***, **Adam Steele,** B. Knuffman, A. Schwarzkopf,* zeroK NanoTech Corporation*; J.J. McClelland,* National Institute of Standards and Technology (NIST) **INVITED**

Performance measurements from a recently constructed focused ion beam (FIB) prototype that employs a new ion source technology will be presented. The performance of any FIB system, and hence the tasks to which it is best suited, are typically determined by its ion source. The high brightness and low energy spread of the Low Temperature Ion Source (LoTIS) employed here has the potential to enable significantly smaller focal spot sizes across a range of beam currents and beam energies in an optimized FIB.

The LoTIS consists of a laser-cooled atomic beam of cesium which is compressed and then photoionized within a volume of a few cubic micrometers. A uniform electric field is applied to form an ion beam. The micro-kelvin temperature of the neutral atoms results in a Cs^+ beam with a low intrinsic transverse velocity spread, yielding low emittance. The small energy spread is determined in this source by the finite spatial extent over which ions are created in a uniform electric field of approximately 10^5 V/m. Previous measurements have shown was shown that LoTIS can achieve a brightness in excess of $1×10^7$ A m^{-2} sr^{-1} eV^{-1} and an energy spread less than 0.34 eV [1].

This brightness and energy spread imply that, when coupled to an optimized ion acceleration and focusing column, a d_{50} spot size of 1 nm should be achievable at 1 pA. The source has also achieved total currents over 5 nA, albeit at a reduced brightness. Among other benefits, these source characteristics are expected to enable a FIB with better nanomachining performance and reduced subsurface damage.

The presentation will also briefly discuss FIB equipped with a similar Li^+ ion source technology that offers a unique capability to site specifically deposit lithium into target substrates.

[1] B Knuffman, AV Steele, and JJ McClelland. *J. Appl. Phys*. **114**, 4 (2013).

9:20am **HI+NS-ThM5 Recent Liquid Metal Ion Source developments for Improving Focused Ion Beam Machines***, **Jacques Gierak,*** LPN-CNRS, Route de Nozay France*; L. Bischoff,* Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, Germany*; P. Mazarov, L. Bruchhaus,* Raith GmbH, Germany*; P. Lozano, C. Perez Martinez,* Massachusetts Institute of Technology **INVITED**

Nowadays Focused Ion Beams (FIBs) machines have become very important tools capable of fulfilling many challenges ranging from micro- to nanofabrication. These tools are widely used both for industrial**[1]** and emerging nanosciences applications**[2]**.

Traditionally FIB technology has been mainly based on gallium Liquid Metal Ions Source. The very high brightness, long lifespan, small source size of the gallium LMIS, and its easy handling, remain its chief and most decisive advantages, but some weaknesses are also well known that inhibit improvements in the resolution of LMIS-based FIB. Therefore progress on ion sources operational characteristics remains very desirable.

In this presentation we will first summarize our recent efforts aiming at optimizing gallium LMIS "needle type" within a dedicated environment for stable operation at lowest possible emission currents. This effort and the important performance gains[3], we will detail, are a firm evidence that progresses can still be expected from this technology.

We will then review and detail the advantages of Liquid Metal Alloy Ion Sources (LMAIS) that represent a promising alternative to expand the already remarkable application field of FIB machines. Incoming ion species are found to influence significantly the properties of FIB-patterned nanostructures, in particular their electrical, optical, magnetic, and mechanical properties. A selection of the best suited elements transported in a focused ion beam will open new nanofabrication routes. In this presentation we will explain how nearly half of the elements of the periodic table can be made available to the FIB technology as a result of continuous research in this area during the last forty years[4] and how, in our opinion, nanotechnology can now take benefit of these.

Finally we will introduce Ionic Liquid Ion Sources (ILIS) that are capable to produce ion beams through field-evaporation from room temperature molten-salts[5]. The possibility of extracting both positive and negative ions having a composition that can be tuned by the selection of the polarity, the liquid chemical composition, the ion emission current and the ion landing energies represents a formidable perspective for FIB technology.

In conclusion we will summarize our vision on the future of FIB technology with improved performances, versatility and on the science frontiers it might help to push.

11:00am **HI+NS-ThM10 Elucidating the Directed Nanoscale Transformations when Building with Ions in Liquid***, A. Ievlev, V. Iberi, J. Jakowski, M.J. Burch, H. Hysmith, A. Belianinov, R.R. Unocic,* ***Olga Ovchinnikova,*** Oak Ridge National Laboratory

In-situ direct writing by ion beams from solutions opens a pathway for resistless fabrication of nanostructures with higher purity than standard gas phase deposition approaches like IBID. In particular the use of the helium ions with the opposite charge and shorter mean free path offers the potential for the localization of the reaction zone on the single digit nanometer scale. However, to fully control the interaction of the ion beam with the liquid to allow for single digit fabrication a comprehensive understanding of the radiolytic process as well as role of secondary iSE generated in solution has to be developed. Here we will present our results on the visualizing nanoparticle nucleation and growth parameters through data analytics on acquired in-situ growth movies and correlate these results to a fully encompassing time-dependent quantum dynamical simulation that takes into account both quantum and classical interactions. Additionally, with optimized instrument parameters and solution chemistry we are able to demonstrate writing of platinum structures from liquid (beam induced electroplating) in a platinum chloride solution using helium ions with sub-10 nm resolution. Furthermore, we will discuss opportunities for using in situ flow cell technology for understating of diffusion processes as they relate to direct writing with ions in solution.

Acknowledgements

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

11:20am **HI+NS-ThM11 Determination of an Upper Limit of Ionization Probability during SIMS Experiments using Laser Post-ionization***,* ***Nicholas Popczun****, L. Breuer,* Pennsylvania State University*; A. Wucher,* University of Duisburg-Essen, Germany*; N. Winograd,* Pennsylvania State University

The prospect of secondary ion mass spectrometry (SIMS) as a method of molecular imaging and molecular depth profiling of organic materials has grown with the implementation of polyatomic primary ion sources. These sources increase the total sputter yield and reduce chemical damage, creating a phenomena where the rate of damage removed by the primary ion beam exceeds the rate of damage created. Improving the sensitivity for molecular imaging and molecular depth profiling further relies on increasing the secondary ion yield of the molecular species. The most obvious suggestion to accomplish this is to increase the ionization probability, which has been estimated to be as low as 10^{-7} for atomic primary ion sources. Our lab has developed a method of directly measuring the total ionized and neutral sputtered molecular species located in the same volume sensitive to extraction. This measurement is accomplished by rastering a mid-IR femtosecond pulse for laser post ionization (LPI) of secondary neutral molecules in a two-dimensional plane perpendicular to the direction of laser propagation. Here, we apply this technique for the first time to organic molecules coronene and guanine. Two-dimensional representations of the spatial distribution of neutral molecular species sputtered by C_{60}^{+} bombardment are presented. Correction for undersampling of the laser volume and subsequent photofragmentation yields an upper limit for the ionization probability for each molecule. In general, this work provides a visual representation of the spatial distribution of sputtered, organic neutral molecules, delivering additional information for the improvement post-ionization techniques.

11:40am **HI+NS-ThM12 Studying Gas Cluster Ion Beam Sputter Yields and Surface Topography in the Helium Ion Microscope***,* ***Anders Barlow****, N. Sano, J.F. Portoles, P.J. Cumpson,* Newcastle University, UK

The applications of ion beams in surface analysis are large and clear in the recent literature. In our multi-user facility most projects benefit from the use of an ion beam processing step, whether for cleaning or oxide removal prior to chemical analysis, or for sputter depth profiling through an interface or layer. In our facility we have access to a number of different ion beams: argon monoatomic and gas cluster ion beams (GCIB), C_{60} ion beams, and on our ORION NanoFab, helium/neon ion beams and a gallium focussed ion beam (FIB). These beams serve numerous purposes, from cleaning of surfaces prior to chemical analysis in X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS), to depth profiling in these techniques, to imaging and FIB milling. In all cases however, the ion beam is interacting with the surface under analysis, and this interaction needs to be studied and well-understood. In chemical analysis such as XPS and ToF-SIMS, this requires knowledge of damage mechanisms that impact the reported chemistry from the technique [1]. Understanding how the ion beam can generate nanoscale topography that directly affects the measurements is paramount [2,3].

We are applying helium ion microscopy (HIM) to studying how the ion beams on our instruments change the surfaces we are analysing. The ultra-high resolution of the HIM allows us to see nanoscale topography on surfaces with new-found sharpness at very high magnification, elucidating the mechanisms behind topography formation during treatment. We have investigated the GCIB etching of indium phosphide (InP) using 8keV Ar_{300} clusters (i.e. 300 Ar atoms per cluster). InP is known to generate significant topography following ion beam irradiation. We observe with a spectacular level of clarity the mechanisms behind topography formation, surpassing other commonly used imaging techniques such as scanning probe and scanning electron microscopy. We can also relate the stages of nanotopography growth with total ion beam dose, from a single GCIB etch crater. With this new technique we can more confidently relate the results we obtain from XPS and ToF-SIMS with the topography we observe in the HIM.

[1] Barlow A.J et al., *J. Appl. Phys.***116**, 054908 (2014)

[2] Radny, T. and Gnaser, H., *Nanoscale Research Letters***9**, 403 (2014)

[3] Seah, M.P. et al., *Applied surface science***144**, 151-155 (1999)

[4] Cumpson, P.J. and Seah, M.P., *Measurement Science and Technology***1**, 544 (1990)

[5] Cumpson, P.J. et al., *J. Appl. Phys.***114**, 124313 (2013)

Advanced Ion Microscopy Focus Topic
Room 104A - Session HI+MI+NS-ThA

Ion Beam Based Imaging and Nanofabrication

Moderators: Jacques Gierak, LPN-CNRS, Shinichi Ogawa, AIST, Japan

2:20pm **HI+MI+NS-ThA1 Mask Repair Technology using Gas Field Ion Source***, **Anto Yasaka**, F. Aramaki, T. Kozakai, O. Matsuda,* Hitachi High-Tech Science Corporation, Japan **INVITED**

We developed a new ion beam based mask repair system using a gas field ion source (GFIS). For conventional photomasks, nitrogen ions were used to repair defects, while hydrogen ions were used for EUVL masks. We evaluated the performance of the mask repar system on MoSi based phase shift masks and EUV masks. The results demonstrates that GFIS technology is a reliable solution of repairing defects on high end photomasks for 1Xnm generation and beyond.

3:00pm **HI+MI+NS-ThA3 Application of an Advanced Bi Cluster LMIS for TOF-SIMS Analysis at the Nano-scale***, F. Kollmer, W. Paul, D. Rading, R. Moellers,* ION-TOF GmbH, Germany*; N.J. Havercroft,* ION-TOF USA*; E. Niehuis, **Julia Zakel**,* ION-TOF GmbH, Germany

In recent years, the application of cluster primary ions has become standard for all kinds of TOF-SIMS applications. Organic surfaces, in particular, benefit from the cluster bombardment due to a more efficient emission of molecular species compared to mono-atomic bombardment. However, the ultimate spot size so far has been obtained by Ga based liquid metal ion sources. In our contribution we will show that a Bi based cluster LMIS has the potential to outperform the established Ga LMIS even in terms of TOF-SIMS imaging at the highest lateral resolution.

We will discuss fundamental emission properties such as energy spread and virtual source size for the main species of a Bi cluster LMIS. Via a consistent optimisation of emission parameters and an adaption of the ion-optical column, a lateral resolution in the 20 nm range can be achieved. At this scale it seems that we are approaching the physical limits since not only the primary ion beam spot size, but also the size of the sputter cascade as well as the signal intensity limit the obtainable useful lateral resolution. Further progress requires the combination of the SIMS data with complimentary imaging techniques of higher lateral resolution or sophisticated sample preparation methods such as bevelling of the surface region with an FIB column.

In this respect we will show that a combined TOF-SIMS Scanning Probe Microscopy (SPM) provides the required information on the nanometer level. Moreover, information on surface topography and other physical properties of the scanned surface area can be obtained in-situ. The investigated samples include inorganic reference samples, alloys, biological samples, hybrid sample systems and thin films.

3:20pm **HI+MI+NS-ThA4 Nanoscale Imaging and Characterization of Interface Driven Assembly of Soft Materials via He-Ion Beam Microscopy***, **Matthew Burch**, A. Belianinov, D. Chang, Y. Luo, K. Hong, O.S. Ovchinikova,* Oak Ridge National Laboratory

The ability to directly image and characterize nanoscale structures and features of soft materials is key to understanding the role growth, interfaces and extrinsic stimuli have on the functionality of these materials. In particular, the arrangement and architecture of bottlebrush block copolymer systems is of interest, as material properties depend greatly on the organization and interfaces of these polymers during growth. However, due to the insulating nature of these materials, directly imaging surface features at the nanoscale using traditional electron microscopy based techniques is challenging. Alternatively, He-ion beam microscopy (HIM) has been developed to the level where it can now characterize and directly image the nanoscale surface features of these soft materials directly.

In this work, He-Ion microscopy is utilized to investigate the nanoscale structures of copolymer systems. In particular, the ordered periodic structures of bottle brush copolymer thin film systems are investigated to understand how different substrates and growth conditions impact the final periodic lamella and domain structures. Of particular interest is how the interface driven separation leads to different short range molecular and long rage surface ordering. Furthermore, we will discuss how surface ordering of the copolymers effects the functionality of the material by correlating HIM imaging results with local probing of electromechanical and electrochemical using scanning probe microscopy.

Acknowledgements

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

4:00pm **HI+MI+NS-ThA6 Advances in *Ex Situ* Lift Out and Manipulation Techniques for FIB Applications***, **Lucille Giannuzzi**,* EXpressLO LLC

The focused ion beam (FIB) *ex situ* lift out (EXLO) technique was the first lift out technique developed for transmission electron microscopy (TEM), surface science, and other site specific analysis of materials [1,2]. EXLO is well known for its ease, speed, and reproducibility, and is perfectly suited for manipulation of thick or electron transparent thin specimens for site specific microscopy or analytical characterization. EXLO is also perfectly suited for manipulation of electron transparent specimens to MEMS carrier devices used for *in situ* TEM holders. Micromanipulation techniques also aid in specimen preparation for particulates and fibers that require subsequent FIB milling. A review of EXLO and advances of the technique using a new slotted grid specimen carrier will be presented. This new grid negates the need for a carbon film specimen support and allows for additional specimen FIB milling or other post processing after manipulation [3].

[1] L.A. Giannuzzi et al., Mat. Res. Soc. Symp. Proc. 480 (1997) 19-27.

[2] F.A. Stevie et al., *Surf. Interface Anal.* 31 (2001) 345–351.

[3] L.A. Giannuzzi et al., *Microsc. Microanal*. 21 (2015) 1034-1048.

4:20pm **HI+MI+NS-ThA7 Helium Ion Microscopy Imaging of Carbon Nanofoams from Hydrothermal Carbonization of Sucrose***, **Natalie Frese**,* Bielefeld University, Germany*; S.T. Mitchell, A. Bowers, K. Sattler,* University of Hawaii*; A. Gölzhäuser,* Bielefeld University, Germany

Carbon nanofoam is considered as potential hydrogen storage material as well as cathode material for metal-air batteries. It is known that carbon nanofoam contains both sp^2- and sp^3-bonded carbon atoms. However, there is still a lack of knowledge about the atomic structure of this material. In this work, different types of carbon nanofoams were produced by low-temperature hydrothermal processing of carbon precursor materials. It was found that the produced foams have a low density and are uniform in their appearance. Helium-ion microscopy, X-ray photoelectron spectroscopy and Raman spectroscopy were used to characterize the foam samples. The results show good consistency between the micro- and nanostructure as well as the elemental composition. We conclude that hydrothermal processing of carbon precursor materials is an effective method to produce high-quality carbon nanofoams of graphitic nature.

4:40pm **HI+MI+NS-ThA8 Nanofabrication Limits in Layered Ferroelectric Semiconductors via He-ion Beam***, **Alexei Belianinov**, A. Ievlev, V. Iberi, H. Hysmith, M.A. Susner, M. McGuire, S. Jesse, S.V. Kalinin, O.S. Ovchinnikova,* Oak Ridge National Laboratory

Manipulating matter at progressively finer and ultimately atomic scales enables new functionality and effectively drives nanoscience. Currently, well understood, robust resist-based lithography, carries the brunt of nanofabrication, however local electron, ion and physical probe methods are improving as well, driven largely in part of their ability to fabricate without multi-step preparation processes that contaminate the sample with processing resists and solvents. Furthermore probe based methods extend beyond nanofabrication to nanomanipulation and imaging, vital ingredients to rapid transition to testing and manufacturing of layered 2D heterostructured devices.

In this work we demonstrate chemical and physical changes induced by a helium ion beam in a Helium Ion Microscope (HIM) with the surface of bulk copper indium thiophosphate (CITP) $CuM_{III}P_2X_6$ (M = Cr, In; X= S, Se) library of compounds of varying copper concentration; from 4–100%. Physical changes in micro- and nano-fabrication are explored via Atomic Force Microscopy, (AFM), and chemical changes are probed by Secondary Ion Mass Spectrometry, (SIMS). Our work illustrates controlled loss of ferrielectric domains, and nanostructure growth with material volumes scaling to the dosage of the helium ion beam. The nanostructures are oxygen rich, sulfur poor, with the copper concentration virtually unchanged. Effects of varying copper concentration on the quality of the fabricated nanostructures, as well as the differences in their chemical make-up will be discussed.

Acknowledgements

Research was supported (A. B., V. I., A. I., H. H., S. J. S. V. K. O. S. O) and partially conducted (AFM, HIM, SIMS) at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy. This work was also supported (M. S., M. M.) and partially conducted (material growth) by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division.

5:00pm **HI+MI+NS-ThA9 Focused Ion Beam Technology Challenges for Circuit Edit***, **Yuval Greenzweig**, Y. Drezner, A. Raveh,* Intel Corporation

The challenges of Circuit Edit (CE) using focused ion beam (FIB) are driven by the perpetual down-scaling of minimum features per VLSI process technology generation. The recent emergence of FIBs with much reduced probe sizes relative to Ga LMIS based tools, may provide a long-needed revitalization of FIB nanomachining capabilities such as FIB image resolution and machining acuity, necessary for nanomachining tasks such as CE. However, other requirements must go along, driving preferences of ion species, ion energies, and requirements for system performance in several areas.

Among the challenging requirements of CE is the task of milling in a controlled and planar fashion through layers of parallel metal lines with intervening dielectric, and end-pointing on a metal layer of choice. The end-pointing is based on the real-time secondary electron (SE) image during ion milling, and the requirement is leaving most of the target metal intact. If linear dimensions of features, such as minimum metal widths, reduce by a factor $\boldsymbol{\alpha}$ from one VLSI generation to the next, then maintaining quality realtime milling images, i.e., sufficient resolution and signal to noise, requires milling vertically through a layer proportional to $\boldsymbol{\alpha}^{-2}$ relative to the previous generation - same number of ions, but in a smaller pixel. On the other hand, the vertical thickness of the metals has also decreased by a, causing the etching to scale as $\boldsymbol{\alpha}^{-3}$ relative to the thinner new metal thicknesses. Previous VLSI process generation scaling factors have been approximately $\boldsymbol{\alpha} = 0.7$, so that the severity of this challenge has been getting worse by ~3X for several generations and is now at the feasibility limit. To improve on this, SE emission and collection efficiency must improve, and in particular SE collection efficiency of normally emitted SEs, which are the bearers of the information from the bottom of these milling boxes. The figure of merit representing this challenge is the SE yield times the SE detector collection efficiency, divided by the sputter yield (or etch rate), this provides opportunity for GFIS sources.

Other challenges of the CE application which providing preferences of ion species and ion energy will be discussed.

5:20pm **HI+MI+NS-ThA10 Ion-milling of Graphene Nanostructures While Supported and Unsupported: Considerations of Graphene Contamination, Substrate Scattering and Beam Tailing***, J. Swett,* Lockheed Martin Space Systems Company*; V. Iberi, D. Cullen, **Adam Rondinone**,* Oak Ridge National Laboratory

Graphene and other 2D materials offer novel characteristics and opportunities compared to traditional thin films. Common nanofabrication techniques including e-beam and nanoimprint lithography can be used to pattern atomically thin 2D systems but the multi-step processes they utilize result in exposure of the film to solvents and resists, and hence degradation of the material's novel electronic properties. Herein we demonstrate that helium and neon-ion milling are effective tools for the creation of very fine features with arbitrary geometries in supported and unsupported graphene, to include conductive structures, arrays of pores, and engineered defects. Properties of graphene, including contamination levels, play an important role in determining millability, as do instrumental parameters such as beam tailing and substrate scattering.

Acknowledgement

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

5:40pm **HI+MI+NS-ThA11 Interaction of Gas Field Ionized Nitrogen with Silicon***, **Marek Schmidt**, Y. Oshima, L.T. Anh, X. Zhang, T. Kanzaki, M. Akabori,* Japan Advanced Institute of Science and Technology, Japan*; A. Yasaka,* Hitachi High-Tech Science Corporation, Japan*; M. Muruganathan, T. Shimoda, H. Mizuta,* Japan Advanced Institute of Science and Technology, Japan

A larger number of gas molecules (among them helium, nitrogen and neon) can be ionized by the gas field ion source (GFIS) and used as projectiles in focused ion beam (FIB) systems. Among them, the nitrogen stands out as it forms a very strong covalent bond. It is not yet fully understood how this N_2 molecule behaves during field ionization and sample interaction, i.e. if and when the bond is broken. Previously, it has been shown that cross section studies are very useful in analyzing beam/sample interaction [1]. Here, we report scanning transmission electron microscopy (STEM) analysis of cross sections extracted from silicon bombarded with ionized N_2 molecules. The extracted implantation depths for ion energies of 25 and 16 keV are compared with theoretical values and suggest that the bond is broken during sample interaction. We use first principle molecular dynamics simulation to support this finding, in particular that the covalent bond is broken within the first few atomic layers of the impinged silicon target.

All nitrogen ion implantation was carried out in the GFIS-FIB nanofabrication system [2] located at the Japan Advanced Institute of Science and Technology. Line implantation was carried out on cleaned silicon. Following the cross section preparation STEM observation was conducted. For the 25 keV beam, an implantation depth of ~75 nm is observed, while this decreases to ~35 nm for the case of 16 keV. These values match the theoretically predicted values for the case that two nitrogen atoms are ionized with a single charge (N_2^+), and split upon impact. The splitting is also predicted by the molecular dynamics simulation we conducted.

These results help to give a clearer picture of the nitrogen ionization in a GFIS and the resulting beam. After ionization of the N_2 molecule through electron tunnelling into the atomically sharp emission tip, the ion is accelerated to the energy $E = E_0$and focused onto the sample. Upon interaction with the sample surface, the covalent bond is momentarily split. Consequently, each of the nitrogen atoms has only half of the energy $E = E_0/2$. The ion charge is dissipated in the substrate by transfer of an electron.

The help of M. Uno with the usage of the GFIS-FIB is acknowledged. The authors thank M. Ito for the help with TEM cross section preparation. This work is supported by the Center Of Innovation (COI) program of the Japan Science Technology Agency.

[1] R. H. Livengood et. al, *Nucl. Instrum. Methods Phys. Res. Sect. Accel. Spectrometers Detect. Assoc. Equip.*, vol. 645, no. 1, pp. 136–140, Jul. 2011.

[2] F. Aramaki et. al, in *Proc. SPIE 8441*, Yokohama, Japan, 2012, vol. 8441, p. 84410D–84410D–6.

6:00pm **HI+MI+NS-ThA12 Spatially Controlled Ripple Formation in the HIM using Low Voltages and High Temperatures***, **Gregor Hlawacek**, L. Sottili, M. Engler, S. Facsko,* Helmholtz-Zentrum Dresden Rossendorf, Germany

Ripple formation is a well known phenomenon that is observed for many materials under low energy ion bombardment. Often broad beam noble gas ion irradiation using energies of a few keV is employed to create these self-organized patterns on various metal, semiconductor and insulator surfaces. In addition to the fundamental interest in the formation and evolution of these structures they can be utilized in a number of new applications. Creating nano scale periodic roughness can be of interest for various microfluidic applications or to control friction in new MEMS and NEMS devices. However, these applications are not realized at their full potential today as the required sub micron patterning which can not easily be realized using broad beams.

Here, we present for the first time ripple patterns that have been created on the GaAs(001) surface using 5 keV Ne ions and elevated temperatures of up to 600 K in a Helium Ion Microscope (HIM). We will present the home built sample heater that can be loaded through the load lock of the Carl Zeiss Orion NanoFab and describe the influence on the device performance, as well as HIM operation at 5 keV.

The evolution of the ripple wavelength changes from 30 nm at low 1e17 Ne/cm² to 80 nm at 1e18 Ne/cm². The orientation of the ripples with respect to the shape can be changed by rotating the pattern on the surface and the influence of the geometrical constrains of the irradiated area on the ripple pattern is studied.

MEMS and NEMS
Room 102B - Session MN+2D+NS-ThA

Focused Session on Atomic Layer Nanomechanics and 2D MEMS

Moderators: Wayne Hiebert, National Institute of Nanotechnology & University of Alberta, Canada, Max Zenghui Wang, Case Western Reserve University

2:20pm **MN+2D+NS-ThA1 Exploring New Degrees of Freedom by Reducing Dimensions***, **Lincoln Lauhon**,* Northwestern University **INVITED**

Nanomechanical resonators fabricated additively from 1-D and 2-D nanomaterials present a wealth of scientific opportunities beyond those of conventional resonators fabricated in a subtractive manner from dielectric thin films. This talk will describe the interesting mechanical behaviors of 1-D VO_2 nanowires and 2-D MoS_2 membranes measured by scanning fiber optic interferometry and modeled using finite element methods. In the first case, nanowire resonators provide a compelling platform to investigate and exploit phase transitions coupled to mechanical degrees of freedom because resonator frequencies and quality factors are exquisitely sensitive to changes in state, particularly for discontinuous changes accompanying a first-order phase transition. To that end, correlated scanning fiber-optic interferometry and dual-beam Raman spectroscopy were used to investigate mechanical fluctuations VO_2 nanowires across the first order insulator to metal transition (*Nano Lett.***14**, 1898 (2014)). Unusually large and controllable changes in resonator frequency were observed due to the influences of domain wall motion and anomalous phonon softening on the effective modulus. In addition, extraordinary static and dynamic displacements were generated by local strain gradients, suggesting new classes of sensors and nanoelectromechanical devices with programmable discrete outputs as a function of continuous inputs. The same interferometric measurement method has been extended to study thermally driven displacements in square few-layer MoS_2 membranes (*Nano Lett.***15**, 6727 (2015)). Mechanical mode frequencies can be tuned by more than 12% by optical heating with the above gap illumination, and modes exhibit avoided crossings indicative of strong inter-mode coupling. When the membrane is optically excited at the frequency difference between vibrational modes, normal mode splitting is observed, and the inter-mode energy exchange rate exceeds the mode decay rate by a factor of 15. Finite element and analytical modeling quantifies the extent of mode softening necessary to control inter-mode energy exchange in the strong coupling regime. The observation of strong coupling suggests the feasibility of coherent control of mechanical modes in TMDs resonators, which would provide novel basis for developing phononic devices or exploring mechanical motions that mimic quantum phenomena.

3:00pm **MN+2D+NS-ThA3 Manipulating Nonlinearities in 2D NEMS***,* ***Akshay Naik,*** Indian Institute of Science, India **INVITED**

Nanoelectromechanical systems (NEMS) are exquisitely sensitive to various stimuli and make fantastic sensors. NEMS devices fabricated using top down fabrication techniques have already demonstrated the ability to measure mass of individual protein macromolecules and their potential use in mass spectrometry applications. NEMS devices fabricated using atomically thin membranes have the potential to bring the resolution of these devices down to single Dalton. However, nonlinearities in these 2D NEMS are quite prominent and can dramatically reduce the dynamic range of these sensors. It is thus imperative to employ strategies to minimize the effect of nonlinearities as well as to exploit them to improve the performance of these devices.

In this talk, I'll present two distinct ways in which we manipulate the nonlinearities in these atomically thin NEMS devices and improve their performance for sensing and oscillator applications. In the first method we manipulate bias voltages and strain in these devices to partially cancel out the nonlinearities present in the system. In the second method, we exploit the strong coupling between various vibrational modes to initiate internal resonance. The frequency stability, and thus the mass resolution, can be improved by orders of magnitude by operating these devices at internal resonances.

4:00pm **MN+2D+NS-ThA6 Wide Bandgap β-Ga_2O_3 Nanomechanical Resonators***,* ***Xu-Qian Zheng****, S. Rafique, J. Lee, L. Han, C.A. Zorman, H. Zhao, P.X.-L. Feng,* Case Western Reserve University

Among wide bandgap oxide semiconductors, β-Ga_2O_3 has recently been emerging as a promising candidate for future high-power electronics. Thanks to its direct wide bandgap, E_g≈4.9eV [1,2], power devices made of β-Ga_2O_3 may provide higher breakdown voltage even than that in high-power devices based on mainstream 4H-SiC and GaN materials. In addition to its excellent chemical and thermal stability [1, 2], β-Ga_2O_3 also possesses excellent mechanical properties (Young's modulus, E_Y≈300GPa) [3], providing opportunities for creating next generation nano- and micro-electromechanical systems (NEMS and MEMS) which can be suited for operations in harsh and extreme environments.

In this work, we describe the construction of β-Ga_2O_3 nanosheets and their suspended structures, toward the first demonstration of vibrating β-Ga_2O_3 drumhead nanomechanical resonators. The nanomaterials were synthesized on 3C-SiC film covered Si substrate using a growth temperature of 950°C for 1.5hrs. No metal catalyst was used for the synthesis of the nanomaterials. The nanosheets have a width of ~2-7μm and thickness of ~20-140nm. The crystal structure and the morphology of the nanosheets were investigated by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). From high resolution FESEM image, it was confirmed that the nanosheets originated from the sidewall of the nanorods. The selected area electron diffraction pattern (SAED) taken along the [10-1] zone axis reveals that the synthesized nanosheets are single crystalline β-Ga_2O_3. We investigate the elastic properties and resonant characteristics of such devices, by measuring flexural-mode resonances using ultrasensitive laser interferometry. We fabricate circular drumhead β-Ga_2O_3 resonators with a diameter of ~3μm using a dry transfer technique. Then, by measuring undriven thermomechanical noise spectra of β-Ga_2O_3 resonators, we observe the resonance characteristics of such resonators at 37MHz to 66MHz in high frequency (HF) range with quality (*Q*) factors ranging 100 to 420. In addition, we observe static mechanical behaviors of β-Ga_2O_3. We perform nano-indentation on these drumhead structures using AFM tips to further study the elastic modulus of β-Ga_2O_3. By combining measured elastic properties from resonances and nano-indentation, this study provides quantitative understanding of mechanical properties of β-Ga_2O_3, and paves the way for future nanomechanical devices engineering based on this new crystal.

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4:20pm **MN+2D+NS-ThA7 Nonlinear Mode Coupling and Internal Resonances in MoS_2 Nanoelectromechanical System***,* ***Chandan Samanta****, P. Gangavarapu, A.K. Naik,* Indian Institute of Science, India

Molybdenum-disulphide (MoS_2), a layered material has attracted attention for nanoelectro- mechanical system (NEMS) applications due to its ultralow mass density and extraordinary mechanical properties. Along with this, its direct band gap of 1.8eV (for monolayer MoS_2) offers the possibility of a new kind of transducer where its mechanical properties can be strongly coupled to its optical properties in visible range. MoS_2-NEMS has been realized recently using optical detection technique. This approach has its own difficulties to drive the resonator into nonlinear regime. On the other hand, mechanical nonlinearities play a crucial role in the performance of NEMS as its dimension shrinks down to atomically thin membrane. A clear understanding of nonlinear effects and the ability to control them are important from both fundamental and application points of view. In this report, we demonstrate fabrication of few layer MoS_2-NEMS and its characterization by three distinct all electrical actuation and detection schemes. We are able to detect multiple vibrational modes in our devices using all the three schemes. We are also able to drive the devices deep into nonlinear regime. Our devices show strong nonlinear coupling between multiple modes. The nonlinear modal coupling is so strong that it leads to multiple internal resonances. Although, there is a report on internal resonance in micromechanical system (MEMS), there is no reported evidence of internal resonance in NEMS made from atomically thin membrane. The observed internal resonances in our devices open the possibility for realizing high stability oscillator in very high frequency range.

4:40pm **MN+2D+NS-ThA8 Very-High-Frequency (VHF) Molybdenum Disulfide (MoS_2) Nanomechanical Resonators Operating in Liquid***, H. Jia,* ***Rui Yang****, P.X.-L. Feng,* Case Western Reserve University

Micro/nanoelectromechanical systems (NEMS/NEMS) have demonstrated versatile device technologies for sensing applications by exploiting their miniaturized dimensions and increasing sensitivities upon scaling.[1,2] However, quite limited flexural-mode resonators (mostly cantilevers and doubly-clamped beams) have been reported, with only fundamental-modes are often utilized that suffer from very low quality factors (*Q*<5) in viscous media.[3-6]

In this work, we experimentally demonstrate the operation of molybdenum disulfide (MoS_2) nanoscale drumhead resonators (1–5μm in diameter, 50–60nm in thickness) in fluidic environment (water), which exhibit robust multimode resonances in the high- and very-high-frequency (HF/VHF) bands. We observe ~10 flexural modes up to ~150 MHz in water. The *Q* factors can easily exceed 10 for fundamental modes, and achieve as high as ~30 for higher modes.

Atomic-layer MoS_2, an emerging two-dimensional semiconductor, has attracted tremendous attention due to its ultralight weight and high surface-to-volume ratio. These attributes suggest that MoS_2 nanoresonators hold potential for ultrasensitive sensing capabilities even in fluids. Meanwhile, drumhead structure exhibits sealed air cavity and multimode resonance characteristics, which help maintain device performance in liquid.

The MoS_2 resonators are directly immersed in water, and optothermally driven by an amplitude-modulated 405nm diode laser. The multimode resonances are interferometrically read out using a 603nm He-Ne laser. We observe ~10 flexural modes up to ~150 MHz with *Q* factors exceeding 10 for fundamental modes, and reach as high as ~30 for higher modes in water. We attribute the improved resonance performance (higher *f* and *Q*, as compared to cantilever beams) to the drumhead structure consisting of an air cavity on one side. We also demonstrate the degradation of resonance characteristics (*f*, *Q* dramatically drop) if water gradually leaks into the imperfectly-sealed nanodrum cavities.

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Nanometer-scale Science and Technology
Room 101D - Session NS+BI-ThA

Applied Nanoscale Microscopy Techniques/Biomaterial Interfaces – New Advances

Moderators: Stephanie Allen, The University of Nottingham, UK, Leonidas Ocola, Argonne National Laboratory

2:40pm **NS+BI-ThA2 Advancing the Development of Nanocrystal Emitters *via* Advanced Electron Microscopy Techniques**, ***James McBride***, *K.R. Reid, S.J. Rosenthal,* Vanderbilt University

The key tool for the characterization of nanoparticles has long been transmission electron microscopy. This technique can provide the size, shape, crystal structure and chemical composition of a nanocrystal. Aberration-corrected Z-STEM has enabled the visualization of the true core/shell structure of colloidal quantum dots, accelerating their commercial development.[1] Through dynamic STEM movies we have visualized the beam-induced motion of the surface atoms of nanocrystals and learned about the instability of the atomic structure of ultrasmall nanocrystals and the surface/sub-surface of large nanocrystals.[2] However, Z-contrast can be difficult to directly interpret due to the choice in shell material or uncertainty of the 3D morphology of large, thick-shelled quantum dots. Advancements in the detector design for performing STEM energy dispersive spectroscopy mapping (STEM-EDS) have greatly facilitated the chemical imaging of nanocrystals, enabling rapid identification of their chemical structure before significant beam damage occurs. With this technological advance, we have obtained the chemical composition of an individual nanocrystal and directly correlated to its individual photophysics using our recently developed correlation technique.[3] The unique combination of optical, structural and chemical information allowed us to determine the origin of the low quantum yield plaguing non-blinking CdSe/CdS quantum dots.[4] Further, STEM-EDS imaging will be presented showing development of InP/CdS and Zn_3N_2 nanocrystals. Included in the presentation will be specifics on sample preparation and the choice of beam current/spatial resolution and sample damage.

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2. McBride, J.R.; Pennycook, T.J.; Pennycook, S.J.; Rosenthal, S.J. The Possibility and Implications of Dynamic Nanoparticle Surfaces *ACS Nano***2013,** *7* (10), 8358-8365.

3. Orfield, N.J.; McBride, J.R.; Keene, J.D.; Davis, L.M.; Rosenthal, S.J. Correlation of Atomic Structure and Photoluminescence of the Same Quantum Dot: Pinpointing Surface and Internal Defects That Inhibit Photoluminescence *ACS Nano***2015,** *9* (1), 831-839.

4. Orfield, N.J.; McBride, J.R.; Wang, F.; Buck, M.R.; Keene, J.D.; Reid, K.R.; Htoon, H.; Hollingsworth, J.A.; Rosenthal, S.J. Quantum Yield Heterogeneity among Single Nonblinking Quantum Dots Revealed by Atomic Structure-Quantum Optics Correlation *ACS Nano***2016,** *10* (2), 1960-1968.

3:00pm **NS+BI-ThA3 Demonstration of Electron Mirror for Quantum Electron Microscopy**, ***Navid Abedzadeh***, *C.S. Kim, R.G. Hobbs, K.K. Berggren,* MIT

Electron mirrors have been used in electron microscopy techniques such as low-energy electron microscopy, mirror-corrected scanning electron microscopy and photoemission electron microscopy due to their ability to introduce chromatic and spherical aberrations of arbitrary sign. More recently, a design for a quantum electron microscope (QEM), an imaging approach based on interaction-free measurement, was proposed that could take advantage of an electron mirror whose surface was patterned with a topographic grating. This grating would produce a periodically varying potential close to its surface when a voltage was applied. As a result, the grating would diffract an incident electron plane wave, presenting an opportunity to develop a low-loss electron beam splitter. The diffracted beams produced by such a beam splitter could be used to probe a sample within an electron cavity to achieve an interaction-free measurement. An electron cavity could be formed when another electron mirror is placed slightly behind the back focal plane of the grating mirror. If a sample were placed inside this cavity, repeated weak interactions with the reflected/diffracted electron beam can be used to image the sample while keeping beam-induced sample damage arbitrarily low.

The approach outlined here will be used to characterize diffraction from the patterned mirror surface. Demonstration of electron diffraction from a patterned surface in a FESEM will represent a significant advancement toward the demonstration of a QEM system.

3:20pm **NS+BI-ThA4 Nanoscale Chemical Imaging by Photo-induced Force Microscopy**, ***Ryan Murdick,*** Molecular Vista

Nanoscale Chemical Imaging with Photo-induced Force Microscopy

Sung Park

Molecular Vista, Inc.

Infrared Photo-induced Force Microscopy (IR PiFM) is based on an atomic force microscopy (AFM) platform that is coupled to a widely tunable mid-IR laser. PiFM measures the dipole induced at or near the surface of a sample by an excitation light source by detecting the dipole-dipole force that exists between the induced dipole in the sample and the mirror image dipole in the metallic AFM tip. This interaction is strongly affected by the optical absorption spectrum of the sample, thereby providing a significant spectral contrast mechanism which can be used to differentiate between chemical species. Due to its AFM heritage, PiFM acquires both the topography and spectral images concurrently and naturally provides information on the relationship between local chemistry and topology. Due to the steep dipole-dipole force dependence on the tip-sample gap distance, PiFM spectral images have spatial resolution approaching the topographic resolution of AFM, demonstrating sub 10 nm spatial resolution on a variety of samples. PiFM spectral images surpass spectral images that are generated via other techniques such as scanning transmission X-ray microscopy (based on synchrotron source), micro confocal Raman microscopy, and electron microscopes, both in spatial resolution and chemical specificity. The breadth of the capabilities of PiFM will be highlighted by presenting data on various organic, inorganic, and low dimensional materials. By enabling imaging at the nm-scale with chemical specificity, PiFM provides a powerful new analytical method for deepening our understanding of nanomaterials and facilitating technological applications of such materials.

Bio: Sung Park is the CEO of Molecular Vista, which he co-founded with Prof. Kumar Wickramasinghe (UC Irvine, formerly of IBM) in 2011 to provide research and industrial tools for rapid and nanoscale imaging with chemical identification. Sung has 25 years of experience of industrial R&D, engineering, marketing and sales, and operations. Sung co-founded Park Scientific Instruments (PSI), which was one of the first commercial companies to develop and sell scanning tunneling microscopes (STM) and atomic force microscopes (AFM); PSI was acquired by Thermo Instruments in 1997, by which point PSI had sold upwards of 1,000 instruments to customers worldwide. Prior to founding Park Scientific Instruments, Sung worked as a post-doc at IBM Watson Research Center. Sung earned a Ph.D. in Applied Physics from Stanford University and BA in Physics from Pomona College.

4:00pm **NS+BI-ThA6 Strong Coupling of Localized Surface Plasmon Resonances to Light-Harvesting Complexes from Plants and Bacteria***, A. Tsargorodska, M. Cartron, C. Vasilev,* University of Sheffield, UK*; G. Kodali,* University of Pennsylvania*; J. Baumberg,* University of Cambridge, UK*; PL. Dutton,* University of Pennsylvania*; CN. Hunter,* University of Sheffield, UK*; P. Torma,* University of Aalto*; **Graham Leggett**,* University of Sheffield, UK

Plants and bacteria harvest solar energy with extraordinary efficiency. In chloroplasts, the quantum efficiency, defined as the fraction of captured photons that goes on to cause charge separation, is estimated to be ca. 90%. The mechanisms by which such extraordinary efficiencies are realised have been the subject of intense interest. We have explored the potential offered by plasmonic techniques for the investigation of biological light harvesting complexes. Macroscopically extended arrays of gold nanostructures are fabricated by interferometric exposure of an alkylthiolate SAM on gold, enabling the fabrication of macroscopically extended arrays of gold nanostructures in a rapid, simple process. After annealing, these structures yield strong localized surface plasmon resonances (LSPRs). In contrast to the behaviour observed for most proteins, the LSPRs are split when light-harvesting membrane proteins from purple bacteria and plants are attached to the gold nanostructures, yielding pronounced changes in their extinction spectra. The splitting is large, and is different for mutant proteins containing different pigment molecules, indicating that it is sensitive to the electronic structures of the membrane proteins. The splitting is attributed to strong coupling between the LSPRs and excitons in the light-harvesting complexes. The splitting is suggestive of an asymmetric Fano-type resonance, and the plasmon-exciton coupling has been modelled with coupled harmonic oscillators. The model yields good fits to the experimental spectra. It indicates that in light harvesting complexes 1 and 2 (LH1/2) from purple bacteria, coupling to the carotenoid *S2* state dominates, with a strength of ~ 0.2 eV. However, in a carotenoid-free mutant of LH1 the LSPR couples with a strength of ~ 0.1 eV to the bacteriochlorophyll Q_x transition, which has a smaller transition dipole moment than do the carotenoids. The coupling varies with the square root of the surface coverage of the protein, consistent with strong coupling theory. Strong coupling was also observed for self-assembling polypeptide maquettes that contain only chlorins. However, it was not observed for monolayers of bacteriochlorophyll, indicating that strong plasmon-exciton coupling is sensitive to the specific presentation of the pigment molecules.

4:20pm **NS+BI-ThA7 Microfluidic Device For Aptamer-Based Cancer Cell Capture And Genetic Mutation Detection***, **Sarah Reinholt**, H.G. Craighead,* Cornell University

Genetic mutations in cancer cells are not only fundamental to the disease, but can also have tremendous impact on the efficacy of treatment. Identification of specific key mutations in a timely and cost-effective way would allow clinicians to better prescribe the most effective treatment options. Here, we present a novel microfluidic device as a platform for specifically capturing cancer cells and isolating their genomic DNA (gDNA) for specific amplification and sequence analysis. To filter out rare cancer cells from a complex mixture containing a diversity of cells, nucleic acid aptamers that specifically bind to cancer cells are immobilized within a microchannel containing micropillars to increase capture efficiency. The captured cells are then lysed and the gDNA is isolated via physical entanglement within a secondary micropillar array. This type of isolation allows the gDNA to be retained within the channel, and enables multiple consecutive rounds of isothermal amplification in which different individual genes are amplified separately. The amplified gene samples undergo sequencing, and the resulting sequence information is compared against the known wildtype gene to identify any mutations. Cervical and ovarian cancer cells have been initially tested for mutations in the *TP53* gene using this technology. This approach offers a way to monitor multiple genetic mutations in the same small population of cells, which is beneficial given the wide diversity in cancer cells, and requires very few cells to be extracted from the patient sample. With this capability for genetic monitoring, precision medicine should be more accessible for the treatment of cancer.

4:40pm **NS+BI-ThA8 Molecular Processes in an Electrochemical Clozapine Sensor***, **Thomas Winkler**,* University of Maryland, College Park*; S.L. Brady,* East Carolina University*; E. Kim,* University of Maryland, College Park*; H. Ben-Yoav,* Ben-Gurion University of the Negev, Israel*; D.L. Kelly,* University of Maryland, Baltimore*; G.F. Payne, R. Ghodssi,* University of Maryland, College Park

Selectivity presents a crucial challenge in electrochemical sensing. One example is schizophrenia treatment monitoring of the redox-active antipsychotic clozapine (CLZ). To accurately assess efficacy, differentiation from its metabolite *N*-desmethylclozapine (NDMC) – similar in structure and redox potential – is critical. Here, we leverage biomaterials integration to study, and effect changes in, diffusion and electron transfer kinetics of these compounds. A key finding in our present work is differing dynamics between CLZ and NDMC once we interface the electrodes with chitosan-based biomaterial films. These additional dimensions of redox information can thus enable selective sensing of largely analogous small molecules.

Our study utilizes gold working electrodes either bare, coated with chitosan, or with our previously demonstrated redox cycling system (RCS). In the RCS, electrodeposited chitosan serves as a matrix to immobilize electroactive catechol near the electrode *via* electrografting. Small redox species diffuse through the film for oxidation at the electrode; the nearby catechol enables subsequent reduction of the analyte, establishing a signal-amplifying redox cycle. We execute cyclic voltammetry at 1m—10V/s sweep rates with CLZ, NDMC, or the model redox couple 1,1′-ferrocenedimethanol (FC).

With bare gold, both CLZ and NDMC exhibit similar (R^2=0.99) drastic increases in peak separation even at 0.5V/s, indicating slow electron transfer kinetics, in contrast to FC (Nernstian up to 3V/s). With both chitosan and the RCS we find that similarity broken. For diffusion, the coefficients D reveal two regimes in chitosan: dominance of bulk solution below 10mV/s (values match those from bare gold and theory), and diffusion inside the film becoming limiting at higher scan rates. This is reflected in *D* decreasing by 1.9× for FC, 17× for CLZ, and 31× for NDMC. The sharp difference between FC and the other larger two suggests a size-restriction phenomenon. The consistently 2× lower *D* for NDMC over the similarly sized CLZ points to possible electrostatic effects. With the RCS, signal amplification translates into apparent *D* increases – 9× over bare for FC, 5× for CLZ, and 3× for NMDC. Only at high scan rates does *D* decrease toward the chitosan-only value as true diffusion asserts dominance.

In conclusion, our results demonstrate the intricate interplay between biomaterials, biomolecules, and electrochemistry. They reveal intriguing distinguishing characteristics of CLZ from both the largely analogous NDMC as well as the model FC. This opens up avenues of utilizing diffusion and kinetics information to enhance selectivity in electrochemical sensing.

5:00pm **NS+BI-ThA9 Quantitative Quartz Crystal Microbalance Measurements across Transients Produced by Switching Fluid Properties***, V. Mugnaini, **Dmitri Petrovykh**,* International Iberian Nanotechnology Laboratory, Portugal

We systematically investigated Quartz Crystal Microbalance with Dissipation (QCM-D) measurements in aqueous solutions of model strong electrolytes that are commonly used in experiments with biological surfaces. In particular, we examined the quantitative behavior of both frequency and dissipation responses in transitions between two different aqueous solutions.

The abrupt changes in the QCM-D responses upon such transitions are sometimes referred to as “jumps” associated with switching the bulk properties of the fluid flowing through the QCM-D cell. Switching between fluids of different compositions may be important in a variety of QCM-D measurements for biointerfaces, e.g., when switching between a baseline/rinsing solution and a measurement solution, or switching between optimal buffers used for probe immobilization and for biorecognition steps [1-3]. In specialized quantitative biointerface measurements, such as measuring stabilities of DNA hybrids [2-3], switching among different solutions multiple times actually provides the basis for the measurement.

In typical QCM-D measurements, the baseline is reset after a “bulk jump”, so the data are typically only quantified between any transients, but not across them, i.e., quantification is carried out for a constant fluid composition, but not between different fluids. By considering the underlying viscoelastic formalism [4-5], we demonstrate in a series of systematic measurements for solutions of strong electrolytes that the QCM-D responses upon switching between different solutions can be quantitatively predicted and exhibit interesting scaling behavior. Classical theory of the viscosity of electrolyte solutions provides additional insight into correlations between the results measured for different salts.

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5:20pm **NS+BI-ThA10 ToF-SIMS/XPS Characterization of Frozen-Hydrated Hydrogels**, ***Michael Taylor***, *M.R. Alexander,* The University of Nottingham, UK; *M. Zelzer,* National Physical Laboratory, UK

Over the last decade the beneficial properties of hydrogels as artificial cell culture supports have been extensively investigated^1. Certain synthetic hydrogels have been proposed to be similar in composition and structure to the native extracellular matrix of the stem cell niche, their *in vivo* cell habitat, which is a powerful component in controlling stem cell fate^2. The stem cell differentiation pathway taken is influenced by a number of factors. When culturing cells within or upon hydrogels this choice can be strongly dependent on the underlying 3D hydrogel chemistry which strongly influences hydrogel-cell interactions^3. The interrelationship between hydrogel chemistry and that of biomolecules in controlling cellular response ideally requires analysis methods to characterise the chemistry without labels and often in 3D. Time-of-flight secondary ion mass spectrometry (ToF SIMS) has the potential to be utilised for through thickness characterisation of hydrogels. The frozen-hydrated sample format is well suited to minimise changes associated with dehydration or the chemical complexity of 'fixation', a challenging aspect in vacuum analysis conditions^4. Frost formation can occur in the ambient atmosphere preventing ready depth profiling of the frozen hydrogels^5. We develop a simple method to remove this frost by blowing with gas prior to entry into the instrument which is shown to produce remarkably good profiles on a poly(2-hydroxyethyl methacrylate) (pHEMA) hydrogel film where a model protein, lysozyme, is incorporated to demonstrate how biomolecule distribution within hydrogels can be determined. A comparison of lysozyme incorporation is made between the situation where the protein is present in the polymer dip coating solution and lysozyme is a component of the incubation medium. It is shown that protonated water clusters $H(H_2O)_n^+$ where n=5-11 that are indicative of ice are detected through the entire thickness of the pHEMA and the lysozyme distribution through the pHEMA hydrogel films can be determined using the intensity of characteristic fragment secondary ions. We also expand the developed methodology to X-Ray Photoelectron Spectroscopy (XPS) for through thickness analysis of the similar pHEMA / lysozyme hydrogels, and show that lysozyme distribution can be quantitatively mapped in hydrogels.

5:40pm **NS+BI-ThA11 GCIB-SIMS for Studying Bacterial Surfaces**, ***John Stephen Fletcher***, *P. Wehrli,* University of Gothenburg, Sweden; *A. Farewell,* University of Gothenburg, Seweden; *T.B. Angerer, J. Gottfries,* University of Gothenburg, Sweden

For many years ToF-SIMS has shown the promise of delivering new information of direct relevance to biological research. However, inadequacies in the ability to generate intact molecular ion species and then detect them with precise mass resolution and accuracy have held the technique back. Recent advances in ToF-SIMS, through the implementation of gas cluster ion beams (GCIBs) coupled to non-conventional MS systems, now permit the analysis of higher mass species from native, underivatised, biological specimen i.e. intact bacterial cells. Being able to characterise and understand changes in bacterial biochemistry as a result of environmental, biological or pharmacological stress is critical to address the global challenge of antibiotic resistance. For example, *E. coli* is able to rapidly adjust the biophysical properties of its membrane phospholipids to adapt to environmental challenges including starvation stress. Here, these membrane lipid modifications were investigated in glucose starved *E. coli* cultures and compared to a D*rel*AD*spo*T (ppGpp^0) mutant strain of *E. coli,* deficient in the stringent response, by means of time-of-flight secondary ion mass spectrometry (ToF-SIMS Cultures in stationary phase were found to exhibit a radically different lipid composition as compared to cultures in exponential growth phase. Wild-type *E. coli* reacted upon carbon starvation by lipid modifications including elongation, cyclopropanation and increased cardiolipin formation. Observations are consistent with variants of cardiolipins (CL), phosphatidylglycerols (PG), phosphatidylethanolamines (PE), phosphatidic acids (PA), and fatty acids. Notably, despite having a proteomic profile and a gene expression profile somewhat similar to the wild-type during growth, the ppGpp^0 mutant *E. coli* strain was found to exhibit modified phospholipids corresponding to unsaturated analogues of those found in the wild-type. We concluded that the ppGpp^0 mutant reacts upon starvation stress by elongation and desaturation of fatty acyl chains, implying that only the last step of the lipid modification, the cyclopropanation, is under stringent control. These observations suggest alternative stress response mechanisms and illustrate the role of the RelA and SpoT enzymes in the biosynthetic pathway underlying these lipid modifications.

2D Materials Focus Topic
Room 103B - Session 2D+NS-FrM

2D Materials: Device Physics and Applications

Moderator: Miguel M. Ugeda, CIC nanoGUNE, Spain

8:20am **2D+NS-FrM1 Direct Writing of 2D Flexible Electronic Devices via Illumination-based Techniques***, M.E. McConney, N.R. Glavin, A.T. Juhl,* Air Force Research Laboratory*; J.E. Bultman, J.J. Hu,* University of Dayton Research Institute/Air Force Research Laboratory*; M.F. Durstock,* Air Force Research Laboratory*; A.A. Voevodin,* University of North Texas*; **Christopher Muratore,*** University of Dayton

Ultra-thin two-dimensional (2D) semiconducting materials possess a combination of large, tunable electronic bandgaps, optical transparency, and mechanical flexibility, and will likely revolutionize electronic devices such as wearable sensors and flexible displays. A primary step in the development of such devices with integrated 2D materials is the development of scalable, transfer-free synthesis over large areas at low temperatures. Electrically insulating amorphous transition metal dichalcogenide (TMD) films can be deposited via physical vapor deposition on large area flexible substrates at room temperature, and crystallized with subsequent illumination with light. Focused laser light with a power density of ~1 kW cm^{2}is suitable for writing micron scale features in semiconducting transition metal dichalcogenides on polymer substrates. Broad band illumination from a xenon lamp can also be used over the large substrate areas (> 100 cm^2), or passed through a physical mask to print features only in desired locations. The semiconducting properties of 2D MoS$_2$ and WS$_2$ materials synthesized in this way have been characterized using conductive atomic force microscopy, and other techniques to observe the expected temperature dependence on electrical conductivity. Structure and composition of the materials can be controlled by altering the incident fluence as well as by controlling the ambient environment during illumination, as verified by Raman spectroscopy, X-ray photoelectron spectroscopy, cross-sectional and plan view transmission electron spectroscopy, and other techniques. Multiple layers of 2D materials can also be treated in this way. For example, both layers in a MoS$_2$/WS$_2$ heterostructure of 10 nm total thickness on a polymer (PDMS) substrate were crystallized upon laser illumination. Diverse 2D architectures and devices built from illumination-based crystallization techniques will be highlighted.

8:40am **2D+NS-FrM2 Resolving and Tuning Mechanical Anisotropy in Black Phosphorus Nanoelectromechanical Resonators***, **Zenghui Wang**, H. Jia, P.X.-L. Feng,* Case Western Reserve University

Black phosphorus (P) has emerged as a layered semiconductor with unique crystal structure featuring corrugated atomic layers and strong in-plane anisotropy in its physical properties. In particular, it is predicted to exhibit strong in-plane mechanical anisotropy, which shall lead to previously inaccessible dynamic responses in resonant 2D nanostructures [1], and new opportunities for studying carrier-lattice interaction in atomic layers. It is therefore of both practical and fundamental importance to systematically investigate the mechanical anisotropy in black P crystal and NEMS devices.

Enabled by the first demonstration of black P resonant nanostructures [2] with multimode responses, we show that the spatial mapping of the multimode resonance mode shapes [3] creates a new means for precise determination of black P crystal orientation (*i.e.*, the anisotropic zigzag and armchair axes) [4] . Further, the multimode technique enables simultaneous quantification of the anisotropic mechanical properties (*i.e.*, elastic moduli along both major crystal axes): combined with finite element method (FEM) modeling, we determine the Young's moduli of multilayer black P to be 116.1 GPa and 46.5 GPa in zigzag and armchair directions, respectively. In addition, we demonstrate that electrostatic gating induced straining can continuously tune the mechanical anisotropic effects on multimode resonances in black P electromechanical devices. Our results show that multimode resonant response manifests the unique mechanical anisotropy effect in black P nanodevices, and provides a new method for determine the material's crystal orientation and elastic properties *in situ*, independent from conventional optical, electrical, and nanoindentation calibration techniques.

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[4] Wang, Z., Jia, H., Zheng, X.-Q., Yang, R., Ye, G.J., Chen, X.H., & Feng, P. X.-L. Resolving and Tuning Mechanical Anisotropy in Black Phosphorus via Nanomechanical Multimode Resonance Spectromicroscopy. *under review.* (2016).

9:00am **2D+NS-FrM3 2D Devices for Flexible and Topological Nanoelectronics***, **Li Tao**, W. Zhu, D. Akinwande,* The University of Texas at Austin **INVITED**

Two-dimensional (2D) buckled atomic sheets, such as silicene and phosphorene, yield collective properties of mechanical flexibility and tunable bandgap, which hold promise for advanced flexible and topological nanoelectronics. Silicene is the 2D silicon equivalent of graphene, and is predicted to offer a host of exotic electrical properties, such as quantum spin Hall effect, subjected to external fields. Despite great theoretical expectations on silicene, air-stability had prevented experimental device studies. Recently, our research progress debuts silicene transistors corroborating theoretically predicted ambipolar transport with Dirac band structure. Electrostatic characterization on non-optimized silicene transistors exhibited carrier mobility ~100 cm^2/V-s and 10× gate modulation in ambient condition. Without non-ideal limiting factors, e.g. phase boundary scattering and electron-phonon coupling, pristine free-standing silicene is predicted to offer intrinsic mobility ~1200 cm^2/V-s. Further optimization is on-going to shed light on the mobility upper bound achievable and aging evolution of silicene devices. It is likely with further experimental study that monolayer or multilayer silicene can be a platform for realizing advanced device concepts, e.g. topological bits, on flexible substrates. The unique allotropic affinity of silicene with crystalline bulk silicon suggests a more direct integration with ubiquitous semiconductor technology.

Phosphorene, few-layer black phosphorus (BP), is another promising candidate for flexible nanoelectronics. Phosphorene exhibits high carrier mobility (100 to 1000 cm^2/Vs) and tunable direct bandgap (0.3 to 2eV) even on plastic substrates, making it the most suitable contemporary 2D semiconductor that combines the merits of graphene and transitional metal dichalcogenides. We reported the first BP based flexible RF transistors with intrinsic f_T=20 GHz and f_{Max}=14.5 GHz, and such performance sustained under ex-situ bending test with tensile strain up to 1.5%. Raman spectroscopy analysis of few-layer BP under tensile strain up to 7% was carried out for the first time to reveal the strain effect on BP. Significant orientation dependence was observed while applying tensile strain along armchair (AC) and zigzag (ZZ) directions, exhibiting the trend of Raman peak shift well agreed with theoretical projections. This recent progress on silicene and phosphorene represent a renewed opportunity for future nanoscale flexible and topological electronics beyond what is available in graphene.

9:40am **2D+NS-FrM5 Optical Detectors Based on Bismuth Telluride Nanowire Arrays Capped by Graphene***, **Tito Huber**, T. Brower, O. Abana,* Howard University

Recently, research on graphene based photodetectors has drawn substantial attention. The gapless nature of graphene and low light absorption can cause low responsivity. The synergetic integration of graphene with other materials is a promising approach to overcome these shortcomings. There have been reports of broadband photodetectors based on heterostructructures of few-layer Bi(2)Te(3)/graphene devices that are very encouraging. Here we discuss a different approach, where single layer graphene caps the top of a bismuth telluride nanowire array (where the wire axis are perpendicular to the graphene surface) . Partially, our motivation was to test the exceptional thermoelectric properties of the interface. The room-temperature thermoelectric efficiencies of bismuth telluride compounds are the highest reported for any material, and, therefore, Bi(2)Te(3) nanowires are interesting as building blocks of nanoscale thermoelectric devices, as in this case. Graphene strong photothermoelectric response is also very well known. We employed devices composed of bismuth telluride nanowire arrays which are capped with single layer graphene. Dense arrays of 200-nm nanowires have been prepared by a nonlithographic fabrication technique consisting of the pressure injection of an alumina template with molten Bi_2Te_3, a method that can be successfully employed with 100-µm thick templates of pore diameters in the range of 2 to 200 nm. Bismuth telluride is a semiconductor with a small gap. The nanowire arrays electronic properties including magnetotransport and thermopower were characterized in separate experiments. The single layer graphene layer was fabricated by transfer by Graphenea. Graphene on the device was characterized using Raman spectroscopy. We observed the D, G and 2D peaks and broadening indicating that graphene is nearly intact. We also observed the Raman peaks of bismuth telluride. The incident surface features very low optical reflectivity and enhanced light trapping. Light trapping causes strong light absorption at the interface, an effect that counteracts the weak absorption of graphene and has not been mentioned in the literature before. The unique attributes of the thermoelectric arrays are the combination of strong temporal and optical wavelength dependences of the photocurrent. Under infrared illumination, the signal can be completely described by thermoelectric effects considering cooling rates given by heat diffusion through the array. We will discuss that, in addition, under visible illumination we observe a photovoltaic response. This work was supported by the National Science Foundation through PRDM 1205608 and STC 1231319

10:00am **2D+NS-FrM6 Graphene Nanoelectromechanical Resonators with Eletrothermal Excitation and Tuning***, F. Ye, **Jaesung Lee**, P.X.-L. Feng,* Case Western Reserve University

Graphene, a hallmark of two-dimensional (2D) materials, has been employed as an atomically thin building block for highly miniaturized nanoelectromechanical system (NEMS) and shown attractive potential for nanoscale actuators and sensors. Thanks to its exceptional elastic modulus (E_Y~1TPa), ultralow mass density (r~2200kg/m^3), and superior strain limits (e_{limit}~25%) [1], high performance and frequency tunable graphene resonators have been demonstrated using photothermal [2] and electrostatic actuation [3] schemes. In addition to excellent mechanical properties, graphene possesses high temperature stability [4] and negative thermal expansion coefficient [5], hence graphene resonators may inherently exhibit better performance under high temperature. In existing reports, graphene resonators are exposed in high temperature using annealing or Joule heating (*e.g,*, applying up to 1.8V from drain to source) only for thermal annealing [3], high temperature operation of graphene resonators has not been demonstrated yet.

In this work, we fabricate mono- and bi-layer (1L and 2L) graphene resonators and investigate their resonance characteristics at high temperature up to ~500 K using Joule heating. We conveniently use DC voltage to heat graphene resonators, and apply AC voltage to excite resonance motion. Then, we simultaneously measure temperature and resonance characteristic of graphene resonators using a home-built, integrated Raman spectroscopy and laser interferometry measurement system. We first test electrothermal frequency tuning and find that frequency of graphene resonators upshift from ~80MHz to ~86MHz as DC voltage increases from 0.5V to 2.5V. Unlike electrostatic force resonance tuning and excitation [3], we do not observe capacitive softening or loaded *Q* effects which may compromise performance of resonators. We then investigate mechanical nonlinearity of graphene resonators in high temperature by changing both DC and AC voltage. This study opens new capabilities for engineering tunable graphene NEMS resonators and oscillators for a number of emerging applications.

[1] C. Lee, *et al.*, *Science***321**, 385-388 (2008).

[2] J. S. Bunch, *et al.*, *Science.***315**, 490-493 (2007).

[3] C. Chen, *et al.*, *Nat. Nanotech.***4**, 861-867 (2009).

[4] K. Kim, *et al.*, *Phys. Status Solidi RRL***4** 302-304 (2010).

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10:20am **2D+NS-FrM7 Pushing the Performance Limit of 2D Semiconductor Transistors***, **Xiangfeng Duan**,* California Nanosystems Institute, University of California, Los Angeles **INVITED**

Two-dimensional semiconductors (2DSCs) such as MoS_2 have attracted intense interest as an alternative electronic material in the post-silicon era. However, the on-current density achieved in 2DSC transistors to date is considerably lower than that of silicon devices. It remains an open question whether 2DSC transistors can offer competitive performance. To achieve a high performance (high on-current) device requires (1) a pristine channel with high carrier mobility, (2) an optimized contact with low contact resistance and (3) a short channel length. The simultaneous optimization of these parameters is of considerable challenge for atomically thin 2DSCs since the typical low contact resistance approaches either degrade the electronic properties of the channel or are incompatible with the fabrication of short channel devices. Here I will first review different strategies that have been developed to optimize these factors, and discuss how we can combine these strategies together to achieve high performance 2DSC semiconductor transistors. In particular, we will discuss a unique approach towards high-performance MoS_2 transistors using a physically assembled nanowire as a lift-off mask for creating ultra-short channel devices with pristine MoS_2 channel and self-aligned low resistance metal/graphene hybrid contact. With the optimized contact in short channel devices, we demonstrate that a sub-100 nm MoS_2 transistor can deliver a record a high on-current density comparing well with that of silicon devices, demonstrating thte exciting potential of 2DSCs for future electronic applications.

11:00am **2D+NS-FrM9 Low Temperature Al_2O_3 ALD on 2D Semiconductors***, **Il Jo Kwak**, J.H. Park, A.C. Kummel,* University of California at San Diego

2D semiconductors have attracted attention for future electronic devices due to their excellent electronic and optoelectronic properties. These devices require few nanometer thick and pin hole-free dielectric layers as gate insulators. However, due to the inert nature of 2D semiconductors such as graphene and Transition Metal Chalcogenides (TMDs), the dielectric layer selectively nucleates on defect sites or step edges. In the conventional atomic layer deposition (ALD) process on graphene or other 2D semiconductors, such non-uniform oxides result in large leakage currents in 2D semiconductor based device. Therefore, for successful integration into device, uniform and insulating gate oxides on 2D semiconductors should be prepared.

In this work, Al2O3 was directly deposited on HOPG and MoS2 surface by low temperature ALD with trimethylaluminum(TMA) and H2O or O3 without any seeding layer or surface treatments. Using short purge time between two precursor pulses at 50C, a CVD growth component was intentionally induced to provide more nucleation sites on the surface. The CVD growth component induces deposition of 1 nm Al2O3x particles on the surface which provide a uniform layer of nucleation centers. Before ALD, HOPG and MoS2 samples were cleaned by mechanical exfoliation method. For HOPG substrate, 50 cycles of ALD Al2O3 was deposited at 50C using 600ms of TMA and 50 ms of H2O pulse time with 500ms purge time between two pulses. In the case of MoS2, 300ms of O3 pulse was employed instead of H2O pulse. The same ALD recipes were performed on SiGe substrates in order to compared the quality of the oxide. After ALD process, MOSCAP devices were fabricated to measure the capacitance and leakage current of the oxide. Non-contact mode AFM was performed to check the topography of the oxide and the results showed that uniform and pin hole-free oxide layer was formed on the surface. The leakage current of the oxide on HOPG and MoS2 was as low as 10^{-5} A/cm^2 which was comparable to the oxide on SiGe substrates.

11:20am **2D+NS-FrM10 Atomic Layer Deposition of High-k Dielectrics on WSe_2 for High Performance Electronic Devices***, **Pushpa Raj Pudasaini**, M.G. Stanford, A. Hoffman,* The University of Tennessee Knoxville*; T.Z. Ward,* Oak Ridge National Laboratory*; D.G. Mandrus, P.D. Rack,* The University of Tennessee Knoxville

The performance of electronic and optoelectronic devices based on two-dimensional (2D) transition metal dichalcogenides (TMDs), such as tungsten diselenide (WSe_2) is significantly affected by the quality of the various interfaces present in the device. Historically, the performance of bottom-gate SiO_2 2D TMDs field effect transistor (FET) devices has been greatly limited by the carrier scattering due to the oxide trapped charges, surface roughness, and surface optical phonons, among others. One approach to mitigate this issue is to explore alternatives to SiO_2 which ideally would involve high-κ dielectrics, in which Coulombic impurity scattering is confirmed to be strongly shielded by the dielectric screening.

However, depositing high quality high-k dielectric film onto the surfaces of TMDs is very challenging due to the chemical inertness of the TMD basal planes. Here, we present an aluminum oxide and hafnium oxide top-gate on WSe_2, deposited using atomic layer deposition (ALD) both with and without hydrogen/oxygen plasma treatments and titanium seed layers. The top gated WSe_2 FET devices are fabricated by employing ALD deposited high k-dielectrics, with promising device characteristics having large current on-off ratio (~10^8), small threshold voltage (~5V) and relatively large field effect mobility (~70 cm^2/V.s) at room temperature. A high performance logic invertor device is also demonstrated.

11:40am **2D+NS-FrM11 Layer-dependent Measurements of Electronic Band Alignment for Individual MoS_2 Flakes Supported on SiO_2 using Photoemission Electron Microscopy (PEEM) with Deep Ultraviolet Illumination***, Morgann Berg,* Sandia National Laboratories*; K. Keyshar,* Rice University*; I. Bilgin, F. Liu,* Northeastern University, Los Alamos National Laboratory*; H. Yamaguchi,* Los Alamos National Laboratories*; R. Vajtai,* Rice University*; C. Chan,* Sandia National Laboratories*; G. Gupta,* Los Alamos National Laboratories*; S. Kar,* Northeastern University*; P. Ajayan,* Rice University*; T. Ohta,* Sandia National Laboratories*; A. Mohite,* Los Alamos National Laboratories

Tailoring band alignment layer-by-layer using heterojunctions of two-dimensional (2D) semiconductors is an attractive prospect for producing next-generation electronic and optoelectronic devices that are ultra-thin, flexible, and efficient. 2D layers of transition metal dichalcogenides (TMDs) in laboratory devices have already demonstrated properties favorable for electronic and optoelectronic applications. Despite these strides, a systematic understanding of how band alignment evolves from monolayer to multilayer for MoS_2, a model TMD system, is still missing owing to the lack of a suitable experimental approach. Quantitative determination of the electronic band alignment necessitates that measurements be performed in a controlled environment (such as vacuum) using a substrate that interacts minimally with the overlying TMDs (preferably insulating) to suppress the electronic influence of supporting substrates and prevent chemical modification of TMDs due to adsorbates (primarily water).

Here we report on the local band alignment of monolayer, bilayer, and tri-layer MoS_2 on a 285-nm-thick SiO_2 substrate, measured using a new approach to probe the occupied electronic states based on photoemission electron microscopy with deep ultraviolet excitation. The spatially-resolved, simultaneous measurements of the vacuum level and the valence band edge at the Brillouin zone center show that the addition of layers to monolayer MoS_2 increases the relative work function, and pushes the valence band edge toward the vacuum level. We also find n-type doping of few-layer MoS_2 and type-I band alignment across monolayer-to-bilayer and bilayer-to-trilayer lateral junctions. Our results differ from some earlier reports based on Kelvin probe and scanning photocurrent microscopies [Sci. Reports, 5, 10990 (2015), Nano Lett., 15, 2278 (2015)], and highlight the strong influence of environmental effects on the band alignment in MoS_2 homojunctions. We are now applying this exciting new metrology to systematically examine the ionization energies of a series of TMDs. The results will provide fundamental information necessary to assess the band alignments of TMD heterojunction devices, and to validate or refine existing theoretical predictions [APL, 103, 053513 (2013), J. Phys. Chem. C, 119, 13169 (2015)].

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12:00pm **2D+NS-FrM12 Visualizing Light Scattering in Silicon Waveguides with few-layer Black Phosphorous Photodetectors***, Tianjiao Wang, S. Hu,* Vanderbilt University*; B. Chamlagain, Z. Zhou,* Wayne State University*; S.M. Weiss, Y. Xu,* Vanderbilt University

We investigate the light scattering properties of a silicon nanobeam waveguide through wavelength- and polarization-dependent scanning photocurrent measurements of a black phosphorus (BP) photodetector on top of the silicon waveguide. The measured photocurrent responses exhibit similar patterns as the light intensity distribution calculated by finite-difference time-domain simulations, suggesting that the light scattering properties of the waveguide can be detected as photocurrent signals by the BP photodetector. Interestingly, no photocurrent signals are observed when the incident photon energy is below the bandgap of silicon, indicating that the photocurrent response generated in the BP photodetector is mainly attributed to the photo-excited electron-hole pairs in the silicon waveguide which can be injected into the BP and dominate its photocurrent generation. Our experimental results suggest that two dimensional (2D) material based photodetectors can offer an effective approach to visualize the light scattering properties of photonic structures by photocurrent mapping, which not only opens up avenues for learning about light matter interaction of photonic structures but also provides a way of engineering future 2D material based optoelectronic devices with integrated photonic structures.

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