MEMS and NEMS Group
Room: 24 - Session MN+BI+NS-MoM

Feature Session: Large Scale Integration of Nanosensors
Moderators: Wayne Hiebert, National Institute for Nanotechnology, Canada, Robert Davis, Brigham Young University

8:20am **MN+BI+NS-MoM1 Large Scale Integration: A Not-so-simple Cure for Loneliness of Silicon Nanoresonators**, ***Sébastien Hentz***, Cea Leti, France **INVITED**

After two decades of pioneering work, Nano Electro Mechanical Systems are only starting to fulfil (some) of their huge promises, in particular for sensing. A few start-up companies have been created in the last few years, but NEMS are still far from the industrial success of their micro- counterparts. Among others, one reason is the increasing difficulty to interface the "real-world" quantities to sense with the extremely small size of nanomechanical resonators. An easy to understand example of this is mass sensing: there is huge size mismatch between the NEMS capture cross section (in the μm^2 range) and an actual particle beam size that one can produce (in the mm to $10mm^2$ range). Most of the particles to detect are lost. Industrial applications may require the use of large arrays comprising from 10's to 10000's NEMS.

LETI has been working on nanomechanical resonators for a number of applications in the last ten years and have been pioneering their fabrication with Very Large Scale Integration processes. State of the art performance (signal to background ratio, signal to noise ratio, frequency stability...) has been reached with single silicon resonators and specific transduction means adapted to VLSI technologies. The real strength of VLSI though, as evidenced every day by microprocessor fabrication is the possibility to process a large number of devices operating in sync with great reproducibility and control.

We investigated several types of NEMS arrays in the past at LETI. Arrays comprising typically a few 1000 resonators all connected in parallel for gas sensing have been demonstrated. Smaller arrays with the ability to weigh and localize single particles via frequency addressing have been tested too for mass spectrometry applications. LETI has also been pioneering NEMS co-integration with CMOS in the last decade or so and several technologies have been explored. We took advantage of this know-how to fabricate large and dense arrays of NEMS-CMOS arrays for mass sensing applications.

9:00am **MN+BI+NS-MoM3 Nanomechanical Sensors (MSS, AMA) Toward IoT Olfactory Sensor System**, ***Genki Yoshikawa***, National Institute for Materials Science, Japan **INVITED**

Owing to their intrinsic versatility, nanomechanical sensors have potential to cover a wide range of olfactory sensing applications in various fields including food, agriculture, medicine, security, and environment. Based on the newly developed platform "Membrane-type Surface stress Sensor (MSS)," we are now trying to realize useful nanomechanical sensor systems which can fulfill the practical requirements, such as portability, low-cost, ease of use, in addition to the basic specifications, e.g. high sensitivity and selectivity. While the MSS provides a practical sensing element, a consumer mobile/IoT sensor system requires further optimization and integration of lots of components including receptor layers, hardware including electronics and sample handling, multidimensional data analysis, and precise calibration for high reproducibility. To establish a de facto standard for odor analysis and sensor systems employing the nanomechanical MSS technology, the "MSS Alliance" was launched jointly with companies and a university. In addition, "Aero-Thermo-Dynamic Mass Analysis (AMA)," which we have recently developed, will provide another approach to characterizing gases by directly measuring molecular weight in ambient condition without a vacuum or ionization. In this talk, the overview of the MSS, AMA, and the related technologies ranging from the optimization scheme of the sensor chip to system level developments will be presented.

9:40am **MN+BI+NS-MoM5 Micro-Gas Chromatography Linked with Nano-optomechanical Systems for Breath Analysis**, ***Khulud Almutairi***, University of Alberta, Canada, *W.K. Hiebert*, National Institute for Nanotechnology, Canada

One of the applications of microfabrication and nanofabrication technologies is fabricating a micro-Gas Chromatography (GC) on a chip. The miniaturized GC system is designed for the rapid determination of volatile organic compounds (VOCs) that can be used in remote locations with low consumptions and cost of utilization. It was reported that specific VOCs can be found in exhaled breath sample from patients suffering from lung cancer [1]. Therefore, designing a µGC device can help in separating and analyzing VOCs that comes from exhaled breath samples, such as acetone, benzene and toluene.

Our group has reported that connecting Nano-optomechanical systems (NOMS) to Gas Chromatography can enhance the detection sensitivity limit of VOCs up to 1 ppb [2]. This presentation will feature our first efforts in connecting µGC with NOMS for higher sensitivity and responsivity. In particular, we will discuss our NOMS sensor chips with microheaters for localized control of sensor temperature. One of our goals is to move toward large scale integration of GC analysis by simultaneously sensing at multiple temperatures.

REFERENCES:

[1] Mazzone, Peter J. "Exhaled breath volatile organic compound biomarkers in lung cancer." *Journal of breath research* 6, no. 2 (2012): 027106.

[2] Venkatasubramanian, Anandram, Vincent TK Sauer, Swapan K. Roy, Mike Xia, David S. Wishart, and Wayne K. Hiebert. "Nano-optomechanical systems for gas chromatography." *Nano Letters* 16, no. 11 (2016): 6975-6981.

10:00am **MN+BI+NS-MoM6 Micro Chladni Figures and Multimode Manipulation of Breast Cancer Cells in Liquid**, ***Hao Jia***, *H. Tang*, Case Western Reserve University, *X. Liu, H. Liu*, Northwestern University, *P.X.-L. Feng*, Case Western Reserve University

Non-invasive, microscale positioning of delicate biological cells can foster fundamental research involving probing cellular properties and controlling cellular behaviors and interactions [1-3], which lead to a multitude of applications, such as disease screening, tissue engineering, *etc.*

Here we demonstrate that microscale manipulation of breast cancer cells can be achieved in a fast and non-invasive manner through exploiting multimode micromechanical systems. We design edge-clamped diaphragm resonators (~300µm in length scale) and piezoelectrically excite their mechanical resonances (within 50–500 kHz) in fluidic environment. The transverse vibrations induce localized, microscale hydrodynamic flow that can aggregate microbeads (3.6µm-diameter) on device surfaces into a variety of one- and two-dimensional (1D and 2D) 'Chladni figures' [4] (optical images in Fig.1a & b). This phenomenon allows us to further manipulate single or a group of breast cancer cells (MDA-MB-231, 15µm-diameter), in both 1D and 2D fashions, at a speed of ~4µm/s (fluorescent images in Fig. 1a & b). By simply programming the piezoelectric excitation frequency, we achieve dynamic control of cancer cell spatial distributions, switching between mode patterns.

We further demonstrate that such multimode resonator platform can facilitate cellular-level biological studies, such as evaluating cellular adhesive interactions and its connection with cancer biomarker (*e.g.*, CD44). As shown in Fig.2, by exploiting the 'Chladni figure' phenomenon, and carefully selecting 2 resonance modes of a square diaphragm, *e.g.*, Mode (1,1) and Mode (3,3), a controlled number of MDA-MB-231 cells can be quickly manipulated into single cluster and then forced to break as the excitation voltage of Mode (3,3) gradually increases. Cancer cells with CD44 gene knocked out by CRYSPR technology are named as $CD44^-$ cells, while those with CD44 gene maintained named as $CD44^+$ (control) cells. The break of $CD44^-$ cell cluster after $0.8V_{pp}$ in Fig. 2 indicates that they form much weaker adhesive interactions than $CD44^+$ cells do, which indicates that CD44 plays a significant role in the metastatic breast cancer cell clustering.

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[2] H. Zhang, *et al.*, J. R. Soc. Interface **5**, 2008.

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10:40am **MN+BI+NS-MoM8 Microfabrication and Assembly Processes for Integrating Microelectrode Arrays into Tissue-Engineered Scaffolds for Novel Nerve Interfaces**, ***Jack Judy***, *C. Kuliasha, P. Rustogi, S. Natt, B. Spearman, S. Mohini, J.B. Graham, E.W. Atkinson, E.A. Nunamaker, K.J. Otto, C.E. Schmidt*, University of Florida **INVITED**

To advance fundamental understanding and develop therapies for neurological disease or injury, microfabricated implantable electrode arrays have been designed and manufactured to stimulate and record neural activity. The materials in these implants, as well as the processes used to integrate them together, must be carefully selected to maximize biocompatibility, device performance, and overall reliability. For upper-limb amputees, nerves are a promising neural-interface target to control sophisticated robotic limbs. Recent advances have shown that nerve stimulation can provide natural sensory feedback. In contrast, it is currently not possible to extract large-scale, high-resolution, and reliable movement-intent signals from nerves. To provide rapid and precise limb control and elicit high-resolution sensory percepts, a nerve interface needs many independent motor and sensory channels. Unfortunately, all existing non-invasive and non-regenerative nerve interfaces grossly under-sample the heterogeneous population of efferent and afferent axons. Although tissue engineering, nerve regeneration, and implantable neural-electronic interfaces are individually well-established fields, the concept of merging these fields to create scalable, and high-performance neural interfaces has not been extensively explored. To overcome the scalability challenge, we present a novel approach. Specifically, we describe a hybrid tissue-engineered electronic nerve interface (TEENI), which consists of multi-electrode polyimide-based "threads" embedded into a biodegradable hydrogel composite scaffold that is sutured to the ends of a transected nerve. Single or multiple thread sets can be incorporated in the hydrogel to enable the TEENI implant to comprehensively engage with the nerve. These polyimide threads will be fully enveloped and held precisely in position during implantation by the hydrogel scaffold, which has properties optimized to reduce foreign-body response. Eventually, the hydrogel will degrade and be replaced with regrown and maturing axons. Since the TEENI approach is scalable to high channel counts over the nerve volume, we believe TEENI nerve interfaces are well positioned to comprehensively capture movement-intent information and impart sensory-feedback information so that upper-limb amputees can get the most out of their prosthetic limbs.

11:20am **MN+BI+NS-MoM10 Magnetically Actuated Synthetic Cilia for Microfluidics**, ***Peter Hesketh***, *S.K.G. Hanasoge, M. Ballard,* Georgia Institute of Technology, *M. Erickson,* University of Georgia, *A. Alexeev*, Georgia Institute of Technology **INVITED**

Many bacteria use cilia for swimming, sensing and signal transduction. These functions are achieved by manipulating the fluid around the cilia with continuous and synchronised asymmetric beating patterns . We have fabricated arrays of synthetic cilia using thin film deposition of NiFe thin films. The cilia are able to manipulate fluid in these creeping flow regimes by creating an asymmetry in the forward and recovery strokes. We propose to use artificial cilia in microfluidic devices to perform different functions including mixing, fluid transport, and particle capture.

We use a simple rotating magnet to actuate the cilia array and observe a large asymmetry in the bending pattern of these cilia in the oscillation cycle. We analyze the asymmetric strokes of the cilia by imaging from the side view and quantify the asymmetry between forward and recovery strokes as a function of drive frequency. These asymmetric oscillations are important in creating any microfluidic transport phenomenon such as pumping, mixing and capture in a microchannel as demonstrated in this work. Computational modeling was also used to simulate the motion of the cilia over a broader range of design parameters. We show the dependence of the ciliary performance on several non-dimensional numbers based on the balance of magnetic, viscous and elastic forces acting on the cilia.

The motivation for this work is to improve the quality of sampling for the detection of bacteria and virus in food. Detecting low concentrations of bacteria in food samples is a challenge. The pre-concentration and separation of the target bacteria from the food matrix can be enhanced using improved fluid handling. We demonstrate particle capture with cilia, by functionalizing the surface of the cilia with streptavidin protein and capturing biotin labelled particles on its surface. The functionalized cilia are incorporated inside a microchannel and biotin labelled particles are introduced into array of the cilia. Likewise, these artificial cilia find varied application in many lab on a chip devices where active fluid transport is needed.

Scanning Probe Microscopy Focus Topic
Room: 10 - Session SP+AS+NS+SS-MoM

New Imaging and Spectroscopy Methodologies
Moderators: Wonhee Ko, Oak Ridge National Laboratory, An-Ping Li, Oak Ridge National Laboratory

8:20am **SP+AS+NS+SS-MoM1 Charge Transport through Nanostructures measured with a Multi-Tip STM**, ***Bert Voigtländer***, Forschungszentrum Juelich, Germany **INVITED**

The use of Multi-Tip STM for transport measurements is another step in the recent paradigm shift in scanning probe microscopy transforming from "just imaging" to detailed measurements at the nanoscale. Multi-Tip STM is an ideal technique to study electronic properties, while a current is running through a nanostructure/nanodevice.

We demonstrate how three requirements have to be combined to perform nanoscale charge transport measurements, using the Multi-Tip STM technique: (a) a stable, versatile, and easy to operate Multi-Tip STM instrument, as well as (b) electronics and software, which allow any possible "concerted" Multi-Tip measurements, and last but not least (c) the new method Multi-Tip STM also requires new methodologies for data analysis.

We demonstrate the capabilities of the Multi-Tip STM method to reveal fundamental nanoscale charge transport properties by the following examples: (a) Mapping of resistance profiles and corresponding doping profiles along freestanding GaAs nanowires, (b) measurement of the surface conductivity at semiconductor surfaces, (c) identification of resistivity dipoles in nanoscale potential maps around defects, using scanning tunneling potentiometry, (d) disentangling *in situ* top and bottom conductance of a topological insulator thin film by gate dependent measurements.

9:00am **SP+AS+NS+SS-MoM3 Robust High-Resolution Imaging and Quantitative Force Spectroscopy in Vacuum with Tuned-Oscillator Atomic Force Microscopy**, ***Omur Dagdeviren***, *J. Goetzen,* Yale University, *H. Holscher,* Karlsruhe Institute of Technology (KIT), Germany, *E.I. Altman*, *U.D. Schwarz*, Yale University

Since the first demonstration of atomic resolution in ultrahigh vacuum more than twenty years ago, frequency modulation-based noncontact atomic force microscopy (FM-NC-AFM) has significantly matured and is now routinely applied to study problems that benefit from high-resolution surface imaging. In FM-NC-AFM, control of the tip's vertical position is accomplished by detecting a shift in the cantilever's resonance frequency upon approach to the sample. Consistently ensuring reliable distance control during extended data acquisition periods has nevertheless remained challenging, as most FM-mode-based control schemes employ three feedback loops that may interfere. As a consequence, sample throughput in FM-NC-AFM is often low compared to ambient condition AFM, where the easy-to-implement amplitude-modulation (AM) control scheme is predominantly used. Transfer of the AM methodology to high-resolution measurements in vacuum is, however, difficult as with AM-AFM, instabilities during approach are common. In addition, the lack of viscous air damping and the related significant increase of the cantilever's quality factor generate prolonged settling times, which cause the system's bandwidth to become impractical for many applications. Here we introduce a greatly simplified approach to NC-AFM imaging and quantitative tip-sample interaction force measurement that prevents instabilities while simultaneously enabling data acquisition with customary scan speeds by externally tuning the oscillator's response characteristics [1]. After discussing background and basic measurement principle, examples for its application to a variety of sample systems are provided [1,2,3,4]. A major advantage of this operational scheme is that it delivers robust position control in both the attractive and repulsive regimes with only one feedback loop, thereby carrying the potential to boost the method's usability.

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[4] O.E. Dagdeviren et al, Advanced Materials and Interfaces, 4, 1601011 (2017)

9:20am **SP+AS+NS+SS-MoM4 Electrical Transport Measurements with Atomically Precise Probes**, ***Markus Maier***, *J. Koeble, R. Thiel, M. Fenner, A. Pirou, D. Stahl, T. Roth*, Scienta Omicron GmbH

A major challenge in the development of novel devices in nano- and molecular electronics is their interconnection with larger scaled electrical circuits. Local electrical probing by multiple probes with precision on the atomic scale can significantly improve efficiency in analyzing electrical properties of individual structures on the nano-scale without the need of a full electrical integration.

The LT NANOPROBE is a sophisticated instrument that merges the requirements of a 4-probe system, efficiently and precisely navigated by a scanning electron microscope (SEM) and at the same time satisfies the needs for high performance SPM. The excellent stability in the pm range allows for atomic resolution in STM and nc-AFM (QPlus) and expands applications from electrical probing on the nanometer scale towards tunneling and force spectroscopy and the creation of atomically precise structures. The system is operated near thermal equilibrium and temperatures below 5K, specifically also during simultaneous SEM imaging and navigation. The system has been developed towards an extremely low thermal drift in the range of 100pm/h, which is the most important ingredient to allow for enough measurement time on extremely small structures.

We will present measurements that prove the performance level of the instrument, specifically the low thermal drift and stability as well as QPlus AFM measurements, which become important if nanostructures are deposited on an insulating substrate for a better electrical decoupling. We will also show the newest technology improvements, such as high frequency capabilities and optical access for pumped probe experiment. Future technology challenges as well as applications and scientific drivers for this type of scientific instrumentation will be discussed.

9:40am **SP+AS+NS+SS-MoM5 Planar Two-probe Scanning Tunneling Spectroscopy Measurements at the Atomic Level**, ***Marek Kolmer***, Jagiellonian University, Krakow, Poland **INVITED**

We present our recent results obtained on the new Scienta-Omicron low temperature ultra-high vacuum 4-probe STM (LT-Nanoprobe). This unique machine is equipped with 4 STM scanners able to operate on the same surface simultaneously with the stability of the *state-of-art* single tip low temperature STMs [1].

Firstly we show our methodology for fine relative positioning of two STM probes on a surface with unprecedented atomic precision and with a lateral exact probe to probe distance below 50 nm. Secondly we discuss our design of the 2-probe STM experiment, in which both tips are kept in tunnelling conditions above a grounded sample. Then, by applying a DC bias voltage between probes in the described configuration we can detect a probe to probe DC current signal. Moreover, we add a small AC component to a varied DC bias voltage and by demodulation of resulting current signals on each of the probes, we extract corresponding dI_1/dV_1 (vertical) and dI_2/dV_1 (planar) STS signals. Our method allows a direct testing of the electronic transport properties of atomic-scale structures in a *fully planar* geometry, what is shown on an example of a model system: bare Ge dimer wires on Ge(001) surface. In this case we determine ballistic charge transport regimes in the atomic wires by systematic 2-probe spectroscopic experiments on the probe to probe distances below 50 nm.

Finally, we discuss perspectives for application of the above methodology in characterization of molecular structures, i.e. molecular wires obtained by the on-surface synthesis approach on metal oxide surfaces [2-4].

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10:40am **SP+AS+NS+SS-MoM8 An Ultrafast Scanning Probe Microscopy Technique for Imaging Polarization Switching in Ferroelectric Materials**, ***Suhas Somnath***, *S.V. Kalinin, S. Jesse*, Oak Ridge National Laboratory

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 extremely sensitive to local defects and structural imperfections at the micro- and nanometer scale, which have undesirable effects on ferroelectric domains. These considerations led to the development of Piezoresponse Force Microscopy (PFM) for imaging and manipulating local polarization states. In PFM, a micro-cantilever with a conductive tip is brought into contact with the sample surface. Periodic bias applied to the tip deforms the sample, which in turn causes the cantilever to vibrate, and these vibrations are recorded using an optical setup in the microscope. The current state-of-art PFM imaging and spectroscopy techniques measure the bias dependent material deformation either at a single frequency (using a lock-in-amplifier) or over a narrow band of frequencies thereby discarding valuable information from higher vibrational modes of the cantilever and multiple harmonics. As an extension, PFM spectroscopy techniques suffer from serious compromises in the measurement rate, voltage and spatial resolutions since they require the combination of a slow (~ 1 sec) switching signal and a fast (~ 1 – 10 msec) measurement signal. The slow measurement speed results in undesirable compromises between the imaged area, spatial resolution, and voltage resolution.

We report on a new voltage spectroscopy technique applied to PFM that rapidly acquires dense 2D maps of local hysteretic material response. This technique combines the acquisition of the complete information about the cantilever response with intelligent signal filtering techniques to enable direct measurement of 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. By rapid acquisition of a large number of hysteretic loops on very dense grids, this technique will enable significant insight into nanoscale polarization dynamics and phenomena such as polarization fatigue or local wall displacements that remain difficult to study at the desired spatial and temporal scales, and are crucial for integration of ferroelectric nanostructures in future electronic devices.

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.

11:00am **SP+AS+NS+SS-MoM9 Direct Probing of the Graphene-Electrolyte Double Layer Potential**, ***Evgheni Strelcov***, NIST Center for Nanoscale Science and Technology / University of Maryland, *A. Tselev*, University of Aveiro, Portugal, *H.X. Guo, A. Yulaev*, NIST Center for Nanoscale Science and Technology / University of Maryland, *I. Vlassiouk*, Oak Ridge National Laboratory, *N.B. Zhitenev, W. McGehee, B. Hoskins, J.J. McClelland, A. Kolmakov*, NIST Center for Nanoscale Science and Technology

Solid-liquid interfaces play an instrumental role in a broad range of natural phenomena in biological, hydrological, chemical and electrochemical systems. The latter include energy conversion and storage applications, such as fuel cells, supercapacitors, electrochromic devices, and batteries, whose performance strongly depends on the state of the solid-liquid interface. Key elements of this interfacial behavior are the formation of the electrical double layer (EDL), ionic transport through it, ionic adsorption, and Faradaic processes. Thus, understanding the structure and properties of the EDL is of critical importance. Despite more than a century of research on the EDL, its molecular structure and electrode potential dependence remain the subject of frontier research. Only a handful of experimental techniques, including surface force and spectral methods, are currently available for direct probing of the EDL, but even they do not offer adequate spatial resolution.

Here, we report on direct measurement of the EDL potential in a copper (II) sulfate electrolyte with Kelvin Probe Force microscopy (KPFM). The aqueous electrolyte is placed in a multichannel array, consisting of high aspect ratio, 2 μm diameter channels, sealed at the bottom and capped with bilayer graphene at the top. The system can be imaged *in vacuo* with high resolution scanning electron microscopy and KPFM, correlatively. The graphene membrane acts as both an electrode and a seal that prevents the electrolyte from evaporating into the vacuum. The KPFM probe scans over the subnanometer graphene membrane of individual channels and records potential of the EDL formed at the electrified graphene-electrolyte interface. Both graphene and bottom platinum electrode can be biased to modulate the response of the system to polarization. The collected data are compared to numerical simulation of EDL formation.

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11:20am **SP+AS+NS+SS-MoM10 Quasiparticle Interference Mapping of ZrSiS**, ***Michael Lodge***, University of Central Florida, *G. Chang, B. Singh*, National University of Singapore, *J. Hellerstedt, M.T. Edmonds*, Monash University, Australia, *D. Kaczorowski*, Polish Academy of Sciences, *M.M. Hosen, M. Neupane*, University of Central Florida, *H. Lin*, National University of Singapore, Singapore, *M. Fuhrer*, Monash University, Australia, *B. Weber*, Nanyang Technological University, Singapore, *M. Ishigami*, University of Central Florida

3D Dirac semimetals are a class of materials whose bulk electronic states are protected by topology, presenting intriguing new systems in which to study the rich physics of the quasiparticles that they host. One such system is the nodal line Dirac semimetal, wherein the conductance and valence bands have a line-like crossing along a closed loop in momentum space and disperse linearly in the vicinity of the resulting line node. This configuration gives rise to the prediction of exotic phenomena such as spin vortex rings, diverging mobility in the limit of vanishing chemical potential, and a linearly increasing dependence of the conductivity on temperature. Many of these compounds have their line node located hundreds of meV above the Fermi level, making direct observation of the line-node inaccessible to experimental techniques such as angle resolved photoemission spectroscopy (ARPES). We employ spectroscopic imaging scanning tunneling microscopy (SI-STM) at 4.5K to visualize the quasiparticle interference with point defects in zirconium silicon sulfide (ZrSiS). In combination with numerical modeling, we identify six groups of quasiparticle scattering vectors allowed within the material, and show that topological protection of the electronic bands is relaxed in the presence of certain defects. We also estimate the location of the line node.

MEMS and NEMS Group
Room: 24 - Session MN+EM+NS-MoA

Nano Optomechanical Systems/Multiscale Nanomanufacturing

Moderators: Robert Ilic, NIST, Meredith Metzler, University of Pennsylvania

1:40pm **MN+EM+NS-MoA1 GHz Integrated Acousto-Optics**, ***Mo Li***, University of Minnesota **INVITED**

Integrating nanoscale electromechanical transducers and nanophotonic devices potentially can enable new acousto-optic devices to reach unprecedented high frequencies and modulation efficiency. We demonstrate acousto-optic modulation of a photonic crystal nanocavity using acoustic waves with frequency up to 20 GHz, reaching the microwave K band. Both the acoustic and photonic devices are fabricated in piezoelectric aluminum nitride thin films. Excitation of acoustic waves is achieved with interdigital transducers with periods as small as 300 nm. Confining both acoustic wave and optical wave within the thickness of the membrane leads to improved acousto-optic modulation efficiency in the new devices than that obtained in the previous surface acoustic wave devices. In a photon-phonon waveguide, we further demonstrate strong Brillouin scattering of light by electromechanically excited acoustic waves. Our system demonstrates a novel scalable optomechanical platform where strong acousto-optic coupling between cavity-confined or guided photons and high frequency traveling phonons can be explored.

2:20pm **MN+EM+NS-MoA3 Coupling Piezoelectric MEMS to Cavity Optomechanics**, ***Kartik Srinivasan***, NIST **INVITED**

Establishing a link between the radio frequency (RF) and optical domains is a topic of relevance to a variety of applications in communications, metrology, and photonic quantum information science. Acoustic wave devices represent an opportunity to mediate such transduction in a chip-integrated format. The approach we are pursuing uses materials that are both piezoelectric, to couple RF waves to strain fields, and photoelastic, to couple strain fields to optical waves.

One architecture that we have recently explored is based on exploiting these effects in GaAs. First, interdigitated transducers (IDTs) convert 2.4 GHz RF photons into 2.4 GHz propagating surface acoustic waves. These acoustic waves are routed through phononic crystal waveguides and are coupled to a nanobeam optomechanical cavity that supports both a highly localized 2.4 GHz breathing mechanical mode and a high quality factor 1550 nm optical mode. In contrast to non-resonant excitation of photonic structures with IDTs, here the phononic waveguide preferentially excites a localized mechanical mode, which in turn strongly interacts with the optical mode through the photoelastic effect. Finally, the optical mode can be out-coupled or excited via an optical fiber taper waveguide. Using this platform, we demonstrate preparation of the breathing mode in a coherent state at any location in phase space, and optically read out an average coherent intracavity phonon number as small as one-twentieth of a phonon. In the time-domain, we show that RF pulses are mapped to optical pulses, forming a resonant acousto-optic modulator with a sub-Volt half-wave voltage. We also observe a novel acoustic wave interference effect in which RF-driven motion is completely cancelled by optically-driven motion, enabling the demonstration of interferometric opto-acoustic modulation in which acoustic wave propagation is gated by optical pulses.

While the above platform has been shown to provide a coherent interface between the RF, optical, and acoustic domains, the overall efficiency is limited by imperfect matching across the various interfaces, e.g., IDT-to-phononic crystal waveguide, etc. In the final part of my talk, I will outline efforts to improve upon the transduction efficiency of the system.

3:00pm **MN+EM+NS-MoA5 Collective Nano-optomechanics for Sensing Applications**, ***Eduardo Gil Santos***, *W. Hease*, Universite Paris Diderot, France, *A. Lemaitre*, Centre de Nanosciences et Nanotechnologies, France, *M. Labousse, C. Ciuti, G. Leo, I. Favero*, Universite Paris Diderot, France

Optomechanical resonators have been the subject of extensive research in a variety of fields, such as sensing, communication and quantum technologies. Our recent investigations on the capabilities of optomechanical semiconductor disk resonators to operate as sensors in liquids have revealed an astonishing potential. Minimum mass detection of $14 \cdot 10^{-24}$ g, density changes of $2 \cdot 10^{-7}$ kg/m^3 and viscosity changes of $5 \cdot 10^{-9}$ Pa·s, for 1s integration time, are extrapolated from our measurements in liquids. After landmark experiments realized on single resonators, the use of multiple optomechanical cavities is essential to further improve their sensing capabilities, as it enlarges the sensing area while keeping their individual assets. This evolution towards collective nano-optomechanics hence bears potential for a variety of sensing applications, but for quantum or topological photonics as well. Unfortunately, the collective configurations are usually impeded by the residual disorder imposed by nanofabrication techniques, which naturally detunes high optical Q resonators and precludes resonant interactions between them. Therefore, overcoming fabrication imperfections and allowing spectral alignment of resonators is essential.

Here, we develop a new simple and scalable post-fabrication method to achieve such alignment in a permanent manner. The method introduces an approach of cavity-enhanced photoelectrochemical (PEC) etching in a fluid (gas or liquid). This resonant process is highly selective and allows controlling the resonator size with sub-pm precision, well below the material's interatomic distance. Light resonantly injected into the optical mode of an optical resonator immersed in a fluid triggers an etching process, leading to a fine-tuning of the resonator's dimensions. The evolution of dimensions is monitored continuously by tracking the resonator's optical resonance with a laser. This tuning process is naturally scalable to multiple resonators. We demonstrate it using a cascaded configuration where optomechanical disk resonators, each supporting its own localized optical and mechanical mode, are unidirectionally coupled through a common optical waveguide. The technique is illustrated by finely aligning up to five resonators in liquid and two in air, opening the way of fabricating large networks of identical resonators.

As an example of application of this tuning technique, we explore the resonant optical interaction of multiple nano-optomechanical systems. We observe a first form of collective behavior involving several distant resonators, where a unidirectional flow of light frequency-locks a chain of nano-optomechanical oscillators.

3:20pm **MN+EM+NS-MoA6 Microporous Nanophotonic Mechanical Cantilevers for Mass Sensing**, ***Anandram Venkatasubramanian***, *V.T.K. Sauer, J.N. Westwood-Bachman*, University of Alberta and The National Institute for Nanotechnology, Canada, *K. Cui, S.K. Roy, M. Xia*, National Institute for Nanotechnology, National Research Council, Canada, *D. Wishart*, University of Alberta, Canada, *W.K. Hiebert*, University of Alberta and The National Institute for Nanotechnology, Canada

The Gas chromatography (GC) – Mass spectrometry (MS) system is the industry benchmark in chemical analysis. However the large size of the Mass spectrometry unit makes it unsuitable for portable applications. Hence a portable universal mass sensing device that can be used with portable GCs needs to be developed. In this regard, recent demonstration with nano opto-mechanical system (NOMS) devices in conjunction with a GC system have proven that these kinds of sensors have the breakthrough potential to improve the sensitivity of portable GCs. Those demonstrations using NOMS devices have shown these sensors to match the mass detection limits of nanoelectromechanical systems (NEMS) sensors and can potentially better their performance owing to their superior displacement sensitivity compared to NEMS.

In this regard, a free space interferometry system based nanophotonic sensor was developed and attached to a conventional GC. The nanophotonic sensor consists of a microring racetrack resonator (for concentration sensing) with a nanomechanical beam (for mass sensing) adjacent to it. Common method to improve the sensitivity of a nanomechanical beam is to apply surface coatings. However, the application of surface coatings can potentially affect its universal sensing characteristics. Hence an alternate way to improve the adsorption sensitivity is to increase the surface area of the nanomechanical sensor to aid in increasing the number of gas adsorption sites.

In this paper we increase the surface porosity of nanomechanical beam by stain etching. Care was taken to protect the adjacent microring resonator from stain etching as surface pores can negatively affect the performance of the ring resonator due to increased scattering. The stain etching was conducted using vanadium oxide/Hydrofluoric acid based chemistry to etch ~ 10nm pores of random morphology on the surface. Based on an estimated porosity of <15% by volume, we have noted an increase in mass adsorption of ≥ 50 - 100% when tests were conducted using different volatile organic compounds. In other words, a mass adsorption enhancement factor of 1.5 to 2 has been achieved. Due to this enhanced adsorption, the mass detection threshold has improved by an order of magnitude ($\sim 10^{-19}$ g). To the best knowledge of the authors, this is the first time NOMS based porous nanomechanical mass sensor has been developed.

Mass Adsorption Enhancement Factor = Adsorption frequency shift for porous beam/Adsorption frequency shift for non porous beam

4:00pm **MN+EM+NS-MoA8 Tunable Resistivity in Inkjet Printed Circuit by Plasma Reduction of Particle-free, Stabilizer-free Ink**, *Y. Sui, S. Ghosh, C. Miller, R.M. Sankaran, **Christian Zorman***, Case Western Reserve University

Inkjet printing offers a low-cost, rapid methodology to produce patterned metal thin films on flexible substrates. The most commonly used ink consists of colloidal suspensions of nanoparticles prepared by wet chemical reduction of metal salts. Even after concentrating the nanoparticles through solution processing, the as-printed ink usually exhibits a low conductivity due to the presence of organic molecules that help stabilize the nanoparticles from agglomeration and precipitation. High temperature (>200 C) treatment is then required after printing to remove the insulating organics and sinter the nanoparticles. The thermal step can limit printing on polymers such as PDMS, paper, and 3D printed polymers.

Here, we present a particle-free, stabilizer-free ink and a low-temperature plasma reduction process to produce electrically conductive metallic patterns on temperature-sensitive without any additional thermal step. The ink is comprised of a metal salt, a solvent, and a viscosity modifier, and is absent of any large organic molecules that cannot be evaporated after printing. The as-printed and dried metal salt is then treated with a plasma formed in a low-pressure argon environment. Even without the presence of highly reactive atomic and molecular hydrogen, this process is found to be sufficient to reduce the metal salt to highly conductive metal with resistivities approaching bulk values. More importantly, we found the resistivity of the printed structure can be tuned over a range of 2 orders of magnitude by varying the plasma power and treatment time. Thus far, we have demonstrated this general approach for silver (Ag) and tin (Sn) from silver nitrate (AgNO3) and tin (II) chloride (SnCl2), respectively. Details of the material properties as assessed by materials characterization and electrical conductivity measurements, device application to RC filter circuits, and applicability to other metals will also be discussed.

4:20pm **MN+EM+NS-MoA9 Cold Forming of Shallow Spherical Micro Caps by Nano Imprinting**, ***Asaf Asher**, E. Benjamin, L. Medina, S. Lulinsky*, Tel Aviv University, Israel, *R. Gilat*, Ariel University, Israel, *S. Krylov*, Tel Aviv University, Israel

Many nonlinear systems are distinguished by bistability, which manifests itself as the coexistence of two equilibria under the same loading. Progress in the development of micro and nano structures stimulated renewed interest in the mechanics of bistable elements. Applications of these devices in the realm of micro and nanoelectromechanical systems (MEMS/NEMS) include switches, sensors, non-volatile memories, micro-pumps, micro-resonators and deformable mirrors. While curved beam-type bistable micro structures were intensively investigated both theoretically and experimentally much less attention was paid to two-dimensional bistable structures such as initially curved plates and shells (caps). One of the reasons is that lithography-based processes commonly used in MEMS/NEMS are essentially planar and are not suitable for fabrication of cap-like structures with an out-of-plane curvature. Existing approaches include gray-scale lithography or a glass blowing technique.

In this work we discuss several approaches for fabrication of shallow micro shells. One of the directions is the use of the cold forming techniques, when stamping changes a flat thin foil of ductile material into double-curvature components. While multiple variations of this process were used at the macro scale, much less works reported the implementation of this technique in MEMS. In the framework of the fabrication process used in our work, a layer of Al or Cu is deposited on top of a Si wafer. Sputtering is implemented for the creation of a thin seed layer, followed by electrodeposition used to increase the layer thickness to a desired value. Next, an opening is etched through the wafer using deep reactive ion etching (DRIE). Finally, the forming process is performed using nano-imprinting lithography tool. The tool allows very precise control of the force applied to the structure as well as the stamp temperature, displacements and rate of loading. Finite elements analysis and compact reduced order models are used for the evaluation of the desired parameters. Prior to forming, residual stress of the thin suspended membranes is estimated using a resonance method, by means of comparison of the measured natural frequencies of the device with the model predictions. We discuss suitability of different structural materials, deposition methods and stamping techniques for the formation of non-planar three-dimensional micro structures.

4:40pm **MN+EM+NS-MoA10 Plate Mechanical Metamaterials: The Thinnest Plates You Can Pick Up by Hand**, ***Igor Bargatin***, University of Pennsylvania **INVITED**

Recently, my group has demonstrated a new class of ultra-lightweight plate-shaped mechanical metamaterials, which we named "plate mechanical metamaterials". Using a periodic three-dimensional patterning, we fabricated free-standing plates up to 1 cm in size out of aluminum oxide (alumina) films as thin as 25 nm. Weighing as little as 0.1 gram per square meter, they are among the thinnest and lightest freestanding solids that can be handled with bare hands. We also combined multiple ultrathin layers of alumina to create a nanoscale analog of paper-based corrugated cardboard. Unlike cardboard, these plates have the ability to “pop back” to their original shape, without damage, even after undergoing multiple sharp bends by more than 90 degrees.

Like the nanotruss -based mechanical metamaterials reported by other groups, plate mechanical metamaterials are extremely lightweight and resilient due to their nanoscale thickness and microscale cellular structure. However, in contrast to the cube-shaped metamaterials that typically form a lattice easily penetrated by the ambient air, our plates form flat continuous plates. Ultralow weight, mechanical robustness, thermal insulation, as well as chemical and thermal stability of alumina make plate metamaterials attractive for numerous applications, including structural elements in flying microrobots, high-temperature thermal insulation in energy converters, testing of nanoscale strength enhancement, new types of optical and acoustic metamaterials, as well as ultrathin MEMS/NEMS sensors and ultra-lightweight hollow MEMS/NEMS resonators.

Nanometer-scale Science and Technology Division
Room: 19 - Session NS+HC+SS-MoA

Oxides in Nanotechnology
Moderator: Nancy Burnham, Worcester Polytechnic Institute

2:00pm **NS+HC+SS-MoA2 Epitaxial Growth and Characterization of WO3 and WO$_{3-\delta}$ Thin Films**, ***Yingge Du**, Z. Yang, Z.H. Zhu, C. Wang*, Pacific Northwest National Laboratory

Tungsten trioxide (WO_3) based thin-film materials are of significant importance because of their diverse structures and wide range of properties. These materials have found widespread applications in display devices, electrochromic “smart” windows, gas sensors, catalysis, and photocatalysis. Investigations of WO_3 films in epitaxial form offer definite advantages over porous or polycrystalline forms for fundamental science studies. For example, the ability to detect and eliminate secondary phases and surfaces simplifies the material system and makes it easier to establish defensible cause-and-effect relationships. While amorphous, polycrystalline, and epitaxial WO_3 films have been prepared by several methods such as evaporation of WO_3, sputtering, and pulsed laser deposition, the growth of epitaxial WO_3 films by molecular beam epitaxy (MBE) is much less explored.

We examined three different ways to grow epitaxial WO_3 films by MBE – by evaporating WO3 powders from an effusion cell, by evaporating WO_x surface layers formed on W metal surface, and by evaporating tungsten metal in an oxidizing environment. Epitaxial films are formed in all three cases but the growth characteristics vary significantly. The films from the first two methods are found to grow as stoichiometric islands first, while the third method leads to layer by layer growth, with significant amount of ordered oxygen vacancies. The films are characterized *in-situ* by RHEED and XPS, and *ex-situ* by XRD, SIMS, and STEM.

2:20pm **NS+HC+SS-MoA3 Oxide Surfaces: Structure, Adsorption, Growth**, ***Ulrike Diebold***, TU Wien, Austria **INVITED**

Fundamental investigations into the surface properties of oxides have experienced a continued growth. The reasons for this increasing interest are quite clear: after all, most metals are oxidized under ambient conditions, so in many instances it is the oxidized surface that deserves our attention. In addition, metal oxides exhibit an extremely wide variability in their physical and chemical properties. These are exploited in established and emerging technologies such as catalysis, gas sensing, and energy conversion schemes, where surfaces and interfaces play a central role in device functioning. Hence a more complete understanding of metal oxide surfaces is desirable from both fundamental and applied points of view.

By using Scanning Probe Microscopy measurements, in combination with Density Functional Theory calculations and area-averaging spectroscopic techniques, great strides have been made in understanding the atomic-scale properties of the surfaces of these complex materials.

In the talk I will give examples drawn from recent studies on several metal oxide systems, including TiO_2, Fe_3O_4, In_2O_3, ZrO_2, and perovskites. I will point out the advantages of directly viewing, and manipulating, point defects and single molecules with atomic precision, and how inspecting central processes such as charge transfer to adsorbates can further a deep mechanistic understanding. I will also discuss new opportunities based on recent technique development such as Scanning Force Microscopy, and the challenges and possible rewards in exploring more complex materials.

3:00pm **NS+HC+SS-MoA5 Imaging and Sensor Applications of infiltrated Zinc Oxide**, ***Leonidas Ocola***, Argonne National Laboratory, *V. Sampathkumar*, University of Chicago, *N. Kasthuri*, *R.P. Winarski*, Argonne National Laboratory, *Y. Wang*, *J.H. Chen*, University of Wisconsin - Milwaukee

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

Most biological materials have problems with charging when imaging with electrons and low contrast when imaging with hard X-rays. In this presentation we describe the use of infiltrated ZnO as a means to address both charge dissipation in electron microscopy and contrast enhancement for X-ray microscopy. With ZnO infiltration it is feasible to coat a 2 – 3 nm conductive metal oxide film throughout a porous biological sample, and image both the surface and the interior of a sample without any further sample recoating. We demonstrate this technique can be applied on tooth and brain tissue samples. We show that high resolution X-ray tomography can be performed on biological systems using Zn K edge (1s) absorption to enhance internal structures, and obtained the first nanoscale 10 KeV X-ray absorption images of the interior regions of a tooth.

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

- Use of the Center for Nanoscale Materials and the Advanced Photon Source, both Office of Science user facilities, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. Additional funding by IARPA, (ARIADNE) under Contract D16P00002

3:20pm **NS+HC+SS-MoA6 Plasma Modified Gas Sensors: Bridging the Gap Between Tin Oxide Nanomaterials and Paper-Based Devices**, ***Kimberly Hiyoto***, *E.R. Fisher*, Colorado State University

Metal oxide nanomaterials are desirable for solid-state gas sensors because of their low manufacturing cost and ability to detect a wide variety of gases through changes in resistance resulting from gas-surface interactions. The substrates that support these materials, however, are often brittle and their smooth surface limits the amount of nanomaterial that can be exposed to target gases. Recent attempts to address these issues utilize paper substrates, that are not only low cost, but flexible to allow for a more robust device. Moreover, the porous, fibrous morphology of paper substrates provides significantly increased surface area for attaching more nanomaterials when compared to a traditional substrate of the same size. Despite recent improvements to paper-based metal oxide gas sensors, tin(IV) oxide (SnO_2) nanomaterials require high operating temperatures, thus have not yet been successfully translated to paper-based sensors. Here, we describe how low power (30 – 60 W) Ar/O_2 plasma modification, can be used to enhance gas-surface interactions of SnO_2 paper-based sensors while maintaining desirable bulk nanomaterial and substrate architecture. X-ray photoelectron spectroscopy revealed plasma treatment increased adsorbed oxygen, which is thought to improve sensor response by promoting gas-surface interactions. Indeed, plasma modified SnO_2 nanomaterials on a paper substrate exhibit improved response to ethanol, carbon monoxide, and benzene at ambient temperature. Furthermore, scanning electron microscopy demonstrates that plasma treatment does not damage the morphology of SnO_2 or the paper substrate. Response and recovery studies on these devices will be discussed along with SnO_2 nanomaterial gas sensors created on more traditional substrates (e.g. ZrO_2) as another measure of sensor performance. A better understanding of how plasma modification and the resulting changes in surface chemistry affect sensor performance is an important step towards achieving improved paper-based gas sensors using SnO_2 nanomaterials.

4:00pm **NS+HC+SS-MoA8 Understanding the Initial Stages of Oxidation in Nickel-Chromium Alloys**, *P. Reinke*, ***William H. Blades***, *G. Ramalingam*, University of Virginia

Through a combined experimental and computational effort, the interaction of oxygen with Nickel-Chromium alloys is studied. Prior to the formation of a full oxide layer, the physical and chemical processes behind the initial stages of oxidation are not well understood. This work fills a significant gap in our understanding of binary alloy oxidation. Scanning Tunneling Microscopy and Spectroscopy were used to observe the onset of oxide formation. These surface techniques are combined with Bandgap and Density of States maps, which lend themselves as powerful tools when studying surfaces with heterogeneity at the nanoscale. Ni-Cr(100) thin films with a range of compositions were prepared on MgO(100) in UHV and exposed to controlled amounts of oxygen up to 400L. Previous experiments have shown chromia to be the dominant oxide when Ni-Cr alloys are oxidized with a partial pressure of $p(O_2)<10^{-7}$mbar at 300ºC. Under these oxidation conditions the Ni prefers the kinetically favorable Ni(100)-c(2x2)-O reconstruction. Our experiments demonstrate that a combination of increased chromium concentration, which locally catalyzes the Ni, and an elevated oxidation temperature of 500ºC can overcome the activation barrier for NiO formation. The statistical analysis of island densities and sticking coefficient, in direct comparison of Ni and Ni-Cr surfaces, support the idea that NiO nucleation is facilitated by the presence of Cr. Early oxidation steps reveal that initial NiO nucleation and growth occurs along the step edges of the Ni-Cr alloy. This is in contrast to Ni(100)-c(2x2)-O where the step edges are passivated and devoid of reactive kink sites. We suggest that the presence of Cr at the step edges lowers the activation barrier and thus promotes rapid NiO formation. Anneal periods have shown that at low coverage, the NiO is readily desorbed from the surface leaving behind small oxides particles and regions with chemisorbed oxygen. Further oxidation steps create a high quality crystalline oxide layer, which is significantly more stable at elevated temperatures. Density Functional Theory is used to develop an understanding of the electronic and geometric structure of the oxidized Ni-Cr alloys and the effect of chromium on the local bonding environment. This collective experimental and theoretical approach has offered greater insight into alloy-oxide interface structure, and the role of transition metal dopants in the oxidation process in the pre Cabrera-Mott regime. This work is supported by the Office of Navel Research MURI “Understanding Corrosion in Four Dimensions,” Grant N00014-14-1-0675.

4:20pm **NS+HC+SS-MoA9 Evaluation of Titanium Doped β-Ga_2O_3 Thin Films in Extreme Environment for Application in Oxygen Sensors**, ***Sandeep Manandhar***, *A.K. Battu*, *C.V. Ramana*, University of Texas at El Paso

The reliable and efficient operation of power generation systems has become one of the grand challenges of today’s research in order to meet the ever-increasing demand for energy and sustainability. The improvement in power/energy generation processes, in particular, for those depend on fossil fuels, the higher temperature and accurate measurement of the combustion environment and the emissions produced by the combustion via proper selection of sensing materials can enhance the efficiency and reliability. While several candidate metal oxides (SnO_2, ZnO, TiO_2, WO_3, and Ga_2O_3) exhibit high sensitivity chemical gases, β-Ga_2O_3 has shown to function as oxygen sensor at high temperatures (>700°C). However, the response time and sensitivity must be improved in order to utilize them in practical applications. While improved sensor characteristics are seen in various metal/ion doped β-Ga_2O_3, fundamental understanding of the long term effects of high temperature exposure on the structure and properties of doped β-Ga_2O_3 films is missing at this time. However, such studies are quite important to predict the thermodynamic stability and performance in extreme environments. In this work, we performed a detailed study to understand the effect of extreme environment on titanium (Ti) doped β-Ga_2O_3. The real environment condition for sensor (>700°C) application were simulated to understand the effect of temperature on the crystal structure, mechanical properties, electronic properties and oxidation states of Ti doped β-Ga_2O_3. The results will be presented and compared with as prepared Ti doped β-Ga_2O_3 films in the context of utilizing these materials in oxygen sensor applications.

4:40pm **NS+HC+SS-MoA10 Characterization of Infiltrated ZnO in PS-b-PMMA Nanostructures**, ***Paris Blaisdell-Pijuan***, University of Chicago, *L.E. Ocola*, Argonne National Laboratory

We have characterized the growth of ZnO using sequential infiltration synthesis (SiS) on PS-b-PMMA block copolymers (BCP) of spherical and cylindrical sub-20nm morphologies and studied how the photoluminescence of these nanostructures varies per its seed layer. Investigation of these structures was done using atomic force microscopy (AFM), spectrofluorometry, Raman spectroscopy, and scanning electron microscopy (SEM). We report blue-shifted photoemission at 335nm (3.70eV), suggesting quantum confinement effects. Samples of ZnO prepared with an alumina seed layer showed additional defect state photoemission at 470nm and 520nm for spherical and cylindrical BCP morphologies, respectively. Defect photoemission was not observed in samples prepared without a seed layer. No Raman peaks were observed for any samples with less than four cycles of ZnO, implying the absence of phonons and the functionality of these ZnO nanostructures as isolated emitters. Rapid thermal annealing of samples in air above 500 ºC began to coalesce and show photoemission characteristic of bulk ZnO at 370nm (3.35eV). Our work demonstrates that ZnO nanostructures grown on PS-b-PMMA via SiS are advantageous in uniformity and size, and exhibit unique fluorescence properties. These observations suggest that infiltrated ZnO in PS-b-PMMA nanostructures lends itself to a new regime of applications in photonics and quantum materials.

Scanning Probe Microscopy Focus Topic
Room: 10 - Session SP+2D+AS+NS+SS-MoA

Probing Electronic and Transport Properties

Moderators: Phillip First, Georgia Institute of Technology, Chuanxu Ma, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

1:40pm **SP+2D+AS+NS+SS-MoA1 Probing Atomic and Electronic Structures of 2D Electronic Materials and their Heterostructures**, ***Chih-Kang Shih***, University of Texas at Dallas **INVITED**

The emerging atomic layer materials offer a remarkably wide range of building blocks of nanostructures ranging from metals (e.g. graphene), large gap insulators (BN), to semiconductors (transition metal dichalcogenides and black phosphorous). Key advantages of these van der Waals materials include a broad span of energy gaps, flexibility of stacking different types of materials to form heterostructures, tunability in material properties by doping and strain, and the relative ease of integration with other electronic and photonic devices. This talk will be focused on the usage of scanning tunneling microscopy and spectroscopy to probe the atomic and electronic structure of transition metal dichalcogenides (TMDs) and their heterostructures, including both vertical and lateral structures.

I will first introduce a comprehensive form of scanning tunneling spectroscopy (STS) which allows us to probe not only the quasi-particle band gaps but also the critical point energy locations and their origins in the Brillouin Zone (BZ) can be revealed using this comprehensive form of STS. By using this new method, we reveal the systematic trend of the critical point energies for TMDs due to atomic orbital couplings, spin-orbital coupling and the interlayer coupling. By using the vertically stacked MoS2/WSe2, I will show how interlayer coupling can be used as a new designing parameter to create a lateral 2D electronic superlattices. I will then turn attention to MoS2/WSe2 lateral heterostructure where I will show a novel method to probe 2D strain tensor and how the strain changes the band profile as well as the band alignment at the interface.

2:20pm **SP+2D+AS+NS+SS-MoA3 SP-STM Study of Antiferromagnetic CuMnAs Thin Film**, ***Giang Nguyen***, Oak Ridge National Laboratory, *P. Wadley, R. Campion, K. Edmonds,* University of Nottingham, UK, *F. Maccherozzi, S. Dhesi,* 3Diamond Light Source, UK, *T. Jungwirth,* University of Nottingham, UK, *A.-P. Li*, Oak Ridge National Laboratory

Antiferromagnetic (AFM) tetragonal CuMnAs thin films have attracted great research interest recently, largely due to the capability of manipulating and detecting of their AFM states with ordinary electric current. Here we report a study on a CuMnAs thin film, grown epitaxially on GaP(001) substrates, using Spin-Polarized Scanning Tunneling Microscopy (SP-STM). An arsenic capping layer is used to protect the sample during transferring through the air which is able to be subsequently removed from the surface by thermal annealing. Atomic resolution STM topographic images of CuMnAs surface are achieved which shows an interesting surface reconstruction. Scanning tunneling spectroscopy (STS) is performed to explore the electronic structure of the thin film as well at the surface step edge. SP-STM study in combination with X-ray magnetic linear dichroism-photoelectron emission microscopic (XMLD-PEEM) measurements provides further understanding of the antiferromagnetic domain structure.

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.

2:40pm **SP+2D+AS+NS+SS-MoA4 Probing Spin-Dependent Chemical Potential in Topological Insulator by Spin-Polarized Four-Probe Scanning Tunneling Microscopy**, ***Wonhee Ko***, *S.M. Hus,* Oak Ridge National Laboratory, *Y.P. Chen,* Purdue University, *A.-P. Li,* Oak Ridge National Laboratory

Conversion between the charge and the spin signal is a core technology for detection of many spin-related phenomena and for the realization of spintronic devices. Topological insulators are promising candidate for such purpose because of their surface states with non-trivial spin texture. The surface states electrons have the spin and the momentum locked to each other, so the electrical current can induce the uneven shift in the spin-dependent chemical potential for different spin directions. In this talk, we utilized spin-polarized four-probe scanning tunneling microscopy to probe the spin-dependent chemical potential of the topological insulators. Utilizing ferromagnetic tips and variable probe-spacing measurements, we detected non-vanishing spin-dependent chemical potential induced by the charge current. Various tip and surface conditions were tested to confirm its origin from the spin of charge carriers through the surface states. The result demonstrates the generation of excessive spins only by electrical means in topological insulators, which would become the critical component for the future spintronic applications.

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

3:00pm **SP+2D+AS+NS+SS-MoA5 Spin-charge Transport Phenomena on the Atomic Scale Studied by Multi-probe STM**, ***Christoph Tegenkamp***, Leibniz Universität Hannover, Germany **INVITED**

Low dimensional metallic structures, e.g. quantum wires and films on surfaces, reveal fascinating phenomena of condensed matter physics. Among others, 2D-superconductvity, formation of charge density waves and topologically protected edge states were realized lately with atomic precision and directly probed by electronic transport. Generally, the surface science approach benefits from the fact that the low dimensional systems can be comprehensively characterized and manipulated in view of their atomic structure and electronic bands. This is a prerequisite to understand electronic transport on the atomic scale.

In this talk I will introduce the technique of surface sensitive transport by means of 4-tip STM technique and highlight some recent examples of our group from seemingly different fields, e.g. spintronic, correlated materials and mesoscopic physics. The talk covers spin-orbit coupling related phase transitions in quasi 1D atomic wire structures (Au/Si(553), Pb/Si(557) [1,2]) as well as ballistic transmittance of electrons in epitaxially grown graphene nanostructures on SiC(0001) [3-5].

[1] C. Tegenkamp, et.al. PRL 109, 266401 (2012)

[2] C. Brand, et.al. , Nat. Comm. 6, 8118 (2015)

[3] J. Baringhaus ,et.al., Nature 506, 349 (2014)

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[5] J. Baringhaus et.al. PRL. 116, 3186602 (2016)

4:00pm **SP+2D+AS+NS+SS-MoA8 Site-specific Superconducting Atomic Contacts Studied by Scanning Tunneling Microscopy**, ***Yukio Hasegawa***, The Institute for Solid State Physics, The University of Tokyo, Japan **INVITED**

In the trend of miniaturization of devices, electrical conductance through atomic-scale contacts is of significant importance for practical application of atom switch and single molecular devices. Because of unknown atomic geometry at the junction, however, the measured conductance often fluctuates. Here in this study we have studied the conductance properties of atomic superconducting point contact with precise control of contact geometry to investigate atomic details of conductance channel formation through it.

Using a low-temperature scanning tunneling microscopy (STM), we measured the conductance between the tip and sample surface from the tunneling to contact regimes [1]. By precisely positioning the tip on atomically specific sites of a sample surface such as on-top and hollow sites, site-specific conductance evolutions were obtained. We found using a Pb tip and Pb thin film as contact forming materials the conductance at point contact is larger at hollow site than at on-top site. Furthermore, it is found that the relation of the conductance measured is reversed just before the contact formation; at 20 pm away from the contact the conductance of the hollow site is smaller than the on-top site. These peculiar conductance behaviors can be explained by the attractive chemical force and subsequent conductance channel formation between the tip apex atom and surface atoms of the thin film.

Since the measurements were performed at low temperature (1.6 K) below the superconducting critical temperature of both materials, we obtained the evolution of the Josephson current and subharmonic in-gap structures due to multiple Andreev reflection (MAR) in the conductance spectra. From the analysis of the MAR structures, the complete set of transmission probability of conduction channels, which is often called personal identification number (PIN) of the junction as it determines all the coherent transport properties, was successfully extracted [2]. We found again site dependent evolution of transmission probabilities and the number of active conduction channels at the contact formation. We will discuss on the mechanism of channel formations based on comparison with the results of theoretical analysis.

References

[1] H. Kim and Y. Hasegawa, Phys Rev Lett 114, 206801 (2015)

[2] H. Kim, M. Kawamura, T. Kato, T. Ozaki, and Y. Hasegawa, in preparation.

4:40pm **SP+2D+AS+NS+SS-MoA10 The Difference between Electron and Hole Dopant of Magnetic Element to the Superconductivity in BaFe$_2$As$_2$**, ***Qiang Zou***, *L. Li, A. Sefat, D.S. Parker, Z. Gai*, Oak Ridge National Laboratory

The effect of magnetism and spin excitation in the Fe-based superconductors (FeSC) is crucial to understand their superconductivity. Both electron-(Ni) and hole-(Cr) dopant of magnetic elements could lead to suppression of the magnetic/structural phase transition in BaFe$_2$As$_2$. However, the Cr doped BaFe$_2$As$_2$ doesn’t show the superconductivity. Using scanning tunneling microscopy/spectroscopy, here, we compared the electronic properties of BaFe$_2$-xNixAs$_2$ and BaFe$_2$-xCrxAs$_2$ at various temperatures. Our results will shed the light on the microscopic understanding of relation between the superconductivity and magnetism in the FeSC. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

5:00pm **SP+2D+AS+NS+SS-MoA11 Rapid Measurement of I-V Curves in Scanning Probe Microscopy via Bayesian Inference**, *S. Somnath, K. Law, R. Archibald, S.V. Kalinin, S. Jesse*, ***Rama Vasudevan***, Oak Ridge National Laboratory

Current-voltage (IV) curve acquisition is the oldest and most common spectroscopic method implemented on virtually every scanning probe microscope (SPM) available. Though in use for three decades, the basic measurement has not altered substantially in this time-frame, with the current being detected during DC pulses applied to the SPM tip. Such measurements include both a delay time after each DC voltage change (to reduce parasitic capacitance influence), as well as a an integration time, to reduce noise, limiting typical measurements to a few Hz at most. Here, we introduce a new method for IV curve acquisition, based on an AC-excitation of the SPM tip, in combination with full information acquisition from the current amplifier and Bayesian inference. IV curves are acquired on a model ferroelectric system, at rates ~500x faster than the current state of the art, with higher spatial and spectral resolution. The obtained results offer a complementary channel of information to supplement existing piezoresponse force microscopy studies, allowing to probe disorder at the nanoscale. Bayesian inference further allows quantification of the capacitance contribution, which can be utilized to estimate the dielectric constant of the ferroelectric, with results agreeing with reported values. These studies highlight the utility of both complete information acquisition, and Bayesian inference, in dramatically increasing the acquisition rates of data from SPM.

This research was sponsored by the Division of Materials Sciences and Engineering, BES, DOE (RKV, SVK, SS). This research was conducted and partially supported (SJ) at the Center for Nanophase Materials Sciences, which is a US DOE Office of Science User Facility. Bayesian inference portion was sponsored by the Applied Mathematics Division of ASCR, DOE; in particular under the ACUMEN project (KJHL, RA).

Electronic Materials and Photonics Division
Room: 14 - Session EM+NS-TuM

Nanostructures and Nanometer Films for Electronic and Photonic Devices
Moderators: Jessica Hilton, RHK Technology, Joseph Tischler, U.S. Naval Research Laboratory

8:00am **EM+NS-TuM1 Spin Properties in Semiconductor Colloidal Quantum Dots**, ***Efrat Lifshitz***, Russell Berrie Nanotechnology Institute, Solid State Institute, Israel **INVITED**

Colloidal semiconductor quantum dots (CQDs) have been at the forefront of scientific research for more than two decades, based on their electronic and optical tunable properties. Recent years show a substantial interest in spin properties with significant importance for spin-electronic, spin-photovoltaic and spin-optical devices.

The talk includes the study of two different CQD platforms: (1) CQDs from the II-VI semiconductors and their diluted magnetic derivatives; (2) Halide perovskite CQDs. Both systems show intriguing spin properties of special scientific and technological interests.

Spins in CdSe/CdS and Mn^{+2}@CdSe/CdS: Unpaired spins generated by an absorption of a phonton (electron and hole) can dictate the magneto-optical properties of the host CQDs. Furthermore, magnetic doping by foreign ions (e.g., Mn), induces internal spin interactions between photo-generated species and the dopant spins, leading to giant magnetization. The current study developed a method to position the Mn ions selectively either at the core or at the shell, by which, controlling the electron-guest versus hole-guest exchange interaction. The materials were characterized by magneto-optical methods, including optically detected magnetic resonance, uncovered individual interactions with resident carriers, thus, revealing understanding of a control of a magnetism with a benefit for spin-based devices.

$APbBr_3$ (A=Cs$^+$, methylamonium)*: The perovskites are minerals that have been studied extensively in the past. They are the focus of new interest in recent years, due to their exceptional performance in photovoltaic cells. Perovskites semiconductors possess high absorption coefficients as well as long-range transport properties. Currently, they are also prepared in the form of CQDs with very interesting properties including ferroelectricity, magnetism and exciton effects. The magneto-optical measurements of excitons in $APbBr_3$ as individuals were investigated by monitoring the micro-photoluminescence spectra in the presence of an external magnetic field, while monitoring either the circular or linear polarization components. Gradual band splitting occurring upon the application of a magnetic field, deviating from a common Zeeman interaction behavior, proposes the existence of a more complex mechanism, when Rashba split is one of the plausible interpretations.

*Collaboration with M. Kovalenko and A. Rappe

9:00am **EM+NS-TuM4 A Platform for Growth of Crystalline Thin-Film Compound Semiconductors on Oxides, Metals, and 2-D Materials**, ***Rehan Kapadia***, *D. Sarkar, W. Wang*, University of Southern California

The electronic and photonic circuits and systems that form the backbone of the modern world are predicated on the ability to create high quality semiconductors. Yet, high-performance electronic and photonic grade semiconductors are nearly exclusively grown on lattice matched substrates. This substrate limitation arises due to the fundamental mechanisms of nucleation and growth in state-of-the-art vapor phase growth techniques, which proves to be extremely limiting and costly. Here we demonstrate a platform for growth of compound semiconductors from microscale liquid metal templates. Using these templates, we can control nucleation and growth of these compound semiconductors, enabling single crystalline devices on non-epitaxial substrates. To grow single crystalline material in the desired form-factors, from liquid metal templates on arbitrary substrates presents a significant challenge, as dewetting of the liquid films prevent control over the ultimate material geometry. Through a basic thermodynamic approach, we show that it is possible to control dewetting on nearly any material, and subsequently grow compound semiconductors on these same substrates. Using this approach, we demonstrate growth and characterization of crystalline InP, InAs, and GaP, on silicon nitride, graphene, gadolinium oxide on silicon, and metals.

Next, we show that compound semiconductors with multiple stable phases can be grown phase-pure using this approach, using tin phosphide as the example. We show that through tuning the growth conditions, we can control which stable phase of tin phosphide precipitates and grows. This control illustrates that our approach is useful for materials beyond simple III-V and II-IV compounds, which only have one stable phase. By carrying out these growths at significantly non-equilibrium conditions, we demonstrate ternary InGaP alloys, with stoichiometry control over nearly the entire In-Ga composition range. Unlike binary III-V or the Sn-P system, where the stoichiometry of the precipitating compound is nearly insensitive to the growth conditions, the ternary systems are alloys, and consequently extremely sensitive to growth conditions, making growth of uniform materials a potential challenge. We show that through control over the growth conditions, we can achieve high-quality, uniform stoichiometry ternary III-V alloys. Finally, we show that by enabling nanoscale phase segregation during growth of these ternary alloys, we can materials with extremely broadband photoluminescence curves, with FWHMs greater than 600 meV, potentially enabling a new class of broadband light sources.

9:40am **EM+NS-TuM6 Nanometer Thick Diffused Metal Oxide Light Sensing Film Structures**, ***Fred Cadieu***, Queens College of CUNY and Graduate Center of CUNY, *J.S. Monaco,* Queens College of CUNY, *L. Mourokh*, Queens College of CUNY and Graduate Center of CUNY

Approximately 10 nm thick light sensing film structures have been fabricated by sequentially sputtering various metals in oxygen, then in argon, and then in oxygen again. The layers have been deposited onto heated silicon substrates to create a diffusion region. The layered thicknesses were calibrated by x-ray reflectivity measurements. The film layers, being mostly oxides, exhibit a high lateral resistivity so that the current path is through the film thickness between a grid of contacts deposited below and on top of the film structures. For such current, a high degree of light sensitivity, and voltage polarity sensitivity, has been observed.[1] Analogous film structures have been fabricated using hafnium,[2] titanium,[2] and aluminum such that exposure to light causes large increases in currents for one voltage polarity, but little or no effect for the opposite polarity. The observed phenomenology has been shown to be consistent with a single-particle model based on the existence of interface states on the metal-oxide interfaces.[2] The details of light sensitivity and current polarity sensitivity are dependent on the deposition temperatures and thicknesses of the film layers. Hafnium based interfaces respond repeatedly to light pulses with current pulses up to several hundred microamperes, while aluminum based interfaces can only respond repeatedly with current pulses up to several tens of microamperes.

1. F.J. Cadieu, Device with Light-Responsive Layers. US Patent No. 9,040,982.

2. F.J. Cadieu and Lev Murokh, Nanometer Thick Diffused Hafnium and Titanium Oxide Light Sensing Film Structures, *World Journal of Condensed Matter Physics***7**, 36-45 (2017).

11:00am **EM+NS-TuM10 Integration of Metallic Nanoparticles in Sensing and Memory Devices for Resistance Modulation and Enhanced Switching**, ***Dimitris Tsoukalas***, National Technical University of Athens, Greece **INVITED**

In this work we present the fabrication of metallic nanoparticles (NPs) in vacuum at room temperature and their incorporation into sensor or memory two terminal devices emphasizing their influence on device resistance modulation or switching. Nanoparticles were manufactured using the gas phase condensation technique with a target of high purity. The NPs production system consists of a smaller vacuum chamber (Nanogen) which is connected via an aperture of diameter ~ 3 mm with a larger central vacuum chamber in which the sample holder is mounted. The Nanogen chamber is equipped with a DC magnetron sputtering head and in between the Nanogen chamber and the central chamber there is a pressure gradient, the pressure in the Nanogen being around 10^{-1} mbar while in the main chamber pressure is 10^{-4} mbar. The atoms produced by the magnetron sputtering because of the high pressure in the Nanogen chamber, undergo a short free path, colliding with the atoms of the inert gas (Ar) and lose part of their kinetic energy. This leads to the creation of a supersaturated vapor of the target material, which is condensed, causing the atoms to form nuclei from the material. Due to the pressure gradient prevailing, these nuclei move towards the central chamber. During this movement they interact among them to form larger NPs finally entering into the central vacuum chamber through the aperture.

Regarding the application of nanoparticle networks to sensors, our group is focusing in the use of metallic NPs in particular for chemical, bio and strain sensing applications. We first review the principle of operation of such devices that is based on the change of percolation current through the NP network when the interspace distance among NPs is modified by an external stimuli. We then discuss the potential of integrating these sensors on flexible substrates as well as the influence on their performance of a protective aluminum oxide coating deposited over the nanoparticle network.

Resistive switching memories (RRAM) based on metal oxides are emerging as a new research field and at the same time are intensively studied as one of the most promising candidates for future non-volatile memory applications. We demonstrate that a wide range of non-volatile memory properties can be affected and improved by embedding NPs into the metal oxide matrix. The concentrated electric field effect around the nanoparticles in combination with the charge trapping effect, are regarded as the driving forces for the recorded switching patterns. As a result NPs increase the on/off switching ratio and at the same time decrease the inherent variability of RRAM.

11:40am **EM+NS-TuM12 Thin-film Metallic Glass: An Effective Diffusion Barrier for Microelectronic Packaging, CIGS Solar Cell and Thermoelectric Modules**, *C.C. Yu,* National Taiwan University of Science and Technology, Taiwan, Republic of China, *H.J. Wu,* National Sun Yat-sen University, Taiwan, Republic of China, ***Jinn Chu***, National Taiwan University of Science and Technology, Taiwan, Republic of China

Thin film metallic glass (TFMG) with its amorphous nature is of great interest owing to its unique properties, including high strength, large elastic limits, excellent corrosion and wear resistance. For many electronics, the atomic inter-diffusion may cause device failure or performance degradation during either fabrication or operation. Thus, the introduction of diffusion barrier layer in the device is a common approach to solve this problem. Crystalline Ni- or Ti-based layers are the most common materials for diffusion barriers. Nevertheless, grain boundaries are generally considered as atomic diffusion path, and thus crystalline metals are not able to block diffusion effectively. TFMG, possessing grain boundary-free structure, is thus thought to efficiently mitigate atomic diffusion.

In this presentation, we report the effects of thin film metallic glass as diffusion barriers on the Sn whisker mitigation in the Cu-Sn couples and the copper indium gallium selenide (CIGS) solar cells on stainless steel (SS) as well as the mid-temperature thermoelectric module. We found that TFMG effectively blocks the Cu/Sn interaction even with the thickness as thin as 25 nm. In addition, with very thin thickness, the introduction of TFMG layer is expected to yield insignificant degrees of compressive stress, which is anticipated to occur when the samples are exposed to thermal cycling. Furthermore, the detrimental iron diffusion from SS into CIGS is found to be effectively hindered by the introduction of a 70-nm-thick TFMG barrier; the cell efficiency is thus from 2.73 for bare sample to 5.25% for the one with TFMG barrier. For application in thermoelectric module, a 200 nm-thick Zr-based TFMG, acting as an effective diffusion barrier layer with low electrical contact resistivity, was deposited on a high-zT Se-doped $AgSbTe_2$ substrate. The reaction couples structured with TFMG/TE were annealed at 673 K for 8–360 hours and analyzed by electron microscopy. No observable intermetallic compounds were formed at the TFMG/TE interface, suggesting the effective inhibition of atomic diffusion.

12:00pm **EM+NS-TuM13 Ultra-Fast Silicon Photodiodes Achieve High Efficiency via the Integration of Light-trapping Micro-/nanoholes**, ***Hilal Cansizoglu****, Y. Gao, K.G. Polat, S. Ghandiparsi, C. Bartolo Perez, A. Kaya, H.H. Mamtaz, A.S. Mayet,* University of California, Davis, *E. Ponizovskaya Devine,* W&WSens Devices, Inc., *Y. Yamada,* University of California, Santa Cruz, *A.F. Elrefaie, S.Y. Wang,* W&WSens Devices, Inc., *M.S. Islam,* University of California, Davis

Surface-illuminated photodiodes (PDs) for ultra-fast data transmission are typically GaAs-based non-CMOS compatible detectors. Silicon (Si) has long been ignored for being a material of choice in ultra-fast communication links due to its poor responsivity for the wavelengths >800 nm at data rates 10 Gb/s or higher. Recent demonstration of CMOS compatible surface-illuminated Si PDs with photon-trapping micro-/nanoholes paves the way for the use of Si at 25 Gb/s or higher data transmission rate. Such PDs provided ≤30 ps full-width at half-maximum (FWHM) and above 50% quantum efficiency (QE) at 850nm, which is over 400% higher than the QE that a similar Si PD without absorption-enhancement micro-/nanoholes can provide. The micro/nanoholes create an ensemble of modes that radiate laterally by photon trapping and slow light effects, resulting in absorption enhancement in a very thin layer of Si (<2µm) which is required for high speed operations. The broadband efficiency enhancement by photon-trapping micro-/nanoholes enable Si to be considered as the PD material at longer wavelengths (>870 nm) which is below the room temperature bandgap of GaAs. Such broadband and enhanced efficiency of Si integrated with micro-/nanoholes can be useful for applications such as short wavelength division multiplexing (SWDM, 850-980 nm) for data centers, automotive laser radar systems (LIDAR, 850 or 905 nm) and high-performance computers (990-1065 nm). The CMOS-compatible fabrication of micro-/nanoholes can allow Si PDs to be monolithically integrated with CMOS/BiCMOS integrated circuits such as transimpedance amplifiers, equalizers, limiting amplifiers and other application specific integrated circuits (ASIC), which can increase the achievable data rate to more than 50 Gb/s.

Nanometer-scale Science and Technology Division
Room: 19 - Session NS+EM+MI+SS-TuM

Nanoscale Electronics and Magnetism
Moderators: Keith Brown, Boston University, Aubrey Hanbicki, Naval Research Laboratory

8:00am **NS+EM+MI+SS-TuM1 Nanometrology and Nanocharacterization in Nanoelectronics**, ***Alain C. Diebold***, SUNY Polytechnic Institute **INVITED**

As the so called technology node for integrated circuits moves below 10 nm, new transistor and interconnect materials as well as new device structures are moving from research into development. Pseudomorphic semiconductor films such as $Si_{1-x}Ge_x$ on Si are expected to transition to $Ge/Si_{1-x}Ge_x/Si$ or to III-V epilayers. The current lithographic processing used to pattern FinFETS is based on the Quadruple Spacer Patterning process which can result in two values of pitch walking. This greatly complicates in-line metrology. The FinFET itself will likely be replaced by nanowire transistors having multiple vertically stacked nanowire channels. Another alternative is the nano-sheet transistor. Beyond these evolutionary changes, longer term devices based on 2D materials are being investigated. These include graphene, transition metal dichalcogenides, and topologically protected materials. This talk will cover the advanced measurements being used to address the challenges associated with these new materials and structures. The talk will cover measurement methods including high resolution X-ray diffraction (XRD), XRD reciprocal space mapping, Mueller Matrix spectroscopic ellipsometry base scatterometry, and advanced electron microscopy.

9:00am **NS+EM+MI+SS-TuM4 Measurement of Resistance Induced by a Single Potassium Atom on Chiral-Angle Known Nanotubes: Understanding the Impact of a Model Scatterer for Nanoscale Sensors**, ***Masahiro Ishigami***, University of Central Florida, *R. Tsuchikawa,* University of Utah, *D. Heligman,* Ohio State University, *B.T. Blue,* University of Central Florida, *Z.Y. Zhang,* Columbia University, *A. Ahmadi, E.R. Mucciolo,* University of Central Florida, *J. Hone,* Columbia University

Even atomic impurities are expected to impact device properties of carbon nanotubes. Such sensitivity makes them ultimately useful for sensor technologies. Rational design for nanotube-based sensors requires precise understanding of how impurities impact transport properties of nanotubes. Such impurity-induced carrier scattering is expected to be dependent on the chirality of nanotubes and the nature of scattering potentials imposed by impurities. Yet until our recent measurements, it has been impossible to measure the impact of impurities on resistance of carbon nanotubes with known chirality.

We have developed arrays of experimental techniques to control experiments down to atomic scale to measure the scattering strength of charged impurities on semiconducting single-walled carbon nanotubes with known chirality. The resistivity of nanotubes is measured as a function of the density of adsorbed potassium atoms, enabling the determination of the resistance added by an individual potassium atom. Holes are scattered 37 times more efficiently than electrons by an adsorbed potassium atom. The determined scattering strength is used to reveal the spatial extent and depth of the scattering potential for potassium, a model Coulomb adsorbate, paving way for rational design of nanotube-based sensors. Our results are published in Phys. Rev. B [**94**, 045408 (2016)].

9:20am **NS+EM+MI+SS-TuM5 Atomic Electronics for Quantum Computing**, ***Michelle Simmons***, University of New South Wales, Australia **INVITED**

Extremely long electron spin coherence times have recently been demonstrated in isotopically pure Si-28 [1] making silicon one of the most promising semiconductor materials for spin based quantum information. The two level spin state of single electrons bound to shallow phosphorus donors in silicon in particular provide well defined, reproducible qubits [2] and represent a promising system for a scalable quantum computer in silicon. An important challenge in these systems is the realisation of a two-qubit gate, where we can both position donors with respect to each other for controllable exchange coupling and with respect to charge sensors for individually addressing and reading out the spin state of each donor with high fidelity.

To date we have demonstrated using scanning tunneling microscope hydrogen lithography how we can precisely position individual P donors in Si [3] aligned with nanoscale precision to local control gates [4] and can initialize, manipulate, and read-out the spin states [5,6] with high fidelity. We now demonstrate how we can achieve record single-electron readout fidelity for each of two donor based dots of 99.8%, above the surface-code fault tolerant threshold. We show how by engineering the quantum dots to contain multiple donors we can achieve spin lifetimes up to 16 times longer than single donors. Finally we show how by optimising the interdonor separation and using asymmetric confinement potentials we can create controllable exchange coupling in these devices. With the recent demonstration of ultra-low noise in these all epitaxial devices [7] these results confirm the enormous potential of atomic-scale qubits in silicon.

[1] J. T. Muhonen et al., Nature Nanotechnology 9, 986 (2014).

[2] B.E. Kane, Nature 393, 133 (1998).

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11:00am **NS+EM+MI+SS-TuM10 Electronically Abrupt Borophene/organic Lateral Heterostructures**, ***Xiaolong Liu***, Z. Wei, I. Balla, A.J. Mannix,* Northwestern University*, N.P. Guisinger,* Argonne National Laboratory*, E. Luijten, M.C. Hersam*, Northwestern University

Two-dimensional (2D) boron, known as borophene, has recently been experimentally realized[1,2] following theoretical predictions.[3] As an elementary 2D material, borophene is determined to be metallic like graphene, but also possesses a high degree of in-plane anisotropy like phosphorene. Thus far, all experimental studies have been performed on borophene alone, whereas borophene-based electronic applications will require precise integration of borophene with other materials. Here, we demonstrate the self-assembly of a borophene/organic lateral heterostructure[4]. Upon the deposition of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on sub-monolayer borophene on Ag(111), the molecules preferentially self-assemble into monolayers on bare Ag(111), forming borophene/PTCDA lateral heterostructures spontaneously. This phenomenon is consistent with a lower adsorption energy of PTCDA molecules on borophene, as modeled via molecular dynamics simulations. The formation of the heterostructure leaves the chemical integrity of borophene unperturbed as supported by in situ X-ray photoelectron spectroscopy. In addition to structural properties, atomic-scale ultra-high vacuum scanning tunneling microscopy and spectroscopy reveal strong electronic contrast between the two materials and an electronically abrupt heterojunction with a transition distance of ~1 nm (i.e., approximately the size of one PTCDA molecule). Across this transition region, the differential tunneling conductance curves change from the metallic electronic structure of borophene to the semiconducting molecular orbitals of PTCDA, suggesting the formation of an atomically abrupt 2D metal-semiconductor junction. Overall, the results of this study are likely to inform future research on borophene functionalization for nanoelectronic applications.

1. A. J. Mannix, X.-F. Zhou, B. Kiraly, J. D. Wood, D. Alducin, B. D. Myers, X. Liu, B. L. Fisher, U. Santiago, J. R. Guest, M. J. Yacaman, A. Ponce, A. R. Oganov, M. C. Hersam, N. P. Guisinger, *Science***350**, 1513–1516 (2015).

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3. Y. Liu, E. S. Penev, B. I. Yakobson, *Angew. Chem. Int. Ed.***52**, 3156–3159 (2013).

4. X. Liu, Z. Wei, I. Balla, A. J. Mannix, N. P. Guisinger, E. Luijten, and M. C. Hersam, *Sci. Adv*. **3**, e1602356 (2017).

11:20am **NS+EM+MI+SS-TuM11 Mechanical Characterization of Heat Dissipation in a Current-driven Ferromagnetic Resonance System**, *S.U. Cho, M. Jo, S. Park, J.-H. Lee, C. Yang, S. Kang,* Seoul National University, ***Yun Daniel Park***, Seoul National University, Republic of Korea

Heat dissipation in current-driven ferromagnetic resonance (FMR) system is characterized by monitoring the mechanical resonance, which shifts are governed by thermoelastic properties. Realization of a free-standing Permalloy (Py)/Pt bilayer strip, with an added mechanical degree of freedom, advantageously integrates means to separately measure mechanical resonance, by piezoresistive transduction in Pt [1], and FMR by using the spin-torque FMR (ST-FMR) measurement technique [2]. Heat generated by the precessing magnetization under an electric driving current are selectively investigated by monitoring the mechanical resonance shift, which are immune and independent to thermoelectric effects. By comparing the angular dependence to the applied magnetic field direction of the two FMR spectroscopies, ST-FMR and mechanical heat reaction, we find that Joule heat resulting from a time-dependent magnetoresistance, which in turn arises from the precessing magnetization and electrical current, cannot be overlooked in addition to the intrinsic FMR heat dissipation.

[1] H. Bhaskaran *et al*. Appl. Phys. Lett. **98**, 013502 (2011).

[2] L. Liu *et al*., Phys. Rev. Lett. **106**, 036601 (2011).

11:40am **NS+EM+MI+SS-TuM12 The Exciting Physics of Spin Chains Coupled to a Metallic Substrate**, ***Roland Wiesendanger***, University of Hamburg, Germany **INVITED**

A magnetic nanowire on the surface of a spin-orbit coupled s-wave superconductor is a fascinating platform, which has been proposed for observing the emergence of zero-energy Majorana bound states at the ends of the wires [1]. Majorana fermions can encode topological qubits and ultimately provide a new direction in topological quantum computation [2]. Most recently, evidences for topologically non-trivial end-states were experimentally found for self-assembled ferromagnetic Fe nanowires on superconducting Pb(110) substrates by using scanning tunneling microscopy and spectroscopy (STM/S) as well as non-contact atomic force microscopy methods [3-6]. However, self-assembled nanowires of Fe on Pb surfaces have unavoidable limitations, such as (1) intermixing of atomic species of the nanowire and the substrate during the annealing process, and (2) uncontrolled length and orientation of the nanowires.

Here, we demonstrate the fully-controlled bottom-up fabrication of artificial 1D atomic chains from individual magnetic Fe adatoms on high spin-orbit coupled non-superconducting Pt(111) and superconducting Re(0001) substrates by utilizing STM-based atom-manipulation techniques at T=350 mK. Spin-polarized STM measurements indicate the presence of non-collinear spin textures, i.e. spin spiral ground states, stabilized by interfacial Dzyaloshinskii-Moriya interactions similar to self-assembled Fe chains on Ir(001) investigated earlier [7]. The problem of intermixing is avoided by the low-temperature fabrication of the chain and an appropriate choice of the substrate, while single-atom manipulation allows the construction of chains with a given number of atoms and orientation. Tunneling spectra measured spatially resolved on the Fe-atom chain on Re(0001) reveal the evolution of the local density of states (LDOS) inside the superconducting gap as well as the development of zero-energy bound states at the ends of the chain, which are distinguishable from trivial end states by systematically increasing the number of atoms within the Fe-atom chain. The experimental results will be compared with model-type calculations supporting the interpretation of the spectroscopic signatures at the ends of the chains as Majorana bound states.

(work done together with Howon Kim and Khai Ton That).

References

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[5] R. Pawlak *et al.*, NPJ Quantum Information **2**, 16035 (2016).

[6] B. E. Feldman *et al.*, Nature Phys. **13**, 286 (2017).

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Scanning Probe Microscopy Focus Topic
Room: 10 - Session SP+AS+MI+NS+SS-TuM

Probing Chemical Reactions at the Nanoscale

Moderators: Tae-Hwan Kim, Pohang University of Science and Technology, Republic of Korea, Giang Nguyen, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

8:00am **SP+AS+MI+NS+SS-TuM1 Single Molecule Junction: Chemical Optimization of Charge Transport through Single Benzene Derivatives**, ***Parisa Yasini**, S. Afsari, P. Pikma, E. Borguet,* Temple University

Single molecules are possible components of miniaturized electronic devices. Interconversion between states using external stimuli is a convenient way to generate single molecule devices such as switches and sensors. In this study, we have devised an electromechanical single molecule junction where molecular orientation is controlled by the working electrode potential in an electrochemical environment. We used the scanning tunneling microscopy (STM)-break junction method to measure the electrical properties of benzene derivatives, e.g., tetrafluoroterephthalic acid (TFTPA), terephthalic acid (TPA) and trimesic acid (TMA), bridged between two gold electrodes (the conducting substrate and STM tip). At potentials more negative than zero charge potential, direct contact between the π –system of a benzene ring and the Au (111) electrode results in the formation of a highly ordered monolayer

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* **NSTD Student Award Finalist**

and a high conductance of 0.24 G_0, 0.22 G_0 and 0.15 G_0 are detected for TFTPA, TPA and TMA, respectively. Moving to potentials more positive than the potential of zero charge triggers an order-disorder transition as revealed by STM. Our results show that charge transport through the π conjugated benzene ring increases by fluorination of TPA and decreases by an addition of a carboxylic acid functional group to the TPA. Accordingly, these results suggest that using functional groups, charge transport can be modified by manipulation of the electronic structure of molecules.

8:40am **SP+AS+MI+NS+SS-TuM3 How is Armchair Graphene Nanoribbon Oxidized?**, ***Chuanxu Ma***, *A.A. Puretzky, A.P. Baddorf,* Oak Ridge National Laboratory, *Z. Xiao, W. Lu,* North Carolina State University, *K. Hong*, Oak Ridge National Laboratory, *J. Bernholc,* North Carolina State University, *A.-P. Li*, Oak Ridge National Laboratory

The stability of graphene nanoribbons (GNRs) in air is crucial for practical applications. Here we study the temperature stability of the armchair GNR with a width of seven carbon atoms (7-aGNR) after exposed to air. Combining scanning tunneling microscopy, Raman spectroscopy, x-ray photoemission spectroscopy, and first-principles theory calculations, the oxidization of the armchair GNRs is found to start from the edges at ab out 520 °C, while below 430 °C the edges are unchanged. Two different types of oxygen species are atomically identified, specifically hydroxyl (OH) and atomic oxygen bridging two carbons, both of which are common oxygen forms in oxidized graphitic lattices. The bandgap is significantly reduced from 2.6 eV to 2.3 eV and 1.9 eV in the vicinity of hydroxyl or bridge O, respectively. Our results suggest that the oxidization will greatly affect the transport properties of GNRs. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

9:00am **SP+AS+MI+NS+SS-TuM4 Molecular Chessboard Assemblies Sorted by Site-Specific Interactions of Out-of-Plane d-Orbitals with a Semi-metal Template**, *T.A. Jung,* Paul Scherrer Institut (PSI), Switzerland, *A. Wäckerlin, S. Fatayer, T. Nijs, S. Nowakowska, S.F. Mousavi, O. Popova,* ***Aisha Ahsan***, University of Basel, Switzerland, *C. Wäckerlin*, Paul Scherrer Institut (PSI), Switzerland

We present a conceptually new approach for the formation of 2D chessboard patterns of molecules which is, unlike the other approaches, not dependent on the molecules being functionalized for self-assembly. The deposited Phthalocyanines (Pcs) are sorted in alternating sequence into the 2D layer by their site-specific interaction with the native reconstruction of the bismuth thin-film. The square p-(10 x 10) layer of bismuth on Cu(100) is characterized by the periodic arrangement of shallow pockets which are separated by rims and nodes which originate from the limited registry between Bi and Cu(100). The symmetry and the pitch of 1.8 nm of the Bi/Cu(100) substrate matches with the 4-fold symmetry of the Pc molecules and the pitch of a Pc chessboard arrangement.

We attribute the sorting mechanism to the site-specific interactions between the Bi layer and the out-of-plane 3d states of Mn- and CoPc leading to preferred adsorption sites. The 3d states also allow for the identification of the molecular components in the STM data: Mn and CoPc exhibit a bright contrast on the central metal atom, while Cu in CuPc in absence of such a d-state close to E_F is depicted as a depression.

Due to this characteristic difference in the 3d states, MnPc + CuPc and CoPc + CuPc sort into chessboard arrays. In these arrays, the molecules with out-of-plane 3d states (CoPc and MnPc) adsorb on the Bi-nodes and the one without (CuPc) adsorbs on the Bi-pores. If both molecules have out-of-plane 3d states around the Fermi level (CoPc + MnPc mixture), the selectivity of adsorption is insufficient and no chessboard layer is formed.

References:

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11:20am **SP+AS+MI+NS+SS-TuM11 Nanoscale Chemical Analysis 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.

11:40am **SP+AS+MI+NS+SS-TuM12 STM Studies of the Molecule-2D Heterointerface**, ***Andrew Wee***, National University of Singapore, Singapore, *Y.L. Huang*, Institute of Materials Research & Engineering, Singapore, *Y.J. Zheng, Z.B. Song,* National University of Singapore, *S.Y. Quek*, Department of Physics, National University of Singapore **INVITED**

We have previously shown that the electronic and chemical properties of graphene can be controllably tuned via molecular functionalization [1]. In this talk, I will focus on our recent work on semiconducting 2D transition metal dichalcogenides (TMDs) with tunable direct bandgaps dependent on the number of atomic layers. We use high resolution scanning tunneling microscopy/spectroscopy (STM/STS) to study the atomic structure, intrinsic electronic properties, and grain boundaries of MoS_2 and WSe_2 layers on HOPG substrates [2,3]. Using PTCDA as a prototype semiconductor organic molecule, we show that a monolayer TMD can effectively screen an organic-inorganic heterointerface [4]. We have also studied how a C_{60}F48 molecular acceptor layer on top of a single-layer WSe_2 acts as p-type dopant, and reveal the electronic structure at a prototypical 1D interface between intrinsic and p-doped WSe_2 [5].

[1] H.Y. Mao, Y.H. Lu, J.D. Lin, S. Zhong, A.T.S. Wee, W. Chen, Progress in Surface Science 88 (2013) 132.

Y.L. Huang, Y.F. Chen, W.J. Zhang, S.Y. Quek, C.H. Chen, L.J. Li, W.T. Hsu, W.H. Chang, Y.J. Zheng, W. Chen, A.T.S. Wee, Nature Comm. 6 (2015) 6298.

[2] Y.L. Huang, Z. Ding, W. Zhang, Y.H. Chang, Y. Shi, L.J. Li, Z. Song, Y.J. Zheng, D. Chi, S.Y. Quek, A.T.S. Wee, Nano Letters 16 (2016) 3682.

[3] Y.J. Zheng, Y.L. Huang, Y.F. Chen, W.J. Zhao, G. Eda, C.D. Spataru, W.J. Zhang, Y.-H. Chang, L.J. Li, D.Z. Chi, S.Y. Quek, A.T.S. Wee, ACS Nano 10 (2016) 2476.

[4] Z.B. Song et al., submitted.

Magnetic Interfaces and Nanostructures Division
Room: 11 - Session MI+2D+AC+NS-TuA

Spin-Orbit Phenomena at Surfaces and Interfaces
Moderators: Markus Donath, Westfälische Wilhelms-Universität Münster, Germany, Axel Hoffmann, Argonne National Laboratory

2:20pm **MI+2D+AC+NS-TuA1 Coherent Control over Spin-polarized Dirac Surface State in Topological Insulators**, ***Kenta Kuroda***, The Institute for Solid State Physics, The University of Tokyo, Japan **INVITED**

A number of challenging efforts have been recently made for a coherent control of highly spin-polarized Dirac surface states in various topological insulators, suggesting ultrafast optospintronic devices. However, these attempts generally neither realized a selective photoexcitation of the surface state, since the optical response is typically governed by the bulk properties, nor do they exclusively probe the excitation of the surface state, because the applied techniques are not surface sensitive.

In my talk, I will report that the difficulty can be overcome by direct band mapping of a photoexcitation in the Dirac surface state with time-resolved two-photon photoemission spectroscopy combined with ultrashort tunable pump pulses in mid-infrared regime. It is revealed that the mid-infrared excitation permits a direct population of the unoccupied Dirac-cone owing to a novel optical coupling across the Dirac point. In addition, the direct optical transition induces a pronounced asymmetry of the transient surface population in *k*-space which indicates an excitation of a net spin-polarized photocurrent even with linear pump polarization [Phys. Rev. Lett. **116**, 076801 (2016)]. Moreover, the pump polarization can control the asymmetric population, *i.e.* the surface photocurrent, through the coherent optical transition of the surface Dirac-cone [Phys. Rev. B **95**, 081103(R) (2017)]. By observing the decay of the asymmetric population, the ultrafast dynamics of the photocurrent in the surface Dirac-cone is directly investigated. Our discovery promises important advantages of photoexcitation by mid-infrared pulses for optspintronic applications.

3:00pm **MI+2D+AC+NS-TuA3 Enhancement of Voltage-Controlled Magnetic Anisotropy Through Metallic Insertion at the CoFeB|MgO Interface**, ***Kevin Fitzell***, *X. Li, C.T. Karaba, A. Buditama, G. Yu, K. Wong,* University of California at Los Angeles (UCLA)*, D. Wu,* UCLA; Fudan University, Republic of China*, N. Altieri, C. Grezes,* UCLA*, N. Kioussis,* CSU, Northridge*, S.H. Tolbert,* UCLA*, Z. Zhang,* Fudan University, Republic of China*, J.P. Chang, P.K. Amiri, K.L. Wang*, UCLA

Paramount to the continued scaling of MRAM devices is a comprehensive understanding and control of the factors affecting the interfacial phenomena that occur at the CoFeB|MgO interface, from which the perpendicular magnetic anisotropy (PMA) of the CoFeB originates. Efficient manipulation of this PMA using an applied voltage, known as the voltage-controlled magnetic anisotropy (VCMA) effect, offers significant energy savings over electric-current-controlled alternatives such as STT-RAM. *Ab initio* studies in the literature on Fe/MgO interfaces revealed a dependence of the VCMA effect on the oxidation state of interfacial Fe atoms[1] and on the addition of various heavy metal insertion layers[2] at the CoFeB/MgO interface. While this effect of metallic insertion layers at the CoFeB/MgO interface has not been extensively studied experimentally, inserting a thin Mg layer at the CoFeB/MgO interface has been shown in the literature to improve the (001) texture of the MgO, the tunneling magnetoresistance (TMR) ratio of the MTJ, and the thermal stress stability of the CoFeB layer's PMA.[3,4] What is lacking in the literature, however, is experimental work studying the dependence on the VCMA effect of Mg insertion layers at the CoFeB/MgO interface.

In this work, the impact of several types of metallic insertion layers (Ta, Pt, and Mg) at the CoFeB|MgO interface on the VCMA characteristics and other magnetic properties is studied. For the case of Mg insertion, four different regimes of materials properties were observed, corresponding to the oxidation state at the CoFeB|MgO interface. Inserting an ultrathin Mg layer of 0.1–0.3 nm yielded a VCMA coefficient of ~100 fJ/V×m, representing more than a factor of 3 improvement over average values of ~30 fJ/V×m reported in Ta|CoFeB|MgO-based structures. Ultrathin Ta and Pt insertion layers also showed a small improvement, yielding VCMA coefficients around 40 fJ/V×m. Electrical, magnetic, and synchrotron-based X-ray diffraction results reveal that a 1.1–1.3 nm Mg insertion layer gives rise to the highest perpendicular magnetic anisotropy and saturation magnetization, as well as to the best CoFe and MgO crystallinity; Mg insertion layers thicker or thinner than this give rise to either under- or over-oxidation of the CoFeB|MgO interface. These results demonstrate that precise control over the oxidation level at the CoFeB|MgO interface is crucial for the development of electric-field-controlled perpendicular magnetic tunnel junctions with low write voltage.

3:20pm **MI+2D+AC+NS-TuA4 THz Radiation Generated from Interfacial Rashba Spin-orbit Coupling**, *M.B. Jungfleisch,* Argonne National Laboratory*, Q. Zhang,* Argonne National Laboratory*, W. Zhang,* Oakland University*, J.E. Pearson, H. Wen,* ***Axel Hoffmann***, Argonne National Laboratory

Electromagnetic terahertz (THz) radiation is a versatile tool for a wide variety of sensing technologies ranging from security systems to medical applications. Commonly THz radiation is generated using semiconducting materials and using their inherent charge dynamics. Recently, it was also demonstrated that optical excitation of fast spin current pulses in magnetic materials may generate strong broadband THz radiation from transverse spin transport phenomena, known as spin Hall effects. These experiments rely on a bulk conversion of spin currents into charge current, which then subsequently generate the THz radiation. Here we investigate whether interfacial spin-orbit coupling phenomena may also be an efficient source for generating THz radiation. For this purpose we combine a bilayer of Ag and Bi, which is known to have strong Rashba-type spin-orbit coupling at its interface with a magnetic CoFeB layer. Upon optical excitation we also observe in this system THz radiation. Additional experiments with individual Ag and Bi layers show that this radiation originates from interfacial spin galvanic effects. Furthermore, we demonstrate that the amplitude of the THz radiation varies with the helicity of the incident optical light pulse. These observations open up new perspectives for the development of ultrafast spintronic devices.

This work was supported by the U.S. Department of Energy, Office of Science, Materials Sciences and Engineering Division. Lithographic patterning was carried out at the Center for Nanoscale Materials, which is supported by DOE, Office of Science, BES (#DE-AC02-06CH11357).

4:20pm **MI+2D+AC+NS-TuA7 Spin-orbit Coupled d-electron Surface States of Delafossite Oxides**, ***Phil King***, University of St Andrews, UK **INVITED**

The ABO_2 family of delafossite oxide metals has recently found renewed prominence due to their remarkable transport properties. The Pd- and Pt-based cobaltates are the most conductive oxides known, with room-temperature resistivities lower per carrier even than copper metal [1,2]. Meanwhile, giant low-temperature mean-free paths of up to 10^5 lattice spacings make hydrodynamic effects of the electron fluid observable in mesoscopic samples [3] and lead to a curious negative longitudinal magnetoresistance [4]. This is all underpinned by extremely broad bandwidths of the bulk electronic structure around the Fermi level, dominated by Pd/Pt-derived carriers that behave remarkably like free electrons [2], in part mediated by an unusual interplay with correlations which renders the Co block insulating. The crystal structure is polar, however, opening the potential for their surface electronic structures to be dramatically different to that of the bulk [5,6]. Here, we will show how these surfaces support strongly spin-split electronic states, and discuss the intriguing interplay of spin-orbit coupling and electronic interactions that they host.

Key collaborators on this work include Veronika Sunko (St Andrews and Max-Planck Institute for Chemical Physics of Solids, Dresden), Federico Mazzola (StA), and Helge Rosner, Pallavi Kushwaha, Seunghyum Khim, and Andy Mackenzie (MPI-CPFS).

[1] Hicks *et al.*, Phys. Rev. Lett. 109 (2012) 116401

[2] Kushwaha *et al.*, Science Adv. 1 (2015) e1500692

[3] Moll *et al.*, Science 351 (2016) 6277

[4] Kikugawa *et al.*, Nature Commun. 7 (2016) 10903

[5] Kim *et al.*, Phys. Rev. B 80 (2009) 035116

[6] Noh *et al.*, Phys. Rev. Lett. 102 (2009) 256404

5:00pm **MI+2D+AC+NS-TuA9 Understanding the Interfacial Interaction and Isotope Effects in Organic Spin Valve Structures**, ***Alexandra Steffen***, *N. Herath, J. Keum, H. Zhang, K. Hong, J. Jakowski, J. Huang, J. Browning, C.M. Rouleau, I.N. Ivanov, V. Lauter*, Oak Ridge National Laboratory

Spin-dependent phenomena, such as the extended spin relaxation time and spin diffusion length due to the very week spin-orbit coupling found in organic spin valves (OSV), are of interest from the view of both fundamental research and development of low power spintronic devices.

While deuteration is widely used for contrast variation measurements under the assumption that the deuterated structure shows identical characteristics in comparison to the protonated version, recently, strong isotopic effect on optoelectronic properties was reported and a remarkable reduction in the open circuit voltage was found [1].

In OSV systems, the interfacial properties are crucial for the understanding of the origin of the macroscopic properties. Still, to identify the exact behavior of the interfaces remains challenging, especially for buried soft matter/hard matter interfaces. Here, we utilize via Polarized Neutron Reflectometry to study depth-resolved the magnetic and chemical structure.

Our system under investigation are prototype spintronic devices with LSMO/polymer/Co trilayer structure, where polyfluorene (PFO) is selected as an optimal 'hole' conducting polymer through the model pre-screening based on the electron affinity and electron's effective mass values obtained from theoretical calculations. Using the exceptional syntheses and deuteration capabilities we have recently completed syntheses of four PFO isotopes, i.e., protonated (P), main-chain deuterated (MD), side-chain deuterated (SD) and fully deuterated (FD) PFOs. By creating such modified polymers, the subatomic, intermolecular and interfacial interactions are modified and characteristics like the π-π interaction become tunable. For neutron scattering experiments, the nuclear cross-section varies with the isotopic substitution, thus via changing the contrast with chain-specific deuteration, different parts of a sample are investigated individually.

While our main goal is the understanding the effect of deuterium substitution on the spin-dependent electron transport, in this presentation, we will focus on the details of the structural and magnetization profiles on both LSMO\polymer and polymer\Co interfaces and their impact on the coupling between magnetic layers. We will present the results obtained via Polarized Neutron Reflectometry and discuss the interpretation of the depth-resolved magnetometry study.

[1] Ming Shao *et al.*, The isotopic effects of deuteration on optoelectronic properties of conducting polymers. *Nature Communications*, 5:3180, January 2014.

5:20pm **MI+2D+AC+NS-TuA10 Dispersion and Spin Structure of Conduction Bands of Single-layer TMDC's on Au(111)**, ***Philipp Eickholt****, *M. Holtmann,* Westfälische Wilhelms-Universität Münster, Germany, *C.E. Sanders, M. Dendzik, M. Bianchi, P. Hofmann,* Aarhus University, Denmark, *M. Donath,* Westfälische Wilhelms-Universität Münster, Germany

In the field of 2D materials, single-layer transition metal dichalogenides, especially MoS_2 , WS_2 , $MoSe_2$ and WSe_2, play an important role. Due to their exceptional optical and electronic properties, they are promising materials for optoelectronical applications [1]. The key to understand the material properties is a profound knowledge of the electronic structure. While the occupied electronic structure was investigated in a number of studies, the crucial information about the dispersion and spin structure of the conduction bands is still missing.

Spin- and angle-resolved inverse photoemission (SRIPE) [2] is the ideal technique to study dispersion and spin structure of the unoccupied electronic bands. In this talk, we present a SRIPE study of the conduction bands of single-layer WS_2 [3] and MoS_2 [4] grown on Au(111).

The focus of the presentation will be on the lowest conduction band near the K valley, which is decisive for the optoelectronic properties of the materials. The results will be discussed in consideration of a recent pump-probe (TR-ARPES) experiment [5], which determined the band gap of the "pumped" system.

[1] D. Xiao *et al.*, Phys. Rev. Lett. **108**, 196802 (2012)

[2] S.D. Stolwijk *et al.*, Rev. Sci. Instrum. **85**, 013306 (2014)

[3] M. Dendzik *et al.*, Phys. Rev. B **92**, 245442 (2015)

[4] A. Bruix *et al.* Phys. Rev. B **93**, 165422 (2016)

[5] A. Grubišic Cabo *et al.*, Nano Lett. **15**, 5883 (2015)

5:40pm **MI+2D+AC+NS-TuA11 Unraveling the Spin Structure of Unoccupied States in Bi_2Se_3**, ***Markus Donath***, *C. Datzer, A. Zumbülte,* Westfälische Wilhelms-Universität Münster, Germany, *J. Braun,* LMU München, Germany, *T. Förster, A.B. Schmidt,* Westfälische Wilhelms-Universität Münster, Germany, *J. Mi, B. Iversen, P. Hofmann,* Aarhus University, Denmark, *J. Minár,* University of Pilzen, Czech Republic, *H. Ebert,* LMU München, Germany, *P. Krüger, M. Rohlfing,* Westfälische Wilhelms-Universität Münster, Germany

In topological insulators, spin-orbit coupling leads to the emergence of metallic topological surface states crossing the fundamental band gap. The optical control of spin currents in topological surface states opens new perspectives in (opto-) spintronics. To understand these processes, a profound knowledge about the dispersion and the spin polarization of both the occupied and the unoccupied electronic states is required. We present a joint experimental and theoretical study on the unoccupied electronic states of the topological insulator Bi_2Se_3 [1]. We discuss spin- and angle-resolved inverse-photoemission results in comparison with calculations for both the intrinsic band structure and, within the one-step model of (inverse) photoemission, the expected spectral intensities. This allows us to unravel the intrinsic spin texture of the unoccupied bands at the surface of Bi_2Se_3.

[1] Datzer *et al.*, Phys. Rev. B **95**, 115401 (2017)

Nanometer-scale Science and Technology Division Room: 19 - Session NS+EM+MN+PS+SS-TuA

Nano-Photonics, Plasmonics and Mechanics

Moderators: Joshua Ballard, Zyvex Labs, Christian Zorman, Case Western Reserve University

2:20pm **NS+EM+MN+PS+SS-TuA1 Nonlinear Interactions of Coupled MEMS Cantilevers**, ***Christopher Wallin***, National Institute of Standards and Technology, Center for Nanoscale Science and Technology, *R. De Alba, D.A. Westly,* NIST/CNST, *S. Grutzik,* Sandia National Laboratories, *A.T. Zehnder, R.H. Rand,* Cornell University, *V.A. Aksyuk,* NIST/CNST, *S. Krylov,* Tel Aviv University, Israel, *B.R. Ilic*, NIST/CNST

Micro- and nano-electromechanical systems (M/NEMS) offer tremendous opportunities for technological advancement in mechanical resonator applications including mass, force and energy sensing, microwave amplification, optomechanics, and energy harvesting. These M/NEMS resonators have many favorable qualities including high mechanical quality factors and compatibility with integrated circuit architectures. More specifically, nonlinear, coupled M/NEMS resonating cantilever arrays have been shown to possess complex system dynamics such as intrinsically localized modes, wave propagation, and sensitivity to defects. The collective behavior of these nonlinear interacting cantilever arrays is remarkably sensitive to the slightest perturbation which makes them an excellent candidate for ultra-sensitive sensors. Moreover, custom device responses can be achieved by tuning the electrostatic fringing field coupling, altering the mechanical coupling via the device's overhang, or by introducing precisely engineered structural imperfections into the arrays. With our work, we have found that the cantilever arrays exhibit distinct propagation bands, abrupt transitions between standing wave patterns, and synchronization.

Various device geometries including interdigitated arrays, opposing element arrays, and di-element arrays were constructed using both silicon and silicon nitride as device layers. The arrays generally consisted of 100 cantilevers or more which limited boundary effects in the devices. Gold electrodes were patterned on top of the cantilevers for parametric electrical actuation and for fringing field electrostatic coupling between adjacent cantilevers. Mechanical coupling in the arrays was achieved through the large overhangs produced during the device release. The amplitude envelope of the out of plane motion of the cantilevers was captured using a CMOS camera using a frame rate of 30 s^{-1}. The devices were driven electrically and using a piezoelectric transducer under ambient and vacuum conditions. Large, nonlinear vibrational amplitudes were observed in the arrays along with hysteresis. The cantilever arrays exhibited unique standing wave patterns which were sensitive to defects and external loading. Since the dynamics of M/NEMS coupled cantilevers are highly sensitive to local changes in their environment, we envision the practical implementation of coupled arrays for ultra-sensitive chemical, biological, and force sensors in the future.

2:40pm **NS+EM+MN+PS+SS-TuA2 Silicon Carbonitride Nanoresonator Arrays for Proteomic Analysis**, *W. Zheng,* University of Alberta, Canada, *R. Du,* University of Alberta and The National Institute for Nanotechnology, *Y. Cao,* University of Alberta and The National Institute for Nanotechnology, Canada, *M.A. Mohammad, S.K. Dew,* University of Alberta, Canada, *M.T. McDermott,* University of Alberta and The National Institute for Nanotechnology, ***Stephane Evoy***, University of Alberta, Canada

Analysis of biological molecules is vital in many fundamental problems of molecular biology. ELISA is a widely employed array-based technique for the parallel analysis of biological analystes. This technique however requires fluorescent tagging, which may disrupt the biochemical properties being investigated. Other platforms such as quartz crystal microbalance (QCM) and surface plasmon resonance sensors (SPR) offer alternatives for the analysis of molecular mixtures. However, these platforms are not readily scalable towards large arrays. Resonant mechanical sensors operate by monitoring shifts of resonance frequencies associated to the binding. Such approach

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* **Falicov Student Award Finalist**

enables the frequency modulation of the output, improving the stability/noise-immunity of the reading. In addition, the adsorption sensitivity per unit area of resonators scales favourably as their dimensions are reduced, offering a compelling path for the development large arrays with exquisite mass-sensitivities.

Suspended silicon resonators as narrow as 45 nm were initially reported by Carr, Evoy et al.[1] The brittle properties of this material however limited the yield of these structures to less than 25 %, precluding their use in large arrays. We have recently reinvented the overall approach employed in NEMS fabrication. This new approach combines surface and bulk machining techniques for the release of the device, as opposed to the widely-accepted sacrificial layer approach. We are now routinely fabricating ultra-large arrays of SiCN nanostring resonators as narrow as 8 nm and a yield approaching 100%. These are the narrowest devices produced by any machining method. Each device offers a detection threshold as small as 200 Da. These arrays have successfully been employed for the detection and analysis of protein mixtures. Diazonium modification was developed onto the SiCN surfaces and validated by X-ray photoelectron spectroscopy. Similarly modified nanostrings were then covalently functionalized with anti-rabbit IgG as molecular probe. Specific enumeration of rabbit IgG was successfully performed through observation of downshifts of resonant frequencies. The specificity of this enumeration was confirmed through proper negative control experiments. Helium ion microscopy further verified the successful functionalization of nanostrings.

[1] D. W. Carr, S. Evoy, L. Sekaric, H. G. Craighead, J. M. Parpia, App. Phys. Lett. 75, 920 (1999).

3:00pm **NS+EM+MN+PS+SS-TuA3 Cavity Optomechanical Coupling in Chip-Scale Plasmonic and Photonic Transducers for Nanoscale Measurements and Optical Signal Control**, ***Vladimir A. Aksyuk***, *S. An*, NIST Center for Nanoscale Science and Technology, *B. Dennis*, Rutgers University and NIST CNST, *T. Michels, B.J. Roxworthy, J. Zou*, NIST Center for Nanoscale Science and Technology **INVITED**

Devices controlling light via mechanical motion are ubiquitous, from a simple camera's zoom lens to arrays of moving mirrors correcting for atmospheric distortions in telescopes and digitally projecting movies on the cinema screens. The same optomechanical coupling provides one of the best known techniques for measuring mechanical motion, covering length scales form atomic force microscopy to kilometer scale LIGO interferometers to the red shift measurements over billions of light years. We study optomechanical coupling in micro and nanoscale systems that combine electromechanics with photonics and plasmonics, and apply such chip based optomechanical transducers to solve nanoscale measurement problems. In one example, integrated cavity-optomechanical sensing breaks the common trade-off between sensitivity and bandwidth in atomic force microscopy, allowing extremely low noise motion readout of very fast, nanoscale/picogram mechanical probes. Reducing the probe size not only increases the transduction bandwidth, but also reduces drag and therefore the fundamental thermodynamic force noise when operating in air. Even though the cantilever crossection is much smaller than the optical wavelength, the near-filed coupled high quality factor photonic cavity makes our motion readout exquisitely sensitive. As a second example, I will discuss nanomechanical plasmonic systems, where extreme confinement of the gap plasmon optical modes leads to some of the largest optomechanical coupling coefficients ever observed. I will present electro-mechanical gap plasmon phase modulators and nanomechanically tunable deep subwavelength gap plasmon resonators with potential applications for motion metrology, novel nanoscale sensing and signal transduction and arbitrary wavefront control via nanoelectromechanically tunable optical metasurfaces.

4:20pm **NS+EM+MN+PS+SS-TuA7 An Active Plasmomechanical System for Optical Modulation and Mechanical Lasing**, ***Brian Roxworthy***, *V.A. Aksyuk*, NIST

Plasmonic structures can couple electromagnetic radiation into volumes much smaller than the limits imposed by diffraction. This strong confinement of light transforms these static metallic nanostructures into sensitive bio-chemical sensors, near-field probes for imaging, nanoscale light sources, and effective optical tweezers [1-4]. Advancing the plasmonics paradigm to include active devices, whose resonant properties can be dynamically tuned *via* various electrical, mechanical, or thermal inputs, has great potential to advance nanoscale optical sensing and transduction and for building functional metamaterial devices [5,6].

We present a tunable plasmomechanical system that couples the localized gap plasmon (LGP) resonances of individual subwavelength structures to mechanical, electrical, and thermal modes. By engineering extremely strong optomechanical coupling of the LGPs, we achieve broad tuning of the localized resonances at megahertz frequencies using small voltages < 5 V, producing ≈ 40 % amplitude in the far field and $> \pi$ phase shift of the re-radiated light. We furthermore show selective, sub-diffraction optical transduction of nanomechanical motion with < 10 fm Hz$^{-1/2}$ sensitivity. Coupling of LGPs to thermal modes results in strong thermomechanical backaction capable of driving regenerative mechanical oscillations of cantilever devices – mechanical lasing – using an isolated, subwavelength plasmonic element. Our platform opens the door to smart metamaterials having programmed responses across physical domains, tunable metasurfaces and optical components, and studying optically-powered nonlinear nanomechanics.

[1] J. Anker *et al.*, Nat. Mater. 7, 442–453 (2008).

[2] D. K. Gramotnev and S. I. Bozhevolnyi, Nat. Photon., 83–91 (2010)

[3] Y-J. Lu *et al.*, Science 337, 450–453 (2012)

[4] B. J. Roxworthy *et al.*, Nano Lett. 12, 794–801 (2012)

[5] N. Zheludev and E. Plum, Nat. Nanotech. 11, 16–22 (2016).

[6] B. J. Roxworthy and V. A. Aksyuk, Nat. Commun. 7, 13746 (2016).

4:40pm **NS+EM+MN+PS+SS-TuA8 Plasmon-enhanced Photo-catalysis Using Collapsible Nano-fingers**, ***Yunxiang Wang***, *B. Song, W. Wu, S. Cronin*, University of Southern California

1. Introduction

Photocatalytic decomposition plays an important role in the treatment of pollutants. It utilizes light radiation to decompose contaminants into non-toxic substances. While TiO_2 is one of the most widely used photocatalysts, visible light can hardly be used to drive TiO_2 due to the short wavelength cutoff of TiO_2. Plasmon-enhanced photo-catalysis can extend the wavelength range due to higher order effects. However, previously reported work has limited efficiency, because the hot spots were not optimized and the TiO_2 located outside the hottest part of the hotspots. Here, we invented a technology to fabricate collapsible nano-fingers to achieve large-area high density optimized hotspots with TiO_2 film located at the hottest part of the hotspots. We demonstrated highest photo-catalysis efficiency that we are aware of.

2. Device fabrication

First, pillar arrays were patterned on the top two layers using UV-curable nanoimprint lithography (NIL) and reactive ion etch (RIE), as shown in Fig. 1(a) (b) (c). Au film was deposited on the sample followed by lift-off process to form gold nanoparticle arrays with diameter of 50 nm and pitch of 200 nm on the bottom layer, as shown in Fig. 1(d) (e). After nano-fingers were fabricated using RIE, 2 nm TiO2 film was deposited on the sample using atomic layer deposition (ALD), as shown in Fig. 1(f) (g). After the arrays were exposed to ethanol solutions and air-dried, the fingers closed together in groups of two or four. The scanning electron microscopic (SEM) image of the collapsed nano-fingers is shown in Fig. 2.

3. Results and Discussion

The photocatalytic activities were tested using methyl orange (MO) photodegradation as the model reaction. The decay in absorbance of the solution was monitored by Varian Cary 50 UV–Vis spectrophotometer after 8 h exposure to green laser (532 nm, 3 W) irradiation. MO solution and sample were added into a standard quartz cuvette sealed with a sealing film.

The absorption spectra taken before and after irradiating are used to quantify the photocatalytic decomposition rate, as shown in Fig. 3. As a control experiment, we firstly performed experiment under same illumination condition with a silicon wafer coated with 2nm TiO_2 film, no MO photodecomposition was observed even after 12 h irradiation. For the monomers, the absorption of the MO solution is observed to drop by 4.9% after 8 h illumination. However, with collapsed sample, a 30% reduction in the MO absorbance is observed. This over 6-fold enhancement demonstrates a stronger plasmonic enhancement after nano-fingers being collapsed, which means this novel structure is a great platform to study plasmonic enhancement.

5:40pm **NS+EM+MN+PS+SS-TuA11 Ultra-High Resolution Photonics-based Thermometry**, ***Nikolai Klimov***, *T. Herman, K.O. Douglass, M.J. Chojnacky, Z. Ahmed*, National Institute of Standards and Technology

Temperature measurements play a crucial role in various aspects of modern technology ranging from medicine and manufacturing process control, to environmental and oil-and-gas industry. Among various temperature measurement solutions, resistance-based thermometry is a time-tested method of disseminating temperature standards [1]. Although industrial resistance thermometers can routinely measure temperatures with uncertainties of 10 mK, their performance is sensitive to multiple environmental variables such as mechanical shock, thermal stress and humidity. Drift of sensor resistance over time necessitates expensive, time-consuming recalibrations using ultra-sensitive reference thermometers. These fundamental limitations of resistance thermometry, as well as the desire to reduce sensor ownership cost have ignited a substantial interest in the development of alternative temperature measurement solutions such as photonics-based temperature sensors. A wide variety of innovative photonic sensors have been proposed recently including functionalized dyes [2], hydrogels [3], fiber optics-based sensors [4], and silicon micro- and nanophotonic devices [5,6]. These innovative temperature sensors have the potential to leverage advances in frequency metrology to provide cost-effective measurement solutions. Here we present the results of our efforts in developing novel on-chip integrated silicon photonic temperature sensors with nanoscale footprint and ultra-high resolution as an alternative solution to legacy-based resistance thermometers. These sensors are Fabry-Perrot cavity type silicon photonic devices that are based on photonic crystal nanobeam cavity (PhCC), whose high-Q resonant frequency mode is highly sensitive to even ultra-small temperature variations. In this talk we describe nanofabrication, fiber coupling and packaging of these thermometers, as well as their performance. We will present a direct comparison of our photonic thermometers to Standard Platinum Resistance Thermometers, the best in class resistance temperature sensors used to disseminate the International Temperature Scale of 1990. The preliminary results indicate that our PhCC nanothermometers are capable of detecting changes of temperature as small as 10 µK and can achieve measurement capabilities that are on-par or even better than the state-of-the-art resistance thermometry.

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[2] Donner et al., Nano Lett. 12, 2107 (2012).

[3] Ahmed, J. Adv. Res. 6, 105 (2015).

[4] Kersey et al., IEEE Photonics Technol. Lett. 4, 1183 (1992).

[5] Kim et al., Opt. Express 18, 22215 (2010).

[6] Klimov et al., Proc. SPIE 9486, 948609 (2015).

6:00pm **NS+EM+MN+PS+SS-TuA12 Size-Controlled Synthesis of Gold Nanostars and their Excellent SERS and Fluorescence Quenching Properties**, ***Waqqar Ahmed***, *H.I. Khan, M.U. Khalid*, COMSATS Institute of Information Technology Islamabad, Pakistan

Noble metal nanoparticles have attracted great attention recently owing to their fascinating optical properties. They work as nanoscopic antennas by amplifying the incident and scattered electromagnetic beam. The incident electromagnetic radiation can excite the surface plasmons of nanoparticles, leading to the confinement of electromagnetic energy around the nanoparticles. This makes the metallic nanoparticles an excellent candidate for the surface enhanced Raman scattering (SERS) applications. Anisotorpic nanoparticles such as nanostars are much superior for SERS applications over their spherical counterparts owing to the special surface morphology.

We have developed a facile method for the synthesis of gold nanostars with tunable sizes ranging from 50nm to about 1µm. To the best of our knowledge, this is the widest size range reported for gold nanostars. More importantly, we have observed that these nanostars are excellent for SERS based detection owing to their large enhancement factors and efficient fluorescence quenching properties. Fluorescence is known to interfere with and overshadow the SERS signal, thus affecting the trace detection capabilities of SERS. Therefore, usually off resonance excitation lasers must be used for SERS studies of fluorophores, which limits the universal applicability of the SERS technique. We believe that non-compact surfactant coating of nanostars in our case give the target fluorophores access to nanostar's surface, thus enabling the quenching of fluorescence through Förster resonance energy transfer (FRET). The absence of fluorescence background markedly enhances the appearance of Raman peaks. We were able to achieve a limit of detection of 10pM using an excitation laser source in resonance with the electronic excitation of the target fluoropore. This makes gold nanostars universal substrates for SERS based trace detection.

Scanning Probe Microscopy Focus Topic
Room: 10 - Session SP+AS+MI+NS+SS-TuA

Probe-Sample Interactions
Moderator: Carl Ventrice, Jr., SUNY Polytechnic Institute

2:20pm **SP+AS+MI+NS+SS-TuA1 Atomic Manipulation of Atomic Oxygen on Graphene**, *H.K. Kim, T. Ahn, T.S. Youn, D.G. Lee,* ***Tae-Hwan Kim***, Pohang University of Science and Technology, Republic of Korea

Graphene, a single sheet of sp^2-bonded carbon atoms, is considered as a promising material for future electronic devices especially due to its superior electron mobility as well as mechanical stability. For various applications of graphene, however, the electronic structure has to be tuned and the diverse functionalization is strongly required. In particular, it has been well known that the oxidation of graphene can alter its electronic and optical properties remarkably. We have investigated the atomic oxygen chemisorbed on the epitaxial graphene using scanning tunneling microscopy (STM). The high-resolution topographic images and tunneling spectroscopy spectra reveal distinctive electronic states of oxygen atoms, which bridge two adjacent carbon atoms and make graphene epoxide. More importantly, using the STM tip can controllably induce the local removal and the rearrangement of the atomic oxygen by applying the appropriate biases. The technique is similar to the STM nanolithography, which has been reported, for example, for hydrogenated Si(001). In principle, a combination of the controlled desorption and hopping of atomic oxygen can be employed to design the local electronic property on graphene with atomic-scale precision, which may lead to advanced atomic-scale devices based on graphene.

2:40pm **SP+AS+MI+NS+SS-TuA2 Revealing Distance-Dependence of Chemical Interactions and Image Contrast Reversal in Noncontact Atomic Force Microscopy: A Case Study on Highly Oriented Pyrolytic Graphite**, ***O.E. Dagdeviren****, *J. Goetzen, E.I. Altman,* ***UdoD. Schwarz***, Yale University

The structural and chemical nature of surfaces governs a material's ability to interact with its surrounding. Designing nanodevices requires tailoring surfaces to meet specific needs and revealing underlying fundamental principles, which determine surface reactivity at the atomic scale. A particularly interesting case occurs when the surface site exhibits varying attraction with distance. To shed light on this issue, noncontact atomic force microscopy experiments combined with scanning tunneling microscopy experiments have been carried out where the evolution of the atom-specific chemical interaction leads to contrast reversal in the force channel. Due to the importance of sp^2-hybridized carbon surfaces in functional nanostructures, we have used highly ordered pyrolytic graphite surface and metal probe tips as the model system. Our experiments reveal that at larger tip-sample distances, carbon atoms exhibit stronger attractions at hollow sites while upon further approach, hollow sites become energetically more favorable [1,2]. The analysis suggests the fundamental factors promoting contrast reversal are local varying decay lengths and an onset of repulsive forces that occurs for distinct surface sites at different tip-sample separations. In addition to these, a change of the hybridization state of carbon atoms from sp^2 to sp^3 under the influence of an approaching reactive probe can also result in contrast reversal. Our experiments address the unexpected nature of contrast reversal due to different governing mechanisms, which are determined by local properties of the sample as well as interacting materials. Combined with in-depth computational analysis, such experiments will lead to a deeper understanding of the fundamental effects that govern how materials interact with their surroundings at sub-nanometer scale. Entangling these fundamental principles with design will enable fabrication and synthesis of better nanodevices with graphene and other layered materials as well as nanotubes.

$^{+}$ Author for correspondence: omur.dagdeviren@yale.edu

[1] O.E. Dagdeviren et al, Nanotechnology 27, 065703 (2016)

[2] O.E. Dagdeviren et al, Nanotechnology, 27, 485708 (2016)

3:00pm **SP+AS+MI+NS+SS-TuA3 Absence of a Band Gap at Metal-Monolayer MoS_2 Interface**, ***Abhay Pasupathy***, Columbia University **INVITED**

Abstract: High quality electrical contact to semiconducting transition metal dichalcogenides (TMDCs) such as MoS_2 is key to unlocking their unique electronic and optoelectronic properties for fundamental research and device applications. Despite extensive experimental and theoretical efforts reliable ohmic contact to doped TMDCs remains elusive and would benefit from a better understanding of the underlying physics of the metal-TMDC interface. Here we present measurements of the atomic-scale energy band diagram of junctions between various metals and heavily doped monolayer MoS_2 using ultra-high vacuum scanning tunneling microscopy (UHV-STM). Our measurements reveal that the electronic properties of these junctions are dominated by 2D metal induced gap states (MIGS). These MIGS are characterized by a spatially growing measured gap in the local density of states (L-DOS) of the MoS_2 within 2 nm of the metal-semiconductor interface. Their decay lengths extend from a minimum of ~0.55 nm near mid gap to as long as 2 nm near the band edges and are nearly identical for Au, Pd and graphite contacts, indicating that it is a universal property of the monolayer semiconductor. Our findings indicate that even in heavily doped semiconductors, the presence of MIGS sets the ultimate limit for electrical contact

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* **NSTD Student Award Finalist**

4:20pm **SP+AS+MI+NS+SS-TuA7 Imaging of MOS Interface Trap Distribution using Local Deep Level Transient Spectroscopy Based on Scanning Nonlinear Dielectric Microscopy**, *N. Chinone*, ***Yasuo Cho***, Tohoku University, Japan

Physical properties of metal-oxide-semiconductor (MOS) interface are critical for semiconductor devices. There are several techniques for characterizing MOS interface properties. Deep level transient spectroscopy (DLTS)is one of powerful techniques capable of macroscopic quantitative evaluation of trap density at/near MOS interface (D_{it}). But it is easily imagined that actual trap is not homogeneously distributed, but has two dimensional distributions in atomic scale and even in mesoscopic scale. Therefore, it is very important to characterize MOS interface microscopically. Unfortunately, it is impossible to observe such inhomogeneity by using conventional macroscopic DLTS method.

In this paper, a new technique for local DLTS imaging based on scanning nonlinear dielectric microscopy (SNDM) is proposed. This method enables us to observe two dimensional distribution of trap density at/near MOS interface and is demonstrated with oxidized SiC wafer.

45-nm-thick thermal oxide layers were formed on three Si-faces of 4°-off n-type 4H-SiC wafers. One of them was labeled as #S-45-1. The other two wafers were subjected to post-oxidation annealing (POA) in nitric oxide (NO) at different conditions as follows: 1250°C for 10 minutes (#S-45-2), 1150°C for 60 minutes (#S-45-3). The average D_{it} values of these samples were measured by conventional High-Low method, which showed that the D_{it} of #S-45-1 was highest and that of #S-45-3 was lowest.

These three samples were scanned on 1.5x1.5μm^2 square area with a resolution of 30x30 pixels and analyzed using the proposed local DLTS method.

By analyzing the acquired images, time-constant τ and magnitude of transient capacitance response were obtained at each pixel. Highest brightness was obtained from #S-45-1 and lowest one was obtained from #S-45-3, which is consistent with macroscopically obtained result. Furthermore, in the local DLTS images, we detected dark and bright areas, which can be translated as two dimensional trap distribution.

Next, quantitative imaging of D_{it} was performed. Distributions of D_{it} for τ = 0.3 μs and 3 μs were imaged for all samples. The time constants 0.3 μs and 3 μs correspond to energy depth of 0.24 eV and 0.30 eV below the conduction band, respectively. All images have dark and bright areas with feature size of a few 100 nm. In addition, the images with different time constant showed different distribution, which implies that the distribution of interface traps depends on time constant, or suggests the physical origin of interface trap with different energy level is different.

This local DLTS technique can contribute to understanding microscopic physical properties of MOS interface.

4:40pm **SP+AS+MI+NS+SS-TuA8 Quantum State Readout of Individual Quantum Dots by Electrostatic Force Detection**, ***Yoichi Miyahara***, *A. Roy-Gobeil*, *P.H. Grutter*, McGill University, Canada

Electric charge detection by atomic force microscopy (AFM) with single-electron resolution (e-EFM) is a promising way to investigate the electronic level structure of individual quantum dots (QD). The mechanical oscillation of the AFM tip modulates the energy of the QDs, causing single electrons to tunnel back and forth between QDs and an electrode. The resulting oscillating electrostatic force changes the resonant frequency and damping of the AFM cantilever, enabling electrometry with a single-electron sensitivity. While quantitative electronic level spectroscopy is possible by sweeping the bias voltage, charge stability diagram of the QD can be obtained by scanning the AFM tip around the QD. e-EFM technique can be applied for the investigation of individual colloidal nanoparticles and self-assembled QDs without defining nanoscale electrodes. e-EFM is a quantum electromechanical system where the back-action of a tunneling electron is detected by AFM and can also be regarded as a mechanical analog of admittance spectroscopy with a radio frequency resonator, which is emerging as a promising tool for quantum state readout for quantum information processing. In combination with the topography imaging capability of the AFM, e-EFM is a powerful tool for investigating nanoscale material systems which can be used as quantum bits such as nanowires and single molecules and dopants.

1 Y. Miyahara, A. Roy-Gobeil and P. Grutter, Nanotechnology 28, 064001 (2017).

5:00pm **SP+AS+MI+NS+SS-TuA9 Cryogenic Near-field Imaging and Spectroscopy at the 10-Nanometer-scale**, ***Max Eisele***, *A. Huber*, neaspec GmbH

Near-field microscopy and spectroscopy has become one of the key technologies for modern optics, combining the resolving power of AFM based measurements with the analytical aspects of optical microscopy and spectroscopy. Near-field microscopy has already proven itself vital for modern nanomaterials and has been used in applications such as chemical identification [1], free-carrier profiling [2], or the direct mapping of propagating plasmons [3,4], phonon [5], and exciton polaritons [6]. Key information like the local conductivity, intrinsic electron-doping, absorption, or the complex-valued refractive index can routinely be extracted from these measurements with a spatial resolution of down to 10 nanometer.

In combination with femtosecond light sources, near-field microscopy has also enabled ultrafast pump-probe experiments [7] with a combined 10-femtosecond temporal and 10-nanometer spatial resolution [8]. Carrier-relaxation dynamics in black phosphorus [9] or graphene [10] are just two examples of the broad range of potential applications for ultrafast near-field nano-spectroscopy.

Within this talk we will introduce the newest technological breakthrough in the field of near-field optics - Cryogenic near-field imaging and spectroscopy. This novel approach has been pioneered by the group of Dimitri Basov at Columbia University and UC San Diego using a home-build cryogenic near-field microscope with a temperature range of 24 – 300 Kelvin. For the first time, this microscope has been capable to spatially resolve the insulator-to-metal phase transition of V2O3 with <25nm spatial resolution [11]. Extending ambient near-field measurements to cryogenic temperatures will open a complete new world for nanoscale optical microscopy and spectroscopy, enabling the direct mapping of phase-transitions in strongly correlated materials or the detection of low-energy elementary excitations at the surface of solid-state systems. A first commercial cryogenic system with a temperature range down to 10 Kelvin is now available from neaspec [12] making this technology broadly available to the community.

References:

[1] I. Amenabar et al., Nature Comm. 8, 14402 (2017)

[2] J. M. Stiegler et al., Nano Lett. 10, 1387 (2010)

[3] J. Chen et al., Nature 487, 77 (2012)

[4] Z. Fei et al., Nature 487, 82 (2012)

[5] E. Yoxall et al., Nature Photon. 9, 674 (2015)

[6] F. Hu et al., Nature Photon. 11, 356 (2017)

[7] M. Wagner et al., Nano Lett. 14, 894 (2014)

[8] M. Eisele et al., Nature Photon. 8, 841 (2014)

[9] M. Huber et al., Nature Nanotech. 12, 207 (2017)

[10] G. X. Ni et al., Nature Photon. 10, 244 (2016)

[11] A. S. McLeod et al., Nature Phys. 13, 80 (2017)

[12] www.neaspec.com

5:20pm **SP+AS+MI+NS+SS-TuA10 Atomic Scale Proximity Effect at a Molecular Superconductor-Metal Boundary**, ***KyawZin Latt***, *S. Khan*, Ohio University, *A. Ngo*, Argonne National Laboratory, *H. Chang*, Ohio University, *A. Hassanien*, J. Stefan Inst., Slovenia, *L. Curtiss*, Argonne National Laboratory, *S.W. Hla*, Ohio University and Argonne National Laboratory

How a superconductor interacts with metal at a superconductor-metal boundary is vital for fundamental understanding of important phenomena such as Andreev reflection, and proximity effect. Here we investigate how the cooper pairs from a charged transfer based molecular superconducting cluster interact with 2-D surface state electrons from Ag(111) surface at the atomic scale using tunneling microscopy, tunneling spectroscopy, and atomic/molecular manipulation schemes at low temperatures in an ultrahigh vacuum environment. The superconducting molecular clusters here are composed of a few molecular chains formed by BETS (donors) and GaCl4 (acceptor). In STM images, these molecular clusters appear as ordered parallel chains resembling the 'rafts'. Using scanning tunneling microscope (STM) manipulation, small molecular clusters are repositioned on the surface at desired locations. From the tip height signals, the dynamics of molecular clusters during their movements across the surface has been unveiled. Repeated manipulation experiments reveal that the rafts move only along [211] surface directions with single atomic site hops. Tunneling spectroscopy measurements across metal superconductor boundary provides variation of electron structures highlighting how surface state electrons interact with the superconducting clusters.

5:40pm **SP+AS+MI+NS+SS-TuA11 Breaking the Time Barrier in Scanning Probe Force Microscopy: Fast Free Force Reconstruction (F^{3}R) for Non-contact SPM**, *L. Collins*, ***Stephen Jesse***, *S.V. Kalinin*, Oak Ridge National Laboratory

In the past 3 decades since its invention, the atomic force microscope (AFM) has offered unparalleled insight into both nanoscale structure and surface functionality. At the same time, the spatial resolution afforded by AFM tip is counterpoised by the slow detection speeds compared to other common microscopy techniques (e.g. optical, scanning electron microscopy etc.). This ultimately limits AFM and related measurements to static or quasi-static processes.

In this presentation, we outline a novel time resolved AFM imaging approach, referred to as Fast free force recovery (F^{3}R)[1] utilizing big data capture and analytics. F^{3}R-AFM is based on the G-mode acquisition platform [2] and allows direct reconstruction of the tip-sample forces with much higher time resolution (~µs) than possible using standard AFM detection methods (~ms). We describe how fast data acquisition, coupled with multivariate statistical denoising methods can be harnessed to overcome the widely viewed temporal bottleneck in AFM, the mechanical bandwidth of the cantilever. Finally, we will demonstrate quantitative recovery of tip-sample forces with <10 µs time resolution, free from influences of the cantilever ring-down as well as discussing the fundamentally time and information limits of the approach.

[1] Collins, Liam, Mahshid Ahmadi, Ting Wu, Bin Hu, Sergei V. Kalinin, and Stephen Jesse. "Breaking the Time Barrier in Kelvin Probe Force Microscopy: Fast Free Force Reconstruction Using the G-Mode Platform." *ACS nano* (2017).

[2] Belianinov, Alexei, Sergei V. Kalinin, and Stephen Jesse. "Complete information acquisition in dynamic force microscopy." *Nature communications* 6 (2015).

6:00pm **SP+AS+MI+NS+SS-TuA12 Ultrafast G Mode-Kelvin Probe Force Microscopy and its application to probing ionic transport mechanisms in perovskite solar cells.**, ***Liam Collins***, *S. Jesse, S.V. Kalinin*, Oak Ridge National Laboratory

Kelvin probe force microscopy (KPFM) is crucial technique for the joint investigations of structural, electronic, and electrochemical functionality on materials ranging from ferroelectrics, and photovoltaics, to battery and fuel cell devices. While KPFM has shown extraordinary success for quantification of equilibrium *or quasistatic* functionalities, this level of information is not sufficient for describing electroactive materials or devices involving fast (< ms) relaxation processes. Practically, the detection methodologies adopted in classical KPFM limit the temporal resolution of the measurement (e.g. ~1-10 MHz photodetector stream is down sampled to a single readout of surface potential per pixel).

In this presentation General Acquisition mode (G-Mode) KPFM[1-3] will be introduced. It will be shown that by harnessing big data acquisition and analytics, it is possible to extract dynamic information on the local electrochemical processes with nanometer spatial and microsecond time resolution. Furthermore, the G-Mode KPFM approach is immediately implementable on all AFM platform, allows capture of numerous channels of information simultaneously (*e.g.* capacitive and potential channels), as well as providing increased flexibility in terms of data exploration across frequency, time, space, and noise domains.

Finally we harness these imaging capabilities to explore non-linear ionic transport in organic-inorganic halide perovskites. We will present imaging of spatio-temporal charge dynamics at the perovskite/electrode interface with <20 µs time resolution and ~10s nm spatial resolution. As will be outlined, based on our observations, we determine that the transport behavior of these materials is considerably more complex than previously argued.

[1] Collins, Liam, et al. "Multifrequency spectrum analysis using fully digital G Mode-Kelvin probe force microscopy." *Nanotechnology* 27.10 (2016): 105706.

[2] Collins, Liam, et al. "Full data acquisition in Kelvin Probe Force Microscopy: Mapping dynamic electric phenomena in real space." *Scientific reports* 6 (2016): 30557.

[3] Collins, Liam, et al. "Breaking the Time Barrier in Kelvin Probe Force Microscopy: Fast Free Force Reconstruction Using the G-Mode Platform." *ACS nano* (2017).

Sustainability Focus Topic
Room: 5 & 6 - Session SU+2D+MS+NS-TuA

Membranes, Thin Films, and Sensors
Moderators: Keith Brown, Boston University, Roya Maboudian, University of California at Berkeley

2:20pm **SU+2D+MS+NS-TuA1 Protecting Food and Water Quality: Considerations for Materials Innovation**, ***Susan Duncan***, Virginia Polytechnic Institute and State University **INVITED**

Innovation in materials and membranes provides opportunity for enhancing water and food safety, diversifying and expanding water and food sources, protecting nutrient quality and bio-availability, and improving human health and well-being. Food and water are transitioned from their original sources into resources for animal feed and human food through production, processing, packaging, and distribution/retail stages. Throughout these stages, membranes and materials for physical and chemical separations, microbiological control, analysis and measurement, capture and containment are required.

Synergistic partnerships, among scientific disciplines and between private-public entities, encourage innovation in the design and applications of materials and membranes for discoveries and advancements in water and food processing and packaging. The objective of this discussion is to showcase the engagement of chemists, engineers, and food scientists in approaching and resolving challenges relating to water and food processing, safety, and quality and the relationship to the consumer. Three featured examples, relating to membranes and materials, include:

Aquaculture: Recirculating water for the purpose of raising fish has high economic and global impact by increasing sustainable supply of high quality food proteins for feeding the growing global population. Challenges include the need for removing biosolids, small molecular weight molecules, and bacteria that influence fish health and quality of the fish as a food source.

Water Safety from Source and Supplier to the Consumer: Protecting public health is the primary role of water treatment. Changes in water disinfectant treatment, e.g. chlorine to chloramine, affect material stability, safety and performance and can lead to significant economic impacts and consumer concerns.

Food Packaging Functionality: Protecting food and beverage freshness from processing to purchase requires understanding of the food system, the process, and storage conditions. Innovative materials that interfere with light energy can protect beverage and food quality for retaining freshness and nutrient retention for enhancing human health.

Expanding our scientific continuum from molecule to materials through process, package and consumer perspective enriches and guides scientific discovery.

3:00pm **SU+2D+MS+NS-TuA3 Real-time Detection of Water Contaminants Using a Graphene-based Field-Effect Transistor Sensing Platform**, ***Junhong Chen***, University of Wisconsin - Milwaukee **INVITED**

The National Academy of Engineering identified “providing access to clean water” as one of the top 10 grand challenges for engineering in the 21st century. A central requirement for safe drinking water is the availability of low-cost and real-time water quality monitoring. Current detection methods for critical analytes in water are often too expensive or unsuitable for in-situ and real-time detection (*an unmet need*). As a result, there is a lack of water quality monitoring along the water distribution line and at the point of use, which is inadequate because of potential deterioration in water quality within water distribution systems (e.g., Flint Water Crisis). This talk will unveil a powerful approach to real-time water sensors through a graphene-based field-effect transistor platform. The working principle of the sensor is that the conductivity of 2D nanomaterial channel (usually measured in resistance) changes upon binding of chemical or biological species to molecular probes anchored on the graphene surface. As such, the presence and the concentration of analytes, such as heavy metals, bacteria, and nutrients, can be rapidly determined by measuring the sensor resistance change. The talk will introduce the performance of the sensor for detection of various water contaminants and focus on the molecular engineering aspects of the sensor device through both theoretical and experimental approaches. The talk will end with a brief introduction on the translation of the platform technology from concept to prototype product through partnership with industries.

5:00pm **SU+2D+MS+NS-TuA9 Nanocellulose Thin Films and Nanocellulose Aerogels**, ***Kenneth Carter***, University of Massachusetts - Amherst, *A. Chang, K.L. Martin, Y. Li*, University of Massachusetts – Amherst **INVITED**

Nanocellulose is an interesting material with unique properties and chemistry. We have worked to exploit these characteristics to develop new functional thin films and aerogels. We have developed a new method for the preparation of well-dispersed cellulose nanofibrils and nanocrystals. Advantageously, the method does not require the use of harsh acids and excludes the use of catalytic oxidants such as 2,2,6,6-tetramethyl-1-piperidine-N-oxy (TEMPO) . Furthermore, the nanofibrils and nanocrystals produced by the method are easily re-dispersible and give stable aqueous dispersions. Transparent, robust nanocellulose thin films were prepared with outstanding anti-fogging properties. Most recently, nanocellulose was used to prepare aerogel/foam materials using a new fabrication method. The aerogels are mechanically stable and robust. Our new aerogel fabrication process obviates the need to use freeze-drying or low pressure solvent removal. We will present data on new nanocellulose aerogels with densities ranging from 5-100 mg/cm^3.

5:40pm **SU+2D+MS+NS-TuA11 Fabrication and Characterization of Thermal Treated Si/Si+Ge Thin Films For Energy Harvesting**, *S. Budak, Z. Xiao,* ***Michael Howard****, B. Rodgers, M. Alim*, Alabama A&M University

Thermoelectric thin film devices were prepared from the alternating nanolayers of Si and Si+Ge to form the Si/Si+Ge thin films structures using DC/RF magnetron sputtering system. Fabricated thermoelectric devices were treated at different temperatures for an hour for each case to form quantum (nano) structures in the alternating nanolayers of Si and Si+Ge to increase both the Seebeck coefficients and the electrical conductivity and decrease the thermal conductivity. The prepared Si/Si+Ge thin film thermoelectric devices were characterized using the Seebeck coefficient measurement; the four probe van der Pauw resistivity measurement and the laser thermal conductivity systems for in-plane geometries. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM+EDS). Thermal treatment showed positive effects on the thermoelectric properties of Si/Si+Gethin films on the selected temperatures. The findings will be presented during the meeting.

Acknowledgement

Research was sponsored by NSF with grant numbers NSF-HBCU-RISE-1546965, DOD with grant numbers W911 NF-08-1-0425, and W911NF-12-1-0063, U.S. Department of Energy National Nuclear Security Administration (DOE-NNSA) with grant numbers DE-NA0001896 and DE-NA0002687.

6:00pm **SU+2D+MS+NS-TuA12 Thermoelectric Properties of Bi_2Te_3/Sb_2Te_3 Thin Films Annealed at Different Temperatures**, *S. Budak, Z. Xiao, M. Howard,* ***Breonna Rodgers****, M. Alim*, Alabama A&M University

Thermoelectric devices were prepared from Bi_2Te_3/Sb_2Te_3 thin films using DC/RF magnetron sputtering system. Fabricated devices were annealed at different temperatures to form nanostructures in the multilayer thin films to increase both the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. The thermoelectric devices were characterized using Seebeck coefficient measurement system; four probe van der Pauw measurement resistivity system and the laser thermal conductivity system. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM/EDS).

Acknowledgement

Research was sponsored by NSF with grant numbers NSF-HBCU-RISE-1546965, DOD with grant numbers W911 NF-08-1-0425, and W911NF-12-1-0063, U.S. Department of Energy National Nuclear Security Administration (DOE-NNSA) with grant numbers DE-NA0001896 and DE-NA0002687.

Applied Surface Science Division
Room: 13 - Session AS+BI+MI+NS+SA+SS-WeM

Beyond Traditional Surface Analysis: Pushing the Limits
Moderators: Svitlana Pylypenko, Colorado School of Mines, Paul Vlasak, The Dow Chemical Company

8:00am **AS+BI+MI+NS+SA+SS-WeM1 Photolysis of Pyruvic Acid in Aqueous Solution as a Source of Aqueous Secondary Organic Aerosol**, ***Yao Fu***, *X.F. Yu, F. Zhang, Z.H. Zhu*, Pacific Northwest National Laboratory, *J.M. Chen*, Fudan University, *X.Y. Yu*, Pacific Northwest National Laboratory

Pyruvic acid are found in fogs, aerosols and clouds. The sunlight driven reaction pathways of pyruvic acid in the aqueous phase are more elusive compared to its well-known gas phase chemistry. Aqueous solutions containing pyruvic acid in a microchannel after different UV photolysis times up to 8 hours have been studied by in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) for the first time. Both positive and negative ion mode mass spectra provided complementary information of the photochemical aging products at the solution surface. Compared with previous results using bulk approaches (i.e., NMR, ESI-MS), our unique liquid surface molecular imaging enables the observation of photochemical products of pyruvic acid at the aqueous solution surface including oxidation products (i.e., acetic acid, oxalic acid, formic acid, lactic acid), oligomers (i.e., dimethyltartaric acid), and water clusters (i.e., $(H_2O)_nH^+$, $(H_2O)_nOH^-$) with submicrometer spatial resolution. Spectral principal component analysis is used to determine similarities and differences among various photochemical aging samples. SIMS three-dimensional chemical mapping permits visualization of the surface mixing state at the molecular level. For example, oligomers and oxidation products become more significant shown in the chemical spatial mapping with increased photolysis time. In situ molecular imaging of the pyruvic acid aqueous solution surface provides new understanding of complex photochemical reactions as an important source of aqueous secondary organic aerosol (SOA) formation in atmospheric chemistry.

8:20am **AS+BI+MI+NS+SA+SS-WeM2 XPS Depth Profiling of $SrTiO_3$ and HfO_2 with Small Argon Clusters**, ***Christopher Deeks***, Thermo Fisher Scientific, UK, *M. Baker*, University of Surrey, UK, *P. Mack*, Thermo Fisher Scientific, UK

Metal oxides are employed in a wide variety of functional applications. There is currently strong technological interest in strontium titanate ($SrTiO_3$) and hafnium oxide (HfO_2) due to their specific band gaps and high dielectric constants. $SrTiO_3$ is being studied for use in photocatalysis, energy storage and electronic sensors, whilst HfO_2 is widely employed for optical coatings and optoelectronic device applications. Both materials are regularly deposited as thin films and doped to optimise their properties for the application. An accurate determination of thin film composition is paramount to the understanding and optimisation of device performance.

In this work, thin films of $SrTiO_3$ and HfO_2 have been deposited onto silicon substrates and XPS depth profiles have been performed through the thin films using both monatomic and cluster argon ion bombardment. The monatomic Ar^+ profiles were performed using an incident ion energy of 500 eV and the gas cluster ion beam (MAGCIS) profiles were recorded using8 keV Ar_{1000}^+ and 8 keV Ar_{150}^+ for $SrTiO_3$ and HfO_2 respectively. For HfO_2 the optimum results were found when the MAGCIS ion beam was incident upon the sample at a glancing angle. These MAGCIS conditions yielded excellent retention of the original $SrTiO_3$ and HfO_2 stoichiometry during the profile, with no evidence of preferential sputtering or ion beam induced reduction. Using 500 eV Ar^+,however, resulted in the preferential sputtering of oxygen leading to the presence of sub-oxide states in the XPS spectra of Ti in $SrTiO_3$ and Hf and HfO_2. The depth resolution was similar between the monatomic and cluster ion depth profiles for both thin film materials. Using the same incident ion beam angle, the etch rate for 8 keV Ar_{1000}^+ was only 2.5 times lower than that for 500 eV Ar^+. The results will be discussed in the light of known ion beam effects when sputtering metal oxide materials.

8:40am **AS+BI+MI+NS+SA+SS-WeM3 Surface Analysis of Intact Biomolecules: the Bigger They Are the Harder They Fly**, ***Nina Ogrinc Potocnik***, *R. Heeren*, Maastricht University, The Netherlands **INVITED**

Secondary ion mass spectrometry (SIMS), as the oldest MSI techniques, gained popularity for analysis of biological samples due to its ability to obtain chemical and spatial information at unmatched lateral resolutions. The use of focused ion beams for desorption and ionization of surface molecules in SIMS affords for this notable spatial resolution over, for example, laser-based MS approaches such as Matrix Assisted Laser Desorption Ionisation (MALDI). However, the excessive energy of the primary ions limits the method to the detection of elements, fragmented molecules and small intact molecular species. This consequently points at the method's major drawback, which is the difficulty to ionize and detect larger, intact molecular species such as peptides and proteins with great sensitivity. Over the last years, SIMS has been pushing the boundaries by redirecting focus into biomedical applications. Tissue sections and cell imaging has become common practice in research labs all over the world. Now, abundant lipids and small peptides can be studied with different sample surface modifications, where the upper most layer of the surface is sputter coated with a thin layer of metal ((MetA) SIMS – metal –assisted SIMS) or covered with the matrix (ME-SIMS). In both cases the sputtering efficiency and the secondary molecular yield have increased. Here, we studied how ME-SIMS can influence the ionization efficiency of desorbed intact molecules in comparison to MALDI.

First, we imaged mammalian tissue sections that were subjected to a variety of different matrices using a home-built sublimation chamber. Matrix sublimation produces small, homogenous crystal sizes, without the need for solvents that delocalize molecular species. The same or consecutive sections were subsequently analyzed by FTICR-SIMS, to accurately identify the enhanced molecular species of interest specifically intact lipids and metabolites, and by the PHI nano-TOF II for high lateral resolution images and confident identification of said species with tandem MS.Second, *de-novo* peptide sequencing was performed on endogenous neuropeptides directly from a pituitary gland. Careful sample preparation and the capability of using a 1 Da mass isolation window of the precursor ion followed by a collision-induced dissociation (CID) at 1.5 keV in an activation cell with argon gas enables the molecules to be fragmented in a specific pattern. Neuropeptides up to *m/z* 2000 were detected and sequenced from the posterior lobe. Further on, we applied it for the characterization of tryptically digested peptides from a variety of tissue sections investigating the applicability to bottom-up proteomics.

9:20am **AS+BI+MI+NS+SA+SS-WeM5 Hydrogen/Deuterium Exchange Using Vapor Phase D_2O to Enhance SIMS Characterizations**, ***Paul Vlasak***, The Dow Chemical Company

Hydrogen/Deuterium exchange of labile hydrogens is a well-known water solution-based phenomenon that has in recent years seen extensive use in the area of protein characterization. This presentation will demonstrate a method to accomplish vapor phase hydrogen/deuterium exchange of solid sample surfaces prior to analysis by SIMS. In many cases, it is not desirable to expose the sample to liquid solvent due to the possibility of dissolving and rearranging or removing surface species of interest. In contrast, the effect of vapor phase D_2O exposure is similar to typical exposures of the sample to humid room air.

The described method is simple and inexpensive in comparison with synthetic isotopic labeling studies. However, it is expected that only the sufficiently labile and sterically accessible H atoms can be tagged, typically those bound to N, O, or S. Possible benefits of this method include isomer differentiation, elucidation of fragmentation pathways, fundamental studies of ionization, differentiation of sterically or otherwise protected vs. unprotected functional groups, and determination of water diffusion or permeability in solid materials.

9:40am **AS+BI+MI+NS+SA+SS-WeM6 Fragmentation and Backscattering of Large Ar_n^+ Clusters as a Probe of Polymer Glass Transition**, *C. Poleunis*, Université Catholique de Louvain, Belgium, *V. Cristaudo*, Université Catholique de Louvain, Belguim, ***Arnaud Delcorte***, Université Catholique de Louvain, Belgium

Gas cluster ion beams (GCIB) have become the standard sources for molecular depth-profiling of organic materials with secondary ion mass spectrometry (SIMS) [1] and X-ray photoelectron spectroscopy (XPS). Since 2009, a number of experimental and theoretical studies were devoted to the investigation of the effects of energy, nuclearity and incidence angle of the Ar clusters on the energy deposition, fragmentation and molecular emission induced in organic solids [2-4]. Recently, Mochiji et al. reported that the backscattered Ar_n^+ clusters observed in the SIMS spectra of pure metal surfaces provide information on the mechanical properties of the surfaces analysed by GCIB [5]. They correlated the ratio of Ar_2^+ to the sum of Ar_n^+ clusters intensities with the impulsive stress caused by the impact, a parameter directly linked to the elastic modulus of the material.

Here, the intensity variations of the backscattered Ar_n^+ clusters are studied as a function of temperature for a series of thermoplastic polymers: high molecular weight polydisperse polyisobutylene and polybutadiene, polystyrene (Standard; $M_w = 4000$) and polymethyl methacrylate (Standards; $M_w = 2000$ and 150000). For all these polymers, our results show a transition of the intensity ratio $Ar_2^+/(Ar_2^++Ar_3^+)$ when the temperature is scanned from

-120 °C to +125 °C. This transition generally spans over a few tens of degrees and the temperature of the inflexion point of each curve is very close to the glass transition temperature (T_g) reported for the considered polymer. Due to the surface sensitivity of the cluster backscattering process (a few nanometers as indicated by molecular dynamics simulations [4]), the presented analysis could provide a new method to specifically evaluate the surface T_g of polymers, with the same lateral resolution as the gas cluster beam. The results are discussed from the point of view of the structure and mechanics of polymers.

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11:00am **AS+BI+MI+NS+SA+SS-WeM10 Evolution of the Bi Cluster LMIS as a Universal Source for High Performance SIMS Analysis**, ***Felix Kollmer****, ION-TOF GmbH, Germany **INVITED**

In 1987 Appelhans and co-workers performed a groundbreaking experiment. They bombarded a polymer surface with a neutral SF6 beam in order to avoid charging effects on insulators. By coincidence they discovered that "the SF$_6$ beam is doing an excellent job of producing secondary ions ... it is unexpectedly efficient at sputtering secondary ions from these polymer surfaces "[1].

In the following years the bombardment of organic surfaces with clusters was investigated by many research groups. The lateral resolution of the applied beams was rather low since the focus at this time was clearly on the fundamentals of the ion solid interaction and the secondary ion generation. However, as early as 1991 Benguerba applied an Au cluster liquid metal ion source (LMIS) for a fundamental study of phenylalanine [2].

At the beginning of the millennium Au cluster LMIS became commercially available for TOF-SIMS instrumentation. This led to a wider application in the SIMS community and to a further improved performance. However, the cluster sources remained an additional option for the SIMS instruments especially since the low cluster currents did not allow the replacement of the reference Ga LMIS for many applications.

With the introduction of a LMIS operated with Bi this changed fundamentally [3]. Roughly 50% of the beam consists of clusters and 50% are emitted as mono-atomic Bi species. This ensures a large flexibility for the analysis of inorganic as well as organic surfaces. Moreover, an uncompromised performance in terms of lateral and mass resolution is achieved, even with cluster beams, and a lateral resolution in the sub 20 nm range has been demonstrated with Bi_3^{++} species [4].

Today, the Bi LMIS is used as the standard analysis source on more than 250 TOF-SIMS instruments for all kinds of applications. In combination with a massive cluster beam that is applied for the erosion of the sample (e.g. Ar_n) even depth profiling or 3D analysis of organic samples is possible.

In this contribution, we will have a retrospective look at the development of high performancecluster SIMS. Besides fundamental capabilities of the Bi LMIS and the secondary ion generation we will discuss milestones of the application as well.

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11:40am **AS+BI+MI+NS+SA+SS-WeM12 Evaluating the Benefits of Cs Cluster Analysis in ToF-SIMS and Cs/Xe Co-sputtering for Depth Profiling Layered Thin Films**, ***James Ohlhausen***, *P.T. Vianco, M.T. Brumbach, R. Chow*, Sandia National Laboratories

Depth profiling with Cs to create MCs^+ clusters can produce semi-quantitative results by greatly reducing the matrix effects observed in common M^+ analysis. Additionally, alkali metal clusters enhance negative ion detection in the form of positive Cs clusters, such as MCs^+ and MCs_2^+. In his review article, Wittmaack[1] discussed the many ways that Cs is used in SIMS analyses to provide this enhancement which includes using Cs as the sputtering species and/or analytical probe and using directed Cs vapor. Unfortunately, high Cs surface concentrations can lead to suppression of Cs cluster formation. Xenon and Cs can be co-sputtered in a ToF-SIMS system to adjust the relative amounts of Cs and Xe in the co-sputtered beam to control Cs surface concentration and optimize Cs cluster formation[2]. Cs/Xe co-sputtered depth profiling has been shown to work well in materials systems such as Au thin film on Si[3] and Pd-Rh thin film[4].

The present paper discusses the use of Cs/Xe co-sputtering to investigate an Au/Pd/Ni electroplated layered system. Gold and to some extent Pd have low positive ionization yields, so typical ToF-SIMS data from these metals can be difficult to interpret. However, Cs/Xe co-sputtering has been found to generate high yield MCs^+ clusters in Au and Pd, thus enabling this analysis. This Au/Pd/Ni metal stack were analyzed in a pristine (as received) condition, after accelerated aging and after exposure to a (very high temperature) solder reflow process. The elemental and molecular sensitivities as well as quantitative results stemming from this analysis will be investigated. The manner whereby these results support the use of Au/Pd/Ni stack in an engineering application will be shown. In particular, interlayer diffusion, trace contaminants and interfacial contamination will be examined. Comparisons will be made to Auger and XRF to assess quantitation and sensitivity and to illustrate the advantage of this SIMS technique.

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12:00pm **AS+BI+MI+NS+SA+SS-WeM13 Real-Time Monitoring Electrochemical Reaction Intermediates using *In Situ* Time-of-Flight Secondary Ion Mass Spectrometry**, ***Jun-Gang Wang***, East China University of Science and Technology; Pacific Northwest National Laboratory (PNNL), *Y. Zhang, X.Y. Yu, Z.H. Zhu*, PNNL

In situ monitoring of electrochemical reactions is traditionally performed by cyclic voltammetry[1], plasmonic spectroelectrochemistry[2, 3], and surface probing techniques such as scanning electrochemical microscopy and scanning ion conductive microscope.[4] However, it has been extremely difficult to obtain direct molecular evidence of the electrochemical reaction intermediates using these traditional techniques. Thus, the debate of rection machnisms has long been an issue. Recently, mass spectrometric techniques have been coupled with electrochemistry to provide the molecular information of intermediates of redox reactions.[5] The advantage of mass spctetrometric techniques is that capture of molecular ions can provide direct molecular information of key chemical species, such as rection intermediates. A novel approach, based on coupling of time-of-flight secondary ion mass spectrometry (ToF-SIMS) and electrochemistry has been developed in Pacific Northwest National Laboratory and it has been used for in situ analysis of reaction intermediates in electro-oxidation of ascorbic acid at the electrode–electrolyte interface.[6] Herein, the electrochemical oxidation of acetaminophen was chosen as a model system, which simulated the function of oxidase enzymes cytochrome P-450 to catalyze the oxidation of acetaminophen.[7] This reaction was real-time monitored using in situ ToF-SIMS. The highly reactive N-acetyl-p-benzoquinone-imine (NAPQI) was captured. The NAPQI subsequently conjuated with glutathione and cysteine was molecularly confirmed. We demonstrated the proof of principle for the use of ToF-SIMS for real-time monitoring of electrochemical reaction with high chemical specificity. Our results demonstrate that the coupling of ToF-SIMS and electrochemistry has great potential to molecularly elucidate reaction machnisms in the oxidative metabolism, pharmaceutical intoxification, and cell toxicology.

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Biomaterial Interfaces Division
Room: 12 - Session BI+NS-WeM

Biomaterials and Nanomaterials Fabrication & In Honor of Dave Castner's 65th Birthday: Multitechnique Bio-Surface Characterization I
Moderator: Caitlin Howell, University of Maine

8:00am **BI+NS-WeM1 Plasma-Enhanced Chemical Vapor Deposition of an Antibacterial Coating from an Essential Oil-Derived Precursor**, ***Michelle Mann***, *E.R. Fisher*, Colorado State University

Polymeric constructs, such as filtration membranes for water treatment and nanocomposite scaffolds for wound healing and drug release, are often chosen for their ideal bulk properties (e.g., porosity, mechanical strength, and chemical inertness). Challenges faced when using such materials in aqueous settings, however, include their hydrophobicity and propensity for bacterial attachment, leading to biofilm formation and degradation of material performance. Modifying the surface of the constructs while simultaneously maintaining the bulk properties offers both the possibility of addressing these limitations and the potential for creating new advanced materials. Plasma processing is a valuable tool often used to improve material wettability and deposit antifouling coatings. Here, plasma-enhanced chemical vapor deposition is used to deposit films from eucalyptol (1,8-cineole), an antibacterial precursor derived from tea tree oil. Although the antibacterial properties of eucalyptol are supported by numerous clinical trials, it is unknown to what extent the monomer structure and biocidal capabilities are maintained in plasma polymerized films. Thus, we have explored the properties of the eucalyptol-based films as a function of plasma parameters (e.g., power, pressure). Surface analyses (contact angle goniometry, X-ray photoelectron spectroscopy, scanning electron microscopy, and optical profilometry) reveal film wettability directly correlates to precursor pressure, with water contact angles ranging from ~50° to 85°. To further improve wettability of these materials, they were subjected to H_2O (v) plasma modification, an approach that has been successful in past studies to improve polymer biocompatibility. After plasma treatment, wettability increased, with water contact angles of ~20-35°, and the films exhibited a significant enhancement in oxygen content (40-150%), while remaining stable in aqueous solutions. Attachment and biofilm formation assays allowed for assessment of bacterial interactions at 1 and 5 days after exposure, respectively, with gram-negative *E. coli* and gram-positive *S. aureus*. Using microscopy techniques, we observed attachment and growth are substantially diminished for as-deposited and H_2O (v) plasma treated films. Moreover, performance data (i.e., flux of coated ultrafiltration membranes) are presented. Surface analysis and performance testing results, combined with information about gas phase excited state species observed using optical emission spectroscopy, guide our development of additional antibacterial essential oil-based films for 2D and 3D constructs used in environmental and biomedical applications.

8:20am **BI+NS-WeM2 Transition Metal Nanoparticles and Quantum Dots with Tunable Electronic Properties by Bacterial Precipitation: Synthesis and Applications**, *K.E. Marusak, Y. Feng, E. Ngaboyamahina, Y. Cao, J.T. Glass, L. You,* ***Stefan Zauscher***, Duke University

We present a new method for the fabrication of semiconducting, transition metal nanoparticles (NPs) with tunable bandgap and useful photoelectric properties, through bacterial precipitation. *Escherichia coli* bacteria have been genetically engineered, by overexpression of a cysteine desulfhydrase gene, to precipitate transition metal NPs from solution, here more specifically, cadmium sulfide (CdS). Transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) revealed that the bacterially precipitated NPs are agglomerates of mostly quantum dots (QDs), with a diameter of 4-5 nm, in a carbon-rich matrix. We discovered that the precipitation conditions of the bacteria can be tuned to produce NPs with bandgaps that range from quantum-confined to bulk CdS. Furthermore, we determined their photoelectrochemical (PEC) properties and their energy band structure by electrochemical measurements. In addition, by taking advantage of the organic matrix, which is residual from the biosynthesis process, we fabricated a prototype photocharged capacitor electrode by incorporating the bacterially precipitated CdS with a reduced graphene oxide (RGO) sheet. Our results show that bacterially precipitated CdS NPs are potentially useful components for PEC devices with applications for energy conversion and storage.

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8:40am **BI+NS-WeM3 Plasma Surface Modification of 2D and 3D Constructs: Creating and Evaluating New Materials for Biomedical Applications**, ***Ellen Fisher***, Colorado State University **INVITED**

Plasma processing represents a powerful approach to modification of 2D and 3D substrates with an array of chemistries appropriate for use in biomedical applications. It is an attractive methodology because of its versatility, low waste, and scalability. The three major plasma surface modification classifications are deposition (film formation, polymerization), etching (removal of material) and functional group implantation (covalent bonding of chemical functional groups), which collectively provide a large landscape for creating materials with specific properties tailored for particular applications. Combining a range of spectroscopic techniques, materials characterization tools, and basic biological interaction studies provides a platform for deeper insight into these underlying mechanisms than just one approach alone. Yet, this can also lead to a range of obstacles, especially when seeking to apply traditional diagnostic methodologies to new systems and materials. For example, data on the surface chemistry of 3D constructs coated with thin films having a range of film chemistries (via utilization of allylamine/allylalcohol mixed gas plasmas) combined with an understanding of the gas-phase chemistry in these systems and cell-surfaces interaction studies highlights key properties required to tune the surface chemistries that can promote or deter cell viability and proliferation. Thus, this presentation will highlight a few key examples, including inherent challenges, where such a unified, comprehensive approach has been fruitful for 2D and 3D materials intended for use as antimicrobial materials, in separations, and for tissue engineering applications.

9:20am **BI+NS-WeM5 The Ins and Outs of Functionalized Natural Materials for Applications in Drug Delivery and Separations**, ***Norma Alcantar***, *R. Toomey, Z. Veisi,* University of South Florida, *A. Cardenas-Valencia, M. Cardenas,* SRI International, *R. Falahat,* Moffitt Cancer Center, *T. Peng, F. Guo,* University of South Florida **INVITED**

In the last decade, numerous natural materials have been investigated as platforms in functionalized surfaces. In our case, we have studied the structure and properties of two natural materials, chitosan from crustaceous shells and cactus mucilage from cactus plants. Those two natural materials have been used as building blocks in drug delivery systems, and as flocculants or adsorbent materials to remove contaminants from water. In the drug delivery systems, the natural material is used as surface membranes capable to respond to external stimuli. Our team has discovered that chitosan has a specific bond with the MUC1 enzyme found in epithelial-type cancers, which can enhance its specificity towards cancer cells when used in drug delivery systems. The results of our research have also shown that depending on the biophysical conditions surrounding the natural materials, their response to hydrophilic and hydrophobic interactions to separate organic and inorganic contaminants are controlled by their structure, which can then be finely tuned to enhance their performance. The use of natural materials for functional applications is an area of study that could lead to discoveries in microfluidic devices, health applications, cosmetics, coatings and paintings, and water purification systems.

11:00am **BI+NS-WeM10 Combinatorial Material Chemistry-Topography Screening: The ChemoTopo Chip**, ***Britta Koch****, University of Nottingham, UK, *A. Vasilevich, N. Beijer, J. de Boer,* Maastricht University, The Netherlands, *M.R. Alexander,* The University of Nottingham, UK

The interaction of cells with their culture substrate is critical to their fate, having a profound impact on cell response and viability. However, complex cell-cell as well as cell-matrix interactions in native tissue make it challenging to emulate *in vivo* cell behavior in the lab. The design of man-made, biomimetic cell environments hold great potential for biomedical

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*** BID Early Career Researchers Award**

applications like tissue engineering, disease modeling and drug screening. Therefore, suitable biomaterials are sought that can interface with cells and provide adequate physical, chemical and biological characteristics to elicit the desired cell response in a well-defined *in vitro* environment.

In recent years, microarray technology in combination with high-throughput surface characterization methods has proven to be a valuable tool for the cost-efficient and rapid screening of large libraries of biomaterial candidates. However, until now screening has been performed either on planar samples, focusing on optimizing sample chemistry rather than topography [1] or on topography with no chemical variation [2]. Here we propose a novel platform that augments the chemical screening approach with deterministic control of the topography. This new platform called the 'ChemoTopo Chip' allows the systematic investigation of combinatorial effects of well-defined surface chemistry and topography and moves closer to recapitulating the range of 3D cues at play *in vivo* within an *in vitro* screen. The first results on the identification of hit combinations supporting mesenchymal stem cell growth are presented and future steps aiming at enhancing our global understanding of the context-dependent cell response are outlined. The ChemoTopo Chip platform contributes to the discovery of novel substrates with the potential to ultimately translate these into biomedical applications. Also, the gathering of data allows to develop surface structure-property relationships from which understanding can be generated to support rational design of the *in vitro* cell environment.

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11:20am **BI+NS-WeM11 Combining Surface Analytical and Computational Techniques to Investigate Orientation Effects of Immobilized Proteins**, ***Elisa Harrison***, *G. Interlandi, D.G. Castner*, University of Washington, Seattle

Controlling how proteins are immobilized (e.g. controlling their orientation and conformation) is essential for developing and optimizing the performance of *in vitro* binding protein devices, such as enzyme-linked immunosorbent assays. The objective of this work is to develop new methodologies to study proteins and complex mixtures of proteins immobilized onto surfaces.

The focus of this study was to control and characterize the orientation of protein G B1, an IgG antibody-binding domain of protein G, on well-defined surfaces as well as measure the effect of protein G B1 orientation on IgG antibody binding using a variety of surface analytical and computational techniques. The goal was to immobilize protein G B1 into well-ordered films with different orientations that control the accessibility of antibody binding sites.

The surface sensitivity of time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to distinguish between different proteins and their orientation by monitoring the changes in intensity of characteristic amino acid mass fragments. Amino acids with asymmetric distributions (Asn, Trp, Gly, Ala, and Thr) were used to calculate peak intensity ratios from ToF-SIMS data in the C- and N-terminus of protein G B1 to determine the orientation of five different cysteine mutants of protein G B1 covalently attached to a maleimide surface.

To study the effect of protein orientation on antibody binding, we formed multilayer protein films. Quartz crystal microbalance with dissipation monitoring (QCM-D) detected protein coverages of 69 - 130 ng/cm^2. QCM-D and X-ray photoelectron spectroscopy (XPS) analysis revealed that packing density along with orientation affected the antibody binding process. Spectra from ToF-SIMS using large Ar gas cluster ion sources distinguished between different proteins in multilayer protein systems.

Additionally, development of computational methods to study proteins on surfaces can complement surface analytical data. A Monte Carlo algorithm was developed to predict protein orientation on surfaces. Two distinct orientations of protein G B1 adsorbed onto a hydrophobic surface were found and characterized as two mutually exclusive sets of amino acids on the outermost β-sheets contacting the surface. This prediction was consistent with sum frequency generation (SFG) vibrational spectroscopy results. In fact, theoretical SFG spectra calculated from an equal combination of the two predicted orientations exhibited reasonable agreement with measured spectra of protein G B1 on polystyrene surfaces. This method has been expanded to predict protein G B1 orientations on more complex surfaces, such as self-assembled monolayers.

11:40am **BI+NS-WeM12 Characterizing the Tumor Microenvironment and Tumor Progression**, ***Blake Bluestein***, University of Washington, *F. Morrish, D. Hockenbery*, Fred Hutchinson Cancer Research Center, *L.J. Gamble*, University of Washington

Solid tumors are not simply masses of malignant cells but are a structurally complex system, composed of a myriad of cells. The interactions between malignant cells and non-transformed cells form the tumor microenvironment. The tumor microenvironment has been associated with regulating tumor cell growth, metastatic potential, and drug resistance. Here, a combination of techniques including imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS), H&E staining, and second harmonic generation (SHG) microscopy are used to analyze pancreatic biopsies from a mouse model with Myc-dependent inducible pancreatic β-cell neoplasia to relate changes in the composition and distribution of metabolic related molecules with tumor development. Myc, one of the most frequently deregulated oncogenes in human cancers, contributes to tumorigenesis through various mechanisms, including the deregulation of cell proliferation and metabolic alterations.

Pancreatic tissues were harvested and frozen in optimal cutting temperature (OCT) at 6 days post Myc induction and without any Myc induction (control). Cryosections (4 µm thickness) were serially cut, with one used for H&E staining and SHG microscopy, and one for ToF-SIMS analysis. ToF-SIMS data was acquired using an IONTOF TOF.SIMS 5. Regions identified by analysis and principal components analysis (PCA) were cross-referenced against immunohistochemical, H&E, and SHG images to differentiate the tumor areas from the surrounding tissue.

PCA analysis of ToF-SIMS image data separate tumor from surrounding tissue and reveal the differences in chemistries between the two regions. The Myc-induced islet tumors exhibit a signal of C14:0, a likely product of *de novo* fatty acid synthesis within the islet tumor. Image data shows higher signal regions within the interior of the tumor. These regions exhibit an increased, localized signal of CN^-, CNO^-, Fe^+, and characteristic histidine fragments, $C_5H_8N_3^+$ and $C_6H_5N_2O^+$. SHG images showed that there were no organized structures in these higher signal regions and immunohistochemistry showed no signs of angiogenic processes, confirming that these areas are blood pools resulting from vascular hemorrhaging. Further metabolic analyses showed that when compared to control islets, Myc-induced tumor islets exhibited increased intensities of amino acids and phosphatidylcholine lipids (30:0, 32:1, 32:2), which are known to be related to tumor growth. Tissue surrounding the Myc islet tumors exhibited lower intensities of serine, glycine, and arginine when compared to the tissue surrounding the control islets, which suggests tumor uptake or an increased catabolism induced by the adjacent tumor.

12:00pm **BI+NS-WeM13 Observing the Molecular Mechanisms of Insect Adhesion by Sum Frequency Generation Spectroscopy**, *J.E. Fowler*, Oregon State University, *S.N. Gorb*, Kiel University, Germany, *T. Weidner*, Aarhus University, Denmark, ***Joe Baio***, Oregon State University

Many insects can walk on a range of natural surfaces through an adhesion process that combines an expansive array of hairy contacts on their feet, known as setae, and an adhesive fluid, forming contact between the setae and a substrate. Previous studies of this adhesion system have focused almost exclusively on the mechanical and kinematic aspects of adhesion, while ignoring the molecular interactions at the fluid – substrate interface. However, recent experiments illustrate that substrate chemistry does influence the adhesive forces produced by this fluid. Additionally, mass spectrometry results demonstrate that this adhesive fluid is a complex mixture containing both hydrophobic (*i.e.* fatty acids and lipids) and hydrophilic (*i.e.* sugars, alcohols, and carbohydrates) compounds. We hypothesize that the molecular structure at the adhesive fluid-substrate interface is dynamic, with different molecules within the fluid selectively organizing at the interface as a function of substrate hydrophobicity. In the work presented here we probe the molecular interactions between the adhesive fluid taken from lady bugs (*Cocinella septempunctata*) and three model substrates, polyethylene oxide, polystyrene and CaF_2 with vibrational sum frequency generation (SFG) spectroscopy and scanning electron microscopy (SEM). The observed water contact angles for the polyethylene oxide, polystyrene and CaF_2 substrates were 66^o, 92^o and 106^o, respectively. High-resolution SEM images of individual seta-fluid footprints on the surfaces indicate localized "water in oil" emulsion de-wetting with no sign of distinct patterning. SFG spectra collected, from the three substrates, at the C-H (2800-3100 cm^{-1}) contain peaks at 2850 cm^{-1} and 2870 cm^{-1}, characteristic of symmetric CH_2 and CH_3 stretches, respectively. The presence of these peaks suggests an ordered hydrocarbon monolayer at the interface. However, subtle changes in ordering of these molecular groups at the interface were observed across substrates by comparing the ratio of the intensities of observed vibrational modes related to the CH_2 and CH_3 modes. Across the three different substrates this ratio increased with surface hydrophobicity suggesting that the fluid-surface interactions adapt to different substrate chemistries.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room: 24 - Session HC+NS+SS-WeM

Nanoscale Surface Structures in Heterogeneously-Catalyzed Reactions
Moderator: Erin Iski, University of Tulsa

8:00am **HC+NS+SS-WeM1 The Role of Nanoparticle Edges in Water Dissociation and Oxidation/reduction Reactions in Layered Cobalt Oxides Supported on Au(111) and Pt(111)**, ***Jakob Fester***, *J.V. Lauritsen,* Aarhus University, Denmark, *M. Garcia-Melchor,* Trinity College Dublin, *A.S. Walton*, University of Manchester, UK, *M. Bajdich*, Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, *A. Vojvodic,* University of Pennsylvania, *Z. Sun, J. Rodríguez-Fernández*, Aarhus University, Denmark

Nanostructured cobalt oxides show great promise as earth-abundant and cheap heterogeneous catalysts, in particular for the oxygen evolution reaction (OER) in electrochemical water splitting and low temperature CO oxidation. However, despite the strong potential in this system as catalysts, we still lack basic knowledge on the active sites and the exact reaction pathways as well as an understanding of the underlying principles behind observed synergistic effects with gold.

To study the possible structure and location of catalytically active sites under controlled conditions, we created a model system consisting of 2-dimensional layered cobalt oxide (CoO_x) nanoislands supported on Au(111) [1] and Pt(111) [2] substrates. This system offers the possibility to reveal the structures in atomic detail by Scanning Tunneling Microscopy (STM) combined with high-resolution X-ray Photoelectron spectroscopy (XPS).

By recording in-situ STM movies during exposure of Co-O bilayer nanoislands to H_2O we showed that H_2O dissociates on edge sites of the nanoclusters followed by migration of H to the basal plane which serves as a reservoir [3] . In combination with Density Functional Theory (DFT) calculations, a preferable dissociation pathway was revealed, also highlighting an assisting role of a second water molecule in the dissociation process.

The determining role of edge sites in the nanoparticle reactivity was further emphasized by STM and XPS studies capturing several stages in both of the gradual oxidation- and reduction processes leading to transitions between layered Co-O bilayer and O-Co-O trilayer morhphologies. In particular, atom-resolved STM images showed changes in edge structure and high densities of defect lines prior to the intercalation of oxygen. The onset of the O-Co-O trilayer formation is located at the island edges on both Au(111) and Pt(111), however several substrate effects were observed on the process rate, mechanism and reversibility. In general, the microscopic picture revealed in these studies suggests that special sites at CoO_x nanoparticle edges may be important for the integral description of CoO_x as a catalyst.

1. Fester, J., et al., Gold-supported two-dimensional cobalt oxyhydroxide (CoOOH) and multilayer cobalt oxide islands. Physical Chemistry Chemical Physics, 2017. **19**(3): p. 2425-2433

2. Fester, J., et al., Comparative analysis of cobalt oxide nanoisland stability and edge structures on three related noble metal surfaces: Au (111), Pt (111) and Ag (111). Topics in Catalysis, 2016: p. 1-10

3. Fester, J., et al., Edge reactivity and water-assisted dissociation on cobalt oxide nanoislands. Nature Communications, 2017. **8**

8:20am **HC+NS+SS-WeM2 Analysis of Bulk and Surface Properties of Catalytically-Active Nickel Carbide/Nitride Nanostructures using X-ray Techniques**, ***Samuel Gage***, *K. Fong, C. Ngo, S. Shulda*, Colorado School of Mines, *C. Tassone, D. Nordlund*, SLAC National Accelerator Laboratory, *R. Richards, S. Pylypenko*, Colorado School of Mines

Transition metal carbides and nitrides are an ever-growing topic in the scientific community. These materials can be synthesized with varying composition and morphology to exhibit properties similar to platinum-group metal catalysts, which are relevant to industrial heterogeneous catalysis and energy development. Studies, which report promising catalytic performances of nickel carbide and nitride catalysts, have continued to increase in recent years. Wet-chemical approaches involving a top-down thermal decomposition of nickel salt precursors in the presence of product-directing solvents are particularly interesting. The degree of nitrogen present in the nickel salt precursor, as well as the choice of molecular ligand-based solvents, can influence the material properties of the nickel carbide/nitride (Ni_3C/Ni_3N) products.

A series of nitrogen-rich and nitrogen-poor nickel salt precursors were thermally degraded in the presence of oleylamine. X-ray diffraction confirms the bulk hexagonal crystal structure belonging to Ni_3C/Ni_3N. However, a combination of bulk and surface X-ray characterization techniques, including the X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS), small angle- and wide angle X-ray scattering (SAXS and WAXS) indicate that the material properties of the Ni_3C/Ni_3N nanostructures do vary depending on the precursor. Computationally guided experiments reveal that the unique bulk and surface properties of these nanostructures influence their catalytic activity, giving Ni_3C/Ni_3N nanostructures the potential to be earth-abundant substitutes for precious metal catalysts.

9:00am **HC+NS+SS-WeM4 Grain-Boundary-Supported Active Sites for Electrochemical Catalysis**, ***Xiaofeng Feng***, University of Central Florida

Identification of active sites on a catalyst surface is the key to a rational design of heterogeneous catalysts. For nanoparticle catalysts, most efforts to tailor their surfaces have focused on controlling particle size, shape, and composition. The atomic surface sites underlying these structural features are mainly facets, steps, edges, and corner sites. These efforts have led to important progresses in heterogeneous catalysis, but it is unclear if the accessible structure space is sufficient for finding optimal catalysts. One alternative is to use bulk defects such as grain boundaries (GBs) to stabilize catalytically active surfaces. Here we show that the GBs in metal nanoparticles create new active sites for electrochemical catalysis. Through a careful design of metal nanoparticle catalysts with different GB densities, extensive TEM characterization, and electrochemical measurements, we discovered that the catalytic activity for CO_2 reduction on Au and CO reduction on Cu is linearly correlated with the GB density in the catalysts [1, 2]. The quantitative GB-activity relationship implicates GB surface terminations as new active sites and lead to highly active and stable electrocatalysts for a two-step conversion of CO_2 to liquid fuels such as ethanol and acetate. In addition, we found that the GBs in Au enhance its activity for oxygen reduction reaction, suggesting that GB engineering may be a general strategy to improve heterogeneous catalysis for renewable energy conversion.

References:

(1) Feng, X.; Jiang, K.; Fan, S.; Kanan, M. W. *J. Am. Chem. Soc.***2015**, *137*, 4606–4609.

(2) Feng, X.; Jiang, K.; Fan, S.; Kanan, M. W. *ACS Cent. Sci.***2016**, *2*, 169−174.

9:20am **HC+NS+SS-WeM5 Molecule-Surface Interaction on TiO_2 and MoS_2**, ***Zhenrong Zhang***, Baylor University **INVITED**

Interaction of molecules with surfaces of catalysts is critical for understanding catalytic reaction mechanisms. We have studied the interaction of various probe molecules with TiO_2 and MoS_2 using scanning tunneling microscopy (STM) and tip-enhanced Raman scattering (TERS). Two-dimensional material, MoS_2, has attracted tremendous attention due to promising applications in electronics, photonics, and catalysis. Here we compared the difference in the interaction of sub-monolayer copper phythalocyanine (CuPc) molecules with MoS_2 and Au. The relative Raman peak ratio and Raman peak position shift from s patial TERS mapping show the difference in the adsorbates-adsorbates interaction and the adsorbates-substrates interaction on Au and MoS_2 substrates. We have investigated the limits of Raman signal enhancement on MoS_2. Employing carboxylic acid, acetone, and formaldehyde as probe molecules, we studied how reactive sites affect the chemical activity of TiO_2(110). This unique methodology enables us to achieve the atomic-level understanding of the key elemental reaction steps — adsorption, dissociation, diffusion, and coupling reaction — taking place in heterogeneous catalytic reactions.

11:00am **HC+NS+SS-WeM10 Enantioselectivity: The Quintessential Structure Sensitive Surface Chemistry**, ***Andrew Gellman***, *P. Kondratyuk, D. Rienicker, M.A. Payne*, Carnegie Mellon University **INVITED**

Enantioselective heterogeneous catalysis and surface chemistry are quintessential forms of structure sensitive surface processes. Selectivity is driven purely by the diastereomeric relationship between the structural handedness of a chiral reagent or transition state and the structural handedness of a chiral surface. Enantioselectivity can be observed on naturally chiral metal surfaces with structures that are described as having flat low Miller index terraces separated by kinked step edges, therefore lacking mirror symmetry. This work has mapped the enantiospecific decomposition kinetics of tartaric acid (TA) and aspartic acid (Asp) on ~500 different single crystal planes exposed by the surfaces of Cu(111) and Cu(100) Surface Structure Spread Single Crystal (S^4C). S^4Cs are single crystals polished into a spherical shape that exposes continuous distributions of surface orientations vicinal to primary orientation. During isothermal decomposition of TA and Asp , XPS has been used to map the temporal evolution of coverage at points across the Cu(111) and Cu(100) S^4Cs. The D- and L-TA (D- and L-Asp) coverage maps across the S^4Cs following heating at 450 K to decompose ~70% of the initially adsorbed molecule reveal the symmetry of the substrate surface and the enantiospecific decomposition kinetics on the chiral surfaces with R- and S- orientations. The fourfold symmetry of the Cu(100) substrate is apparent, and the enantiospecificity of the decomposition kinetics is revealed by the spiral nature of the two maps and their opposite sense of handedness for D- and L-TA. These data can be analyzed to yield the enantiospecific rate constants for TA decomposition as functions of surface orientation.

11:40am **HC+NS+SS-WeM12 Understanding the Growth and Chemical Activity of Pt-Re Clusters on HOPG and Titania Surfaces**, ***Donna Chen***, *T.D. Maddumapatabandi, A.J. Brandt, G. Seuser*, University of South Carolina

The growth and chemical activity of bimetallic Pt-Re clusters supported on highly-oriented pyrolytic graphite (HOPG) and $TiO_2(110)$ surfaces are studied as model systems for understanding Pt-Re catalysts in the water gas shift (WGS) and methanol oxidation reactions. STM experiments demonstrate that both Pt and Re atoms are mobile on unmodified HOPG surfaces and form large clusters that preferentially located at step edges. However, Ar^+ sputtering creates defect sites that serve as nucleation sites and result in smaller clusters with uniform size distributions. At high metal coverages, exclusively bimetallic clusters are formed from both the deposition of Pt on Re or Re on Pt. The cluster surfaces are Pt-rich even for the Re on Pt clusters due to the lower surface free energy of Pt compared to Re and the high mobility of atoms within clusters. Similarly, Pt-rich Pt-Re clusters have also been grown on titania supports. The activities of the Pt-Re bimetallic clusters are investigated in a microreactor coupled to an ultrahigh vacuum chamber so that the surfaces can be characterized by X-ray photoelectron spectroscopy (XPS) before and after reaction. In the WGS reaction, Re remains metallic, and Pt on Re surfaces exhibit higher activity than pure Pt. In methanol oxidation, oxygen-diffusion of Re to the surface occurs under reaction conditions, and the formation of volatile Re_2O_7 results in Re sublimation from the surface. Furthermore, the titania support appears to stabilize Re_2O_7 against sublimation, whereas Re oxidation is enhanced by the presence of Pt in the bimetallic clusters.

12:00pm **HC+NS+SS-WeM13 *Single Atom Alloys* for Efficient and Cost-effective Catalysis**, ***E. Charles Sykes***, Tufts University

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 demonstrated for the first time how single palladium atoms can convert the otherwise catalytically inert surface of an inexpensive metal into an ultraselective catalyst. 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. Palladium/copper nanoparticles containing <2% palladium exhibited highly selective hydrogenation of phenylacetylene under realistic reaction conditions and platinum/copper nanoparticles perform the industrially important butadiene hydrogenation at lower temperature using just 1% platinum. 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.*

Nanometer-scale Science and Technology Division
Room: 19 - Session NS+SS+SU-WeM

Nanotechnology for Renewable Energy
Moderator: Robert Ilic, NIST

8:40am **NS+SS+SU-WeM3 Can “Photovoltaic” Halide Perovskites ($MAPbI_3$ & $MAPbBr_3$) be Ferroelectric?**, ***David Cahen***, Weizmann Institute of Science, Israel **INVITED**

Ferroelectricity, well-known in oxide perovskites, was suggested as possible reason for the outstanding solar-to-electrical energy conversion of $MAPbI_3$ & $MAPbBr_3$-based halide perovskite PV cells, esp. because ferroelectric domain wall conduction was thought to keep photogenerated charges separated.(à low carrier recombination rate à high photovoltage efficiency).

Contradicting experimental evidence, relevant to ferroelectricity, is based on structural diffraction, electric field vs. polarization plots, second harmonic generation and piezoelectricity measurements . To resolve this debate we first asked if

· the materials are pyroelectric, direct evidence for *spontaneous polarization*, a necessary condition for ferroelectricity.

· polar-domains exist in the structure, as often found in many ferroelectric materials.

Using home-grown, well-characterized single crystals, we find the cubic phases of $MAPbI_3$ (>330K) and $MAPbBr_3$ (>236K) phase to be non-polar, excluding ferroelectricity in them. The tetragonal phase of $MAPbI_3$, however, shows clear evidence of pyroelectricity when probing the potentially-polar, [001], crystallographic orientation, proving its polar nature. By adding low-temperature electric field vs. polarization and room temperature SHG studies and optical observations of polar domains, we arrive at a clear-cut conclusion that MAPbI3 is ferroelectric in the tetragonal phase. I will briefly dwell on the remaining question, i.e., “does that really matter?”.

* work done by Yevgeny Rakita, Dr . David Ehre, Omri Bar-Eli, Elena Meirzadeh, Hadar Kaslasi, Yagel Peleg, with Profs. Gary Hodes, Igor Lubomirsky, Dan Oron, all from the Weizmann Inst.

9:20am **NS+SS+SU-WeM5 NSTD-Recognition Award Talk: Mixed-Dimensional Nanomaterial Heterostructures for Electronic and Energy Applications**, ***Mark Hersam***, Northwestern University **INVITED**

Layered two-dimensional (2D) nanomaterials interact primarily via van der Waals bonding, which has created new opportunities for heterostructures that are not constrained by epitaxial growth. However, it is important to acknowledge that van der Waals interactions are not limited to interplanar interactions in 2D materials. In principle, any passivated, dangling bond-free surface interacts with another via non-covalent forces. Consequently, the emerging layered 2D nanomaterials can be integrated with a diverse range of other materials, including those of different dimensionality, to form van der Waals heterostructures. This talk will explore mixed-dimensional combinations of 2D + n-D (n = 0, 1 and 3) materials, thus significantly expanding the van der Waals heterostructure concept [1]. In order to efficiently explore the vast phase space for mixed-dimensional heterostructures, our laboratory employs solution-based additive assembly [2]. In particular, constituent nanomaterials (e.g., carbon nanotubes, graphene, transition metal dichalcogenides, black phosphorus, and boron nitride) are isolated in solution, and then deposited into thin films with scalable additive manufacturing methods (e.g., inkjet, gravure, and screen printing) [3]. By achieving high levels of nanomaterial monodispersity and printing fidelity, a variety of electronic and energy applications can be enhanced including digital logic circuits [4] and lithium-ion batteries [5]. Furthermore, by integrating multiple nanomaterial inks into heterostructures, unprecedented device function is realized including anti-ambipolar transistors [6], gate-tunable photovoltaics [7], and neuromorphic memristors [8]. In addition to technological implications for electronic and energy technologies, this talk will explore several fundamental issues including band alignment, doping, trap states, and charge/energy transfer across previously unexplored mixed-dimensional heterointerfaces.

[1] D. Jariwala, *et al., Nature Materials*, **16**, 170 (2017).

[2] J. Zhu, *et al., Advanced Materials*, **29**, 1603895 (2017).

[3] J. Kang, *et al., Accounts of Chemical Research*, DOI: 10.1021/acs.accounts.6b00643 (2017).

[4] M. Geier, *et al., Nature Nanotechnology*, **10**, 944 (2015).

[5] K.-S. Chen, *et al., Nano Letters*, **17**, 2539 (2017).

[6] D. Jariwala, *et al., Nano Letters*, **15**, 416 (2015).

[7] D. Jariwala, *et al., Nano Letters*, **16**, 497 (2016).

[8] V. K. Sangwan, *et al., Nature Nanotechnology*, **10**, 403 (2015).

11:00am **NS+SS+SU-WeM10 Magnetron Sputtered Nanostructured TiO_2 Thin Films for Dye Sensitized Solar Cells Applications**, ***Pierre-Antoine Cormier**, J. Dervaux,* ChIPS, University of Mons, Belgium, *Y. Pellegrin, F. Odobel,* CEISAM, University of Nantes, France, *R. Snyders*, ChIPS, University of Mons, Belgium

Among the many advantages of Dye Sensitive Solar Sells (DSSCs), their non-toxic and low cost components, their lightweight and their high performances under diffuse light and high temperatures are very interesting. DSSCs are therefore considered as a promising alternative to conventional Si and chalcogenide based solar cells. In DSSCs, the light is absorbed by dye molecules inducing an electron injection into a TiO_2 nanoparticles (NPs)-based photo-anode. Although this allows a high photon collection, the charge transport is limited by charge recombination at the NPs boundaries limiting the solar to conversion efficiency [1]. Many efforts have been devoted to rule this problem such as replacing NPs by nanofils, nanotubes or hierarchical nanostructured thin films which offer a direct path way to electrons [1]. We previously shown that such hierarchical structure can be obtained by reactive magnetron sputtering (RMS) at grazing incidence which allows to tune the film morphology from slanted nanoculmns, to zigzag or pillars [2].

In this work, such films were synthesized and annealed during 2h at 773 K under atmospheric pressure in order to obtain nanocolumns composed by a single anatase crystal as verified by TEM. These films were used as photo-anode in liquid DSSCs, which were characterized under simulated AM1.5 Global spectrum and 1sun illumination. Different morphologies (slanted columns, zigzag and pillars) and different thicknesses of slanted columns based films were studied. In addition, the dye grafting efficiency on these structures was evaluated by absorbance measurements performed by UV-Visible spectrophotometry.

The slanted columns-based cells present the best performances followed by zigzag and pillar based ones. This result is directly related to the corresponding specific surface area which is the highest for the slanted columns films. By increasing the thickness of the slanted films from 1.2 to 4.3 μm, the cell efficiency increases from 1.2 to 2.6 %. As the short-circuit current density also increased while the open circuit voltage was not affected, it was concluded that the critical parameter limiting the cell efficiency is the adsorbed dye density, which is enhanced for thicker films

To overcome this limitation still using thin films, the slanted columns films were impregnated by TiO_2 NPs (~20nm). This allows for an enhancement of the cell efficiency by 2.2% attributed to a synergetic effect between: (i) a higher dye adsorption and (ii) and the very good charge transport through the single crystalline columns.

[1] A. Hagfeldt et al. "Dye-Sensitized Solar Cells," 2010

[2] J. Dervaux et al., Vacuum, vol. 114, pp. 213–220, Nov. 2014.

11:20am **NS+SS+SU-WeM11 Spectroscopic Evolution of Halide Perovskite Growth on Graphene Oxide Surfaces for Photovoltaics**, ***Muge Acik***, Argonne National Laboratory, *G. Lee,* Ulsan National Institute of Science and Technology, Korea, *R.A. Rosenberg*, Argonne National Laboratory

High power conversion efficiency of perovskite-based solar cells offers promise for low-cost and scalable production of renewable energy. Hybrid organic-inorganic methylammonium lead halides, $MAPbX_3$ (X=I, Br, Cl)/mixed-halides ($I_{3-x}Cl_x$, $I_{3-x}Br_x$) have been reported as light harvesting layers with tunable bandgaps, long electron-hole diffusion lengths and high electron/hole mobility. Nevertheless, halide-based perovskites require *in situ* investigation for film growth mechanisms to overcome detrimental effects of incomplete lead precursor conversion, inconsistent crystallite formation/film uniformity, and weak cation-anion-solvent coordination (1). Graphene-derived hybrids has recently emerged as an ETL/HTL replacement in these devices. Graphene/perovskite structure-property relationships are, however, not well understood due to unclear chemistry at the ETL/perovskite/HTL interfaces (2). Moreover, effect of film thickness, lead content, stoichiometry control, and overlayer/underlayer morphology/composition ought to be examined for better charge transport at the graphene/perovskite interfaces. Stability factors also need to be studied for charge mechanisms to unravel device performance challenges. Indeed, underlayer ETLs (TiO_2/Al_2O_3) and overlayer HTLs (spiro-OMeTAD) were rarely studied with graphene. To address scalability and stability issues, we investigated degradation, nucleation and growth mechanisms in reduced graphene/graphite oxide (RGO) upon halide-based (I, Cl, Br) perovskite deposition. Chemical interactions were interpreted at perovskite/RGO interfaces for the grain size, orientation, boundaries, and surface/bulk effects using variable-temperature (≤600°C, Ar(g)) *in situ* spectroscopy (infrared absorption and micro-Raman). Controlled perovskite formation was achieved at room temperature for bromide-based perovskites resulting in improved chemical stability (vs. iodide/chloride derivative). Perovskite decomposition was observed at ≥150°C on RGO surfaces. Oxygen-induced chemical reactions occurred at ≤150°C, initiated at room temperature because of precursor interactions forming carbonyls upon perovskite deposition (3), and eliminated hydroxyls reducing GO during perovskite growth. Poor perovskite formation was observed on RGO due to varying electron affinity and reactivity of precursor halides, resulting in film degradation in air (O_2, H_2O). Film morphology was explored by SEM, XRD, XPS, AFM, and the reaction mechanisms were studied by first principles calculations that bring insights for solar cell design principles.

Acknowledgement

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11:40am **NS+SS+SU-WeM12 2D Material Laminates for Ultra-fast and Selective Molecular-scale Separation**, ***Saeed Moghaddam***, University of Florida

Due to their intrinsic properties, 2D materials have provided a unique opportunity to develop membranes with ultrafast and highly selective permeation capability. Graphene oxide (GO) is among 2D materials that has garnered significant attention in the past several years and numerous studies have been conducted on transport characteristics of its laminates. However, a comprehensive understanding of the effect of synthesis conditions on physicochemical conditions of GO that dictate transport characteristics of its laminates is lacking. In this study, the effect of oxidation conditions during the synthesis process of GO flakes on transport characteristics of GO laminates are investigated. Transport properties of the GO laminates are observed to be significantly different. It is determined that i) mean-flake size, ii) surface defects, and iii) inter-layer spacing are the key parameters.

The fundamental knowledge gained has been utilized to developed membrane separators for energy and water applications. To enhance performance of DMFCs, it was determined that at a constant oxidation level methanol permeability decreases linearly with increasing the GO mean flake size while changes in proton conductivity remain insignificant. This behavior is attributed to difference in adopted conduction pathways of protons and methanol molecules. With increasing the oxidation level, proliferation of surface defects is deductively reasoned to be the dominant factor responsible for a large increase in the measured methanol permeability. The proton conductivity is also significantly increased with increasing the oxidation level because of greater number of ion exchange sites, shortened transport pathway and increased GO flakes inter-layer spacing. The observed transport characteristics are attributed to either different adopted conduction pathways or surface mobility of protons and methanol molecules. The findings imply that the GO nanoplatelets contain atomic formations that are more selective to protons than to methanol molecules.

We have also utilized the superior water selective transport properties of GO laminates as filtration membranes for Endocrine Disrupting Compounds (EDCs) with high permeate flux rates. A layer-by-layer (L-b-L) approach was utilized to prepare thin film composite membranes with a polymer support and a few layers of GO interlinked via poly(allylamine hydrochloride) (PAH). The prepared membrane showed a fourfold increase in the permeate flux in comparison to the commercially available nanofiltration (NF) membranes. The rejection performance of the membrane was evaluated by studying the permeation of ibuprofen and a rejection rate of 75% was obtained.

Plasma Science and Technology Division
Room: 22 - Session PS+NS+SS-WeM

Plasma Processing for Nanomaterials & Nanoparticles
Moderators: Hisataka Hayashi, Toshiba, Japan, Kazunori Koga, Kyushu University, Japan

8:00am **PS+NS+SS-WeM1 Plasma Catalysis: a Powerful Blend of the Four States of Matter**, ***Kostya (Ken) Ostrikov***, Queensland University of Technology and CSIRO, Australia **INVITED**

Plasma catalysis is a rapidly emerging multidisciplinary field at the interface of catalysis, nanotechnology, physical chemistry, materials and plasma science. Relevant applications include plasma-assisted catalytic reforming of gas mixtures into fuels, chemicals and synthesis of functional nanomaterials. Plasma-specific effects play a major role in nanoscale catalytic phenomena. The process outcomes are improved when catalysts with nanometer-scale surface features are used along with atmospheric-pressure plasmas (APPs). It is possible that plasmas and catalysts act synergistically.

I will review the APP interactions with the nanometer-size features on the surface of catalyst nanoparticles (NPs). Basic understanding of plasma-catalyst interactions is achieved through nd the effects of these modified surfaces on catalytic reactions. Nanoscale interactions of APPs with the NPs and synergistic effects are related to plasma modifications of catalyst structure and reactivity. The synergistic effects may increase the yield and selectivity of catalytic reactions of importance to chemical and energy resource industries.

The focus is on gas mixtures relevant to natural reforming or hydrogen production by water splitting. The selected nanomaterials catalyze the conversion of the above gas mixtures into higher-value products such as synthetic gas (syngas), hydrogen, fuels, etc. of demand in a variety of industrial applications (e.g., methanol production). The plasmas induce "epigenetic" modifications of catalytic materials and the plasma process parameters are customized to maximize both the conversion rates and the process gas flow, i.e., both the outcome (selectivity) and the productivity (rates) of the gas conversion.

I will discuss the most effective nanoscale plasma-surface interactions. The focus will be on surface modifications (e.g., functionalization, expression of crystal facets, changes in reactivity of near-surface atoms, oxidation or reduction states, etc.) of localized surface areas induced by the nanoscale plasma-surface interactions and chemical reactions. The plasma effects enhance reactivity of the "epigenetically" modified surface areas of the NPs. The expected effects include better adsorption, higher conversion rates of reactant species on the modified surfaces, larger surface areas for reactions, higher catalytic activity through more effective electron transfer, reduced reaction activation barriers, photon- and ion-assisted reactions, new plasma-enabled reaction pathways, etc.

8:40am **PS+NS+SS-WeM3 Vaporization of Nanoparticles in Low Temperature Plasmas**, ***Necip Berker Uner***, *E. Thimsen*, Washington University in St. Louis

Particle nucleation is a major problem that occurs in many thin film processing plasmas. The resultant "killer particles" can create defects upon deposition on the film and they can consequently decrease device functionality. A change of perspective, within the last two decades, the aptness of low temperature plasmas (LTP) for particle nucleation has been successfully exploited to synthesize monodisperse, free standing, spherical and crystalline semiconductor nanocrystals from vapor precursors. These impressive properties of particles synthesized in LTPs stem from particle charging and ion bombardment. When the particle number density is smaller than the ion density, it is proposed that the particles experience unipolar charging. The negative charge acquired by the particles suppresses coagulation and leads to uniform growth. On the other hand, ion bombardment elevates particle temperatures above the surrounding gas temperature and provides crystallinity. By using LTPs, nanocrystals of silicon, germanium, various oxides, sulfides and compound semiconductors of high quality have been produced, whereas production of metal particles were less successful, which indicates incomplete understanding.

In this study, we focus on the interaction between the plasma and metal nanoparticles. In an environment free of vapor precursors, we demonstrate that particle growth in LTPs follows a reversible path. Instead of continuous growth, ion bombardment can lead to extensive vaporization, depending on the plasma density and vapor pressure. By sending in a premade aerosol of bismuth particles through a capacitively coupled radio frequency argon plasma, we observed complete vaporization of the metal at moderate power inputs. Interestingly, at low power inputs, vaporization resulted in significant restructuring of the particle size distribution. Polydispersed size distributions were transformed into monodispersed distributions, with relatively high mass yields reaching 65%. Based on spatial Langmuir probe measurements and detailed aerosol dynamics modelling, we propose that upon exposure to different plasma densities, particles can vaporize and then the resultant vapor can either nucleate into particles or recondense on the remaining clusters, eventually leading to the modification of the size distribution. When particles vaporize completely and the vapor is conserved, the result is the conversion of a polydispersed size distribution into a monodispersed size distribution. This unusual mechanism that involves vaporization at low temperature will be detailed with further experimental observations with different materials. Methods of tuning the final size will be elaborated.

9:00am **PS+NS+SS-WeM4 Nanowires, Trusses and Pillars Produced by Assembly of Plasma Generated Nanoparticles**, ***Ulf Helmersson***, *S. Ekeroth, S. Askari, R. Boyd, N. Brenning*, Linköping University, Sweden

Nanoparticles generated or supplied to a plasma attains a negative potential due to the nature of the plasma. This open up interesting possibilities in synthesis and assembly of the nanoparticles creating structures in the nano- and micro-range. In this work, we use hollow cathode sputtering powered with high-power pulse to ensure close to full ionized of the source material. This promotes rapid growth of the nanoparticles to desired sizes and the negative charge makes it possibility to guide nanoparticles for assembly and collection on desired positions. This is demonstrated by attracting nanoparticles to substrate positions with a positive potential and focusing nanoparticles through a matrix of electrostatic lenses to assemble the nanoparticles into pillars. For ferromagnetic nanoparticles, we also demonstrate generation of nanowires as well as nanowires cross-linked into trusses. Since the iron nanoparticles are generated under relatively pure condition they assemble into wires without oxides in the interfaces. Nanowires and trusses assembled on conducting substrates can potentially be used as low cost large area electrodes.

9:20am **PS+NS+SS-WeM5 Non-Equilibrium Plasmas for Nanoparticle Synthesis: from Semiconductors to Metals**, ***Rebecca Anthony***, Michigan State University **INVITED**

Nonthermal plasmas have been increasingly popular for synthesis of nanocrystals. Generally, these flow-through reactors are radiofrequency (RF) plasmas operated at reduced pressure (2-10 Torr) into which vapor-phase precursors are entrained. The nanocrystals form following dissociation and clustering of the precursor molecules. Among the advantages offered by plasma reactors are low-temperature environment, avoidance of liquid-phase reactants, tunable nanocrystal properties via reactor parameters, and scalability. In addition, the nanocrystals can be collected as powders for post-processing, or directly impacted onto substrates in thin-film form, sidestepping the need for additional steps such as spin- or drop-casting. Combined with the solvent-free, low-temperature, all-gas-phase nature of nonthermal plasma reactors, this opens the door to direct incorporation of nanocrystals into functional layers on arbitrary substrates - without concern about solvent orthogonality or thermal susceptibility.

Here we present our work focusing on exploiting the non-equilibrium of plasma reactors for high-quality nanocrystal growth. First we discuss silicon nanocrystals for optical applications. The properties of these nanocrystals, such as size, crystallinity, and surface, can be altered in-flight using the plasma reactor parameters - and they can be inertially impacted onto a variety of substrates. These nanocrystals exhibit efficient and tunable photoluminescence, and we have deployed them in LEDs, luminescent layers on stretchable substrates, and as sensitizers for pollutant photodegradation. The non-equilibrium environment of the plasma also allows growth of even higher-melting-point nanocrystals, and we will share our work on GaN nanocrystal growth using plasma reactors. These freestanding nanocrystals are size-tunable and have excellent crystal quality despite GaN having a bulk melting temperature of 2500°C. Finally, we will discuss formation of metal nanoparticles in the plasma using an altered-geometry RF plasma with a central consumable ground electrode, working towards expanding the range of optoelectronically functional nanomaterials that can be made using nonthermal plasmas.

11:00am **PS+NS+SS-WeM10 Photochemical Insulator-Metal Transition in Plasma-Synthesized ZnO Nanocrystal Networks**, ***Benjamin Greenberg***, *Z. Robinson, K. Reich*, University of Minnesota, *C. Gorynski*, University of Duisburg-Essen, Germany, *B. Voigt*, University of Minnesota, *G. Nelson*, Creighton University, *L. Francis, B. Shklovskii, E.S. Aydil, U.R. Kortshagen*, University of Minnesota

Nonthermal plasma synthesis has recently emerged as a promising method for producing highly conductive ZnO nanocrystal (NC) networks. The plasma-synthesized NC surfaces are free of ligands, which enables high interparticle electron mobility. In this work, we produce ZnO NC networks using nonthermal plasma synthesis integrated with supersonic inertial impaction deposition, and we manipulate their electron transport properties with a combination of UV illumination and NC surface modification via atomic layer deposition (ALD). Specifically, we use these treatments to increase the free electron density, n, and the interparticle contact radius, ρ, and thereby induce a transition from variable range hopping to metallic transport. We determine n from the NCs' localized surface plasmon resonance (LSPR) and ρ from the subtle increase in the ZnO volume fraction, and we use Fourier transform IR spectroscopy (FTIR) to ascertain the underlying NC surface photochemistry.

11:20am **PS+NS+SS-WeM11 Elucidating Energetic Trends in Hydrocarbon Plasma Systems for Plasma-Assisted Catalysis**, ***Tara Van Surksum***, *E.R. Fisher*, Colorado State University

Plasma-assisted catalysis (PAC) has been investigated as a promising method for pollution control, specifically for conversion or removal of volatile organic compounds. The utility of PAC is severely limited by an overall lack of understanding of plasma chemistry and the reactions occurring at the plasma-catalyst interface. The present work focuses on investigating fundamental gas-phase chemistry in hydrocarbon inductively-coupled plasma systems to understand energy partitioning in PAC systems for decomposition of volatile organic compounds. We have employed broadband absorption and optical emission spectroscopies to determine rotational and vibrational temperatures (T_R and T_V, respectively) for multiple species (e.g., CH, C_2) in a variety of hydrocarbon-containing plasma systems. For example, in CH_4 plasmas, T_V(CH) ranges from ~3000 to ~5000 K, whereas T_R(CH) generally reaches values ranging from 1000-2000 K. Energy partitioning for the same species has also been assessed when a catalytic material (e.g., flat and nanostructured SnO_2 and TiO_2, micro-structured zeolites) is placed in the plasma. In some cases, the substrate has a measureable effect on the gas-phase chemistry, whereas in others the substrate does not appreciably alter the gas-phase of the plasma. Catalytic material properties were also evaluated via surface analysis tools (e.g., X-ray photoelectron spectroscopy, scanning electron microscopy, and Fourier transform infrared spectroscopy) and will be presented in conjunction with energy partitioning data to further elucidate information on the molecular-level processes occurring at the plasma-catalyst interface. Collectively, these data aim to unravel the complex chemistry of hydrocarbon plasma systems for PAC to achieve a viable method of pollution control.

11:40am **PS+NS+SS-WeM12 Synthesis of Metal Nanoparticle Electrocatalysts for Fuel Cell Applications by Atmospheric-Pressure Plasma Reduction**, ***Joffrey Baneton****, Université Libre de Bruxelles, Belgium, *Y. Busby,* Université de Namur, Belgium, *W. Debouge,* Université Libre de Bruxelles, Belgium, *G. Caldarella,* Université de Liège, Belgium, *J.-J. Pireaux,* Université de Namur, Belgium, *V. Debaille,* Université Libre de Bruxelles, Belgium, *N. Job,* Université de Liège, Belgium, *M.J. Gordon,* University of California at Santa Barbara, *R.M. Sankaran,* Case Western Reserve University, *F. Reniers*, Université Libre de Bruxelles, Belgium

Nanoparticles composed of one or more metals particularly platinum (Pt) are used as electrocatalysts in hydrogen fuel cells for the cathodic reduction of dioxygen [1]. Several challenges remain in their synthesis including controlling their morphological features (e.g. size, shape, etc.), maximizing the amount of Pt exposed while minimizing the overall amount of the expensive metal, and eliminating the presence of organic capping groups or other contaminants that cover the active surface.

Here, different atmospheric plasma devices including a microplasma and a radio-frequency (RF) plasma torch are shown to be capable of producing Pt and Pt-based alloy nanoparticles without any organic capping molecules and minimal chemical additives. The as-synthesized nanoparticles are characterized by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) to assess their chemical purity and morphology. We find that when using the microplasma to reduce a Pt precursor in solution, small and non-agglomerated Pt nanoparticles can be directly produced in liquid phase (organic or water based). By controlling the initial amount of the Pt precursor dissolved in solution and the charge injected in the system, the nanoparticle concentration can be tuned [2]. Moreover, this methodology can be applied to bimetallic alloys to reduce the amount of Pt in the electrocatalyst.

In comparison, when using a RF plasma torch, Pt nanoparticles can be produced in the solid phase by plasma reduction of a Pt precursor dispersed on the surface of a carbon support (carbon black, carbon xerogel, carbon nanotubes or graphene) [3]. A mechanism for the plasma reduction of Pt is proposed. It is shown that the size distribution of the particles, their dispersion at the surface, and their quantity in the bulk determined by inductively coupled plasma mass spectrometry (ICP-MS), can be fully controlled by the plasma and preparation parameters.

The Pt nanoparticles synthesized by either method are finally used to fabricate the cathode of a proton exchange membrane fuel cell (PEMFC) using a gas diffusion layer as a substrate. The cell performance, represented by the ratio of the electrochemically active surface area (ECSA) and the catalytic activity, which are comparable to commercial cells, will be discussed in detail.

[1] H.A. Gasteiger et al. *In*: W. Vielstich, A. Lamm and H.A. Gasteiger (eds.), Handbook of Fuel Cells – Fundamentals, Technology and Applications, Wiley, Chichester (UK), **2003**, Vol.3, p. 593.

[2] C. De Vos et al. *J. Phys. D: Appl. Phys.* (**2017**), 50, 105206.

[3] D. Merche et al. *Plasma Process. Polym.* (**2016**), 13, 91–104.

12:00pm **PS+NS+SS-WeM13 Microplasma Spray Deposition of Metal Oxide Nanostructures for Energy Applications**, ***Katherine Mackie***, *M.J. Gordon*, University of California at Santa Barbara

A general, substrate-independent method for plasma deposition of nanostructured, crystalline metal oxides is presented. The technique uses a flow-through, micro-hollow cathode plasma discharge (supersonic microplasma jet) with remote anode to deliver a highly-directed flux of growth species to the substrate. A diverse range of nanostructured materials (e.g., CuO, α-Fe_2O_3, and NiO) can be deposited on any room temperature surface, e.g., conductors, insulators, plastics, fibers, and patterned surfaces, in a conformal fashion. The effects of deposition conditions, substrate type, and patterning on film morphology, nanostructure, and surface coverage will be highlighted. Energy storage application examples to be discussed include NiO on carbon for supercapacitors and CuO for conversion-type Li-ion batteries. The synthesis approach presented herein provides a general and tunable method to deposit a variety of functional and hierarchical metal oxide materials on many different surfaces.

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* **Coburn & Winters Student Award Finalist**

2D Materials Focus Topic
Room: 16 - Session 2D+EM+MN+NS-WeA

2D Device Physics and Applications
Moderator: Humberto Gutierrez, University of South Florida

2:20pm **2D+EM+MN+NS-WeA1 Capacitance-voltage Characteristics of Graphene-gate MOS Devices: The Effect of Graphene Quantum Capacitance**, ***Ruixue Lian***, *A. Ural*, University of Florida

There has been significant research interest in graphene for electronics applications, due to its good electrical conductivity, high optical transparency, mechanical flexibility, and two-dimensional structure. However, the potential of graphene as a channel material replacing silicon is limited due to the absence of a bandgap. On the other hand, graphene is an excellent candidate as a transparent, conductive, and flexible electrode for electronic and optoelectronic devices.

Unlike conventional metals, whose Fermi level is typically pinned at the surface, the Fermi level and hence workfunction of graphene can be tailored by electrostatic gating, chemical doping, or surface engineering. As a result, graphene is also a promising candidate as the gate electrode in metal-oxide-semiconductor (MOS) devices, particularly when transparency or workfunction tunability is a requirement.

In real graphene sheets, charged impurities cause electron-hole puddles and random local electrostatic potential fluctuations (statistically described by a Gaussian distribution), which leads to a modified density of states (DOS). In this work, using this modified DOS, we numerically compute the quantum capacitance of graphene as a function of the graphene electrostatic potential at different temperatures and strengths of the potential energy fluctuations. We compare the exact results to various approximations made in the literature when fitting experimental data. We find that the largest discrepancy between the exact results and the approximations occurs near the Dirac point.

In capacitance-voltage (C-V) characterization of graphene-gate MOS devices, what is measured is not the quantum capacitance versus the graphene potential, but the total gate capacitance versus the gate voltage. We numerically compute the gate voltage as a function of the graphene potential and the resulting C-V characteristics at different temperatures, strengths of the potential energy fluctuations, and equivalent oxide thicknesses. We also consider the effect of series and parallel parasitic impedance to the overall shape of the C-V curves. Furthermore, we numerically compute the full C-V characteristics at different values of the equivalent oxide thickness, silicon doping density, and Dirac voltage of graphene. Finally, we fit our recent experimental C-V data with these theoretical calculations to extract the strength of the potential energy fluctuations and the parasitic impedances.

These results provide important insights into the effect of the graphene quantum capacitance on the C-V characteristics of MOS devices and the potential of graphene as a gate electrode in future MOS technology.

2:40pm **2D+EM+MN+NS-WeA2 *in-situ* Electrical Characterization of Surface Functionalization and Gate Dielectric Deposition Processes on 2D Transition Metal Dichalcogenides Transistors**, ***Antonio T. Lucero***, *J.B. Lee, L. Cheng, H.S. Kim, S.J. Kim, J. Kim*, University of Texas at Dallas

Two-dimensional transition metal dichalcogenide (TMD) materials are a subject of intense research for use as future, low-power semiconductors. The successful fabrication of TMD based transistors requires a scalable dielectric deposition process. Atomic layer deposition (ALD) is commonly used to grow high-k gate dielectrics, though deposition of thin, pin-hole free dielectrics is challenging due to the chemically inert basal plane of most TMD materials. To overcome this limitation, surface functionalization processes have been developed to improve ALD nucleation.

In order to elucidate the effects of surface functionalization and subsequent ALD on the electrical characteristics of TMD transistors we use an *in-situ* electrical characterization system to measure the electrical properties of TMD transistors at various steps during the deposition process. MoS_2 backgated transistors are loaded into an ultra-high vacuum (UHV) cluster tool where samples can be transferred under UHV conditions between various chambers. The cluster tool is equipped with a thermal ALD chamber, a hollow cathode plasma enhanced ALD chamber, a plasma enhanced chemical vapor deposition chamber, and a UHV electrical probe station. Results for ozone, nitrogen radical, and nitrogen plasma functionalization will be presented. The effect of surface dipoles, precursor adsorption and coverage, and nucleation during the ALD process will be discussed as they relate to the electrical characteristics of the device.

This work was supported by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST, and by NRF (No. 2015M3D1A1068061) in Korea. We thank TMEIC for providing the ozone generator and nitrogen radical generator used in this work.

3:00pm **2D+EM+MN+NS-WeA3 High-K Gate oxide by Low Temperature ALD Technique for 2D Materials and Inert Metal Surfaces**, ***Il Jo Kwak***, *J.H. Park*, University of California at San Diego, *S. Fathipour, A. Seabaugh*, University of Notre Dame, *C.S. Pang, Z. Chen*, Purdue University, *A.C. Kummel*, University of California at San Diego

2D materials such as TMDs(Transition Metal Dichalcogenides), Graphene and BN have attracted great attention as new channel materials for future devices due to their excellent electronic and optical properties. For such devices, sub nanometer thick and defect free gate oxide is an essential part. However, due to the inert surface of the materials, high K oxide such as Al_2O_3 and HfO_2 selectively nucleates on defect sites or step edges. Therefore, for successful integration, preparation of uniform and insulating gate oxides are a matter of importance. In this study, Al_2O_3 was deposited on 2D materials surface by low temperature ALD using trimethylaluminum(TMA) and H_2O without any seeding layer or surface treatments. Using short purge time between two precursor pulses at 50C, a CVD component was induced to provide uniform nucleation sites on the surface. The CVD component generates subnanometer AlOx particles[s1] [file:///C:/Users/kwak1/Downloads/2017_AVS_abstract_bilayer_oxide.docx#_msocom_1] on the surface which provide uniform nucleation sites. In order to obtain lower EOT layer, 10 cycles of Al_2O_3 ALD was deposited at 50C as a seeding layer and 40 cycles of HfO_2 ALD was deposited with Tetrakis(dimethylamido)hafnium (TDMAH) and H_2O at 250C. The same oxide was deposited on a SiGe substrate to compare the oxide characteristics. After ALD, MOSCAPs were fabricated to measure electrical properties. AFM measurement revealed that uniform and defect free oxide layers were nucleated on the surfaces. Capacitance-voltage measurement showed that Cox of the bilayer oxide was 2.5 uF/cm2 and the gate leakage current of the oxide was about 10^{-5} A/cm^2 which was comparable to the oxide on a SiGe substrate. Identical bilayer oxide layer was deposited on a dual gated WSe_2 FETs . Top gate oxide leakage of the device was about 10^{-6} A/ cm2. In order to assess the quality of the oxide, a benchmarking study of current density versus EOT of 2D semiconductor FET devices and Si based devises was investigated. The study showed that record-low EOT (1.2 nm) and leakage current (10^{-8} μA/ μm^2) comparable to the best Si devices with La_2O_3 gate oxide by Iwai *et al* was achieved by the WSe2 FET. This technique was also applied to initiate nucleation[s2] [file:///C:/Users/kwak1/Downloads/2017_AVS_abstract_bilayer_oxide.docx#_msocom_2] on inert metal surfaces which are important for logic memory devices including selectors. Using the bilayer oxide, insulating oxide was prepared on Au electrodes of a MOSFET device. The leakage current of the oxide was as low as 10^{-7} A/ cm^2.

3:20pm **2D+EM+MN+NS-WeA4 Exploration and Comparison of Optoelectronic Properties of MoS_2 Monolayers with Multilayer Flakes and $Mo_xW_{1-x}S_2$ Ternary Compounds**, ***Sourav Garg***, *J. Waters, A. Mollah, S. Kim, P. Kung*, University of Alabama

2D transition metal dichalcogenide (TMDC) semiconductors, including MoS_2, WS_2, and more recently ternary compounds, exhibit exceptional structural, electrical and optical properties that make these materials of great interest for nano-optoelectronic devices. For example, unlike graphene, TMDCs have a bandgap, which has the remarkable characteristic of becoming direct when the material is in monolayer form, while it is indirect when the material is composed of multiple layers.

Here, we report the synthesis of monolayer MoS_2, WS_2, ternary $Mo_xW_{1-x}S_2$ ternary compounds and MoS_2/WS_2-based heterostructures, by chemical vapor deposition (CVD) process at temperatures in the range 950-1000 C, without the use of seeds to avoid contamination. The material was extensively characterized using micro-Raman spectroscopy, micro-photoluminescence, and electron microscopy.

Using such large area CVD grown materials, large-area MoS_2 photoconductive detector devices were fabricated using conventional photolithography to realize of interdigitated metal fingers. The electrical and spectral photoresponse from monolayer and multilayer MoS_2 have been compared, in terms of responsivity and specific detectivity. The monolayer devices exhibited high photoconductive gain and detectivity near 10^{12} Jones, which was also found to be higher than in the case of multilayer MoS_2 devices. The rise and decay time of passivated monolayer devices was investigated and shown to be much faster than the unpassivated devices.

4:40pm **2D+EM+MN+NS-WeA8 Dielectric Properties of Carbon Nanomembranes prepared from aromatic Self-Assembled Monolayers investigated by Impedance Spectroscopy**, ***Paul Penner****, E. Marschewski, X. Zhang,* Bielefeld University, Germany*, T. Weimann, P. Hinze,* Physikalisch-Technische Bundesanstalt, Germany*, A. Beyer, A. Gölzhäuser*, Bielefeld University, Germany

Carbon nanomembranes (CNMs) are two-dimensional materials made by cross-linking self-assembled monolayers (SAMs) of aromatic molecules via low energy electron irradiation. Previous study of molecular junction incorporating SAMs and CNMs of oligophenyl thiols has been carried out by using conical eutectic Gallium-Indium (EGaIn) top-electrodes[1] and conductive probe atomic force microscopy (CP-AFM). Here we investigate the dielectric properties of pristine SAMs and CNMs with an EGaIn top electrode by impedance spectroscopy. Analysis and comparison of the tunneling resistance and capacitance density of pristine and cross-linked SAMs revealed a thickness dependent capacitance associated with the monolayer as well as a thickness independent capacitance. We adopted an equivalent circuit to take into account the contribution of the interfacial capacitance as well as the oxide layer of the EGaIn top electrode. The obtained tunneling decay constant remains unaffected after electron irradiation, which exhibits a value of about 0.5 $Å^{-1}$ for both systems. A determination of dielectric constants of SAMs and CNMs from the impedance spectra will also be analyzed and discussed. Furthermore we characterize stacks of CNMs sandwiched with graphene and other 2D materials.

[1] P. Penner, X. Zhang, E. Marschewski, et. al, J Phys Chem C 2014, 118, 21687.

5:00pm **2D+EM+MN+NS-WeA9 2D Crystals for Next-Generation Ultra Energy-Efficient Electronics**, ***Kaustav Banerjee***, University of California at Santa Barbara **INVITED**

I will highlight the prospects of two-dimensional (2D) materials for innovating energy-efficient transistors, sensors, and interconnects targeted for next-generation electronics needed to support the emerging paradigm of the *Internet of Things*. More specifically, I will bring forward a few applications uniquely enabled by 2D materials and their heterostructures that have been demonstrated in my lab for realizing ultra-energy-efficient electronics. This will include the world's first 2D-channel band-to-band tunneling transistor that overcomes a fundamental power consumption challenge in all electronic devices since the invention of the first transistor in 1947 (Nature 2015), as well as a breakthrough interconnect technology based on doped-graphene-nanoribbons, which overcomes the fundamental limitations of conventional metals and provides an attractive pathway toward a low-power and highly reliable interconnect technology for next-generation integrated circuits (Nano Letters 2016). I will also bring forward a new class of ultra-sensitive and low-power sensors as well as area-efficient and high-performance passive devices, both enabled by 2D materials, for ubiquitous sensing and connectivity to improve quality of life.

Applied Surface Science Division
Room: 13 - Session AS+2D+NS+SA-WeA

2D, 3D and nD Imaging of Surfaces, Buried Interfaces and Nanostructures

Moderators: Michael Brumbach, Sandia National Laboratories, Kathryn Lloyd, DuPont

2:20pm **AS+2D+NS+SA-WeA1 Laser-SNMS Imaging of Organic and Biological Systems in Two and Three Dimensions.**, ***Bonnie June Tyler****, A. Pelster, M. Heeger, H.F. Arlinghaus*, Universität Münster, Germany

The introduction of commercial large argon gas cluster ion sputter sources has enabled routine molecular depth profiling and 3D imaging of organic materials with ToF-SIMS. 3D molecular imaging has been demonstrated for a wide variety of organic and biological systems. Despite these advances, sensitivity and quantitation continue to limit applications of the technique for many important systems such as pharmaceuticals. Laser post-ionization of sputtered neutral species is one potential solution to the problems of both low sensitivity and matrix effects.

In this work, we have compared ToF-SIMS and Laser-SNMS for 2D and 3D imaging of several organic systems, including biological samples, pharmaceuticals, and polymeric materials [1-3]. Sample analysis and sputtering were performed using combinations of Bi_3^+ and Ar_n^+ ions. Laser post-ionization was performed using either a 157 nm excimer laser or a 195 nm excimer laser. For organic molecules, superior results are obtained using the shorter wavelength laser at lower power density whereas higher power density with the longer wavelength laser is superior for elemental analysis. Increases in ion yield of as much as 4 orders of magnitude have been observed for both elemental and molecular species.

ToF-SIMS and Laser-SNMS show complementary strengths. For high intensity ion signals, ToF-SIMS allows for faster data acquisition. Laser-SNMS, on the other hand, reduces artefacts from topography and matrix effects and enhances measurement efficiency. Higher efficiency reduces the amount of matter that must be sputtered to obtain a given signal, which facilitates measurement of lower concentrations with higher ultimate spatial resolution.

[1] Nees, R.et al., Biointerphases, 2016. 11(2): p. 02A305.

[2] Pelster, A., et al., Analytical Chemistry, 2016. 88(19): p. 9638-9646.

[3] Pelster, A., et al., Biointerphases, 2016. 11(4): p 041001.

2:40pm **AS+2D+NS+SA-WeA2 Distribution of Surfactants and Polymer in a Coating using GCIB-SIMS**, ***Michaeleen Pacholski****, Z. Qu, W. Ouyang*, The Dow Chemical Company

Water-based coatings are commonly composed of a latex polymer with additional formulation ingredients such as surfactants, defoamers, etc. The distribution of the additives can have a large role in product performance affecting properties such as adhesion, gloss, water whitening, cohesion, etc. Using GCIB-SIMS profiling the distribution of the additives throughout a film can be shown to relate to the particle size and expected film formation theoretical results. The data from this study show, for the first time, that polymer, surfactant and salts can be monitored as a function of film depth with superior sensitivity and specificity to previous literature studies.

3:00pm **AS+2D+NS+SA-WeA3 Correlation of Morphological and Hyperspectral Characterization Techniques for Nanoelectronic and Energy Applications**, ***Jean-Paul Barnes****, A. Priebe, G. Goret, I. Mouton, A. Grenier, G. Audoit, P. Bleuet, Y. Mazel, E. Nolot,* Univ. Grenoble Alpes, CEA, LETI, France*, S. Legendre, A.L. Tempez*, Horiba France S.a.s., France*, R. Estivill, M. Juhel,* STMicroelectronics, France*, S. Duguay, F. Vurpillot, D. Blavette*, Normandie Univ, UNIROUEN, INSA Rouen, CNRS, Groupe de Physique des Matériaux, France **INVITED**

The integration of a growing variety of materials in increasingly complex structures drives the need to correlate characterization techniques. In this presentation we will discuss the advantages of correlating pairs of techniques such as focused ion beam-time of flight-secondary ion mass spectrometry (FIB-TOF-SIMS) and X-ray computed nanotomography (CNT); atom probe tomography (APT) and electron tomography (ET); and TOF-SIMS depth profiling and plasma profiling time-of-flight mass spectrometry (PPTOFMS).

FIB-TOF-SIMS tomography extends the capacity of TOF-SIMS instruments to analyze large heterogeneous samples of several tens of microns in size as well as porous samples or those with strong surface topography. Standard depth profiling is often not possible as the depth scale information is rapidly lost in such samples. Examples include copper pillars used in 3-D integration in nanoelectronics and solid oxide fuel cells (SOFCs) which have a complex porous multilayer (sandwich) structure. Whilst FIB-TOF-SIMS provides unique information on the sample chemical composition, there may be morphological artefacts such as curtaining. These may be identified and corrected by analyzing the sample beforehand by X-ray CNT in an SEM. We have developed a method to analyze the same object by both techniques by using novel sample preparation protocols [1].

The correlation of morphological with hyperspectral data can also be applied to APT and ET. APT is increasingly used for the analysis of semiconductor devices because of its unique ability to measure composition in 3D at the atomic scale with high sensitivity. However the APT data sets are often distorted and care must be taken in quantifying composition. The morphological information obtained from analyzing the APT tip beforehand by ET can be used to optimize the parameters when reconstructing the APT data.

PPTOFMS is a rapid depth profiling technique that uses a plasma to etch away the sample and analyze the composition as a function of depth. Unlike SIMS based techniques, the ionization takes place in the plasma and the ratio of ions extracted from the plasma is directly representative (within a factor of 2-3) of the sputtered sample composition. However, the sensitivity and depth resolution are worse than for TOF-SIMS. Combining PPTOFMS with TOF-SIMS depth profiling enables the standard-free quantification and rapid sample screening capabilities of the PPTOFMS to be combined with the sensitivity and high depth and lateral resolution of TOF-SIMS [3].

[1] A. Priebe et al. Ultramicroscopy. 173 (2017):10-13.[2] A. Grenier et al APL 106, 213102 (2015). [3] A. Tempez et al., J. Vac. Sci. Technol. B (2016) 34

4:20pm **AS+2D+NS+SA-WeA7 Insights into Corrosion and Radiation Damage Processes Through 2D and 3D Imaging at the Nanoscale**, ***Karen Kruska**, D.K. Schreiber, D.J. Edwards, Z. Zhai, M.J. Olszta, I. Arslan, M.A. Conroy, C. Wang, R.J. Kurtz, S.M. Bruemmer*, Pacific Northwest National Laboratory **INVITED**

There is an increasing demand for characterization of materials for nuclear reactors with advanced microscopy techniques. Intelligent materials selection requires a fundamental mechanistic understanding of environmental and irradiation damage processes at the nanoscale.

Current and future nuclear power generating systems require materials that can withstand extreme environments. Long-term resistance to environmental degradation is critical for light water reactors as evidenced by stress corrosion cracking concerns in structural alloys for both primary and secondary systems. Resistance to radiation damage further challenges material selection in current and advanced reactors with unique issues for plasma facing components in tokamak-style fusion energy systems where materials must tolerate extended neutron (14 MeV) and He$^+$ ion (3.5 MeV) irradiation at extreme temperatures (up to 1300 K). Accumulation of metallic fission products in LWR fuels may cause cracking and has been linked to cladding erosion.

2D analytical electron microscopy techniques have and continue to provide key insights into the evolution of local microstructure and chemistry. More recently, these traditional 2D imaging techniques have been complemented by novel 3D imaging methods, including serial sectioning using a focused ion beam, electron tomography and atom probe tomography. When paired with 2D imaging methods, the 3D microscopy provides deeper insights into the hierarchy of the degradation and damage processes, improved statistical relevance and a greater sensitivity to highly localized effects that were not apparent from 2D imaging alone. Going one step further, dynamic processes (such as oxidation and vacancy injection) can be directly imaged by in situ and operando techniques in transmission electron microscopy. Each technique has its own set of strengths and weaknesses, and in this talk we will emphasize how combining these complementary techniques provides a more comprehensive understanding of material degradation than could be obtained from any individual imaging method.

5:00pm **AS+2D+NS+SA-WeA9 XPS Spectroscopic Imaging of 2D-Materials**, ***Olivier Renault***, CEA-Leti, France, *H. Kim,* EPFL, France, *D. Ferrah,* UCI, France, *N. Fairley,* Casa Software, France, *M. Gay,* CEA-Leti, France, *M. Frégnaux,* UVSQ, France, *A. Kis*, EPFL, France

The recent advent of two dimensional semi-conducting materials of the post-graphene era, such as transition-metal dichalcogenides (TMDs- such as MoS$_2$, WSe$_2$, …) has amplified the need for advanced analytical diagnostics. One of the main issues to tackle are directly related to the atomically-thin character of the samples, first concerning the low elemental concentrations and second, the invasive character of most of the characterization techniques implemented. As a photon-probe technique, XPS has a key role to play in the analysis of TMDs but highly sensitive and versatile microscopic capabilities are needed: this is because the physics of TMDs, notably the indirect-to-direct band gap transition in the monolayer limit, requires spatially-resolved information not only on the chemical composition but also on the electronic band structure. Short analysis times are required because a screening of these properties depending on processing conditions (at the material or the device level) is needed. PEEM-based instruments are the only class of XPS microscopes able to offer both type of analysis. In this presentation, we will review recent studies of 2D materials using XPEEM for chemical imaging and *k*PEEM for band structure imaging, with a particular emphasis on instrumental requirements (excitation source, transmission and detection) and post-processing of the 3D spectroscopic image data sets. The examples will range from graphene doping [1] and cleaning [2], to single layer MoS$_2$ [3-4], including also novel materials and 2D heterostructures.

This work was performed at the Platform For Nano-Characterization of CEA-MINATEC.

[1] H. Kim, O. Renault *et al*., *Appl. Phys. Lett*. **105**, 011605 (2014).

[2] M. Frégnaux, O. Renault *et al*., Surf. Interface Anal. **2016**, 48, 465-469.

[3] D. Ferrah, O. Renault et al., Surf. Interface Anal. **2016**, 48, 451-455.

[4] H. Kim, M. Frégnaux, A. Kis, O. Renault, *et al*., *Phys. Rev.* B **34**, 081401 (R) (2016).

5:20pm **AS+2D+NS+SA-WeA10 Carboxylic Acid Headgroups – Towards a New Standard in SAMs**, ***Anna Krzykawska***, Jagiellonian Univeristy, Poland*, J. Ossowski, T. Żaba, P. Cyganik*, Jagiellonian University, Poland

Self-assembled monolayers (SAMs) prepared from biphenyl-substituted molecules chemisorbed on the Ag(111) substrate via an -SH or -COOH headgroup were characterized using scanning tunneling microscopy (STM), infrared reflection absorption spectroscopy (IRRAS), and X-ray photoelectron spectroscopy (XPS). The objective of this work was to determine which of these headgroups, -SH or -COOH, will provide better 2D ordered SAMs. Importantly, to make such comparison valuable, i.e., to correlate the reduction in the concentration of surface defects with the particular headgroup, we need to compare the two systems, which are chemical analogues, and it would be desired that both systems form SAMs of similar packing density. Only under such conditions can the difference in intermolecular interactions in both systems be minimized to determine the role of headgroup bonding to the substrate in the 2D structural ordering of the resulting SAMs. Our results[1] obtained for monolayers meeting the above criteria show that SAMs with carboxylic headgroups can form, at room temperature and within a very short time of just a few minutes well-ordered 2D structures on Ag(111) with surprisingly large domains. In contrast, the thiol analogue formed at the same temperature reveals poor 2D ordering, with approximately 30 times smaller structural domains. Importantly, this pronounced difference in 2D ordering is observed despite the approximately 300 times longer incubation process of the thiol analogue. We also demonstrate that formation of the thiol analogue at elevated solution temperature (60°C) can significantly increase the size of its domains, which is, however, still approximately 5 times smaller in comparison to the carboxylic analogue formed at room temperature. Moreover, the structure of the carboxylic analogue on Ag(111) also shows better 2D order compared with the former data obtained for the thiol analogue SAMs formed on the Au(111) substrate at room temperature. Only the formation of thiol analogue SAMs at elevated solution temperature (60°C) on the Au(111) substrate with 300 times longer formation time provides comparable 2D ordering to that obtained at the room temperature for the carboxylic analogue SAMs on the Ag(111) substrate.

Our results indicate, therefore, that SAMs based on carboxylic head group can be considered an interesting alternative for the curren t standard based on the sulfur headgroups, particularly when 2D ordering, SAM fabrication time and stability in the ambient conditions are of great importance.

References

[1] A. Krzykawska, J. Ossowski, T. Żaba and P. Cyganik, *Chem Comm* **2017** accepted

5:40pm **AS+2D+NS+SA-WeA11 2-D and 3-D Characterization of Functionalized Nanostructured Carbons**, ***Chilan Ngo**, D.R. Diercks, M.B. Strand, M.J. Dzara, J. Hagen, S. Pylypenko*, Colorado School of Mines

Low cost, versatility, and a broad range of properties make carbon a widely studied material with numerous practical applications. Functionalization/doping with heteroatoms is an effective method to tailor the composition and structure of carbon, in order to adjust its properties for various applications. Significant efforts have been dedicated to elucidation of the composition, structure and properties of doped carbon materials, however atomic scale visualization of high-surface area carbons in 3-D has not been achieved. Here, by utilizing a combination of techniques, we focus on understanding the 2-D and 3-D distribution of nitrogen and iron dopants in high-surface area carbons. Information on surface composition evaluated using X-ray photoelectron spectroscopy (XPS) is complemented by 2-D bulk measurements using energy dispersive X-ray spectroscopy (EDS) through transmission electron microscopy (TEM). 3-D distribution of dopants is studied using atom probe tomography (APT), providing novel insight into the properties of high-surface area carbon materials. This type of investigation necessitated the fabrication of a diverse set of materials with defined shape and morphology, along with variation in the distribution of nitrogen and iron species relative to each other. Nitrogen-doped carbon nanospheres (NCs) were prepared by hydrothermal treatment of resorcinol, formaldehyde, and ethylenediamine, followed by pyrolyzation under flowing nitrogen, producing materials with different dopant concentrations and varied relative distribution of nitrogen functionalities. Iron- and nitrogen-doped nanospheres (FeNCs) were prepared by two routes. For the first set of materials, addition of an iron-containing precursor to the NC synthesis was done prior to hydrothermal treatment, to incorporate Fe throughout the bulk of the nanosphere. The second set is expected to deposit iron only on the surface of the carbon, and is prepared by addition of the iron precursor after the NC pyrolysis, followed by a second pyrolysis. A dual-beam focused-ion beam scanning electron microscope (FIB/SEM) was used to isolate nanospheres into a workable APT tip. Combination of 2-D and 3-D analysis are expected to further the understanding of N-doped carbon materials and N-containing Pt-group metal free catalysts employed in a variety of important catalytic reactions. This work also serves as a foundation to prepare model high-surface area materials that are compatible with *in situ* liquid and electrochemistry TEM techniques, to allow further investigations of these catalytically active materials under conditions relevant to their applications.

6:00pm **AS+2D+NS+SA-WeA12 Characterization of Natural Photonic Crystals in Glitterwing (*Chalcopteryx rutilans*) Dragonfly Wings using 3D TOF-SIMS**, ***Ashley Ellsworth***, *D.M. Carr, G.L. Fisher,* Physical Electronics, *W.W. Valeriano, R.R. de Andrade, J.P. Vasco, E.R. da Silva, A.B.M. Machado, P.S.S. Guimarães, W.N. Rodrigues,* Universidade Federal de Minas Gerais, Brazil

The male Amazonian glitterwing (*Chalcopteryx rutilans*) dragonfly has transparent anterior wings and brightly colored iridescent posterior wings. The colors are important for dragonflies with regard to sexual recognition, mating, and territorial behavior. The source of the varying colors was determined by Valeriano [1] using electron microscopy and optical reflectance to analyze the internal microstructures. SEM and TEM images revealed that the iridescent wings have multiple alternating layers with different electronic densities. The variation of the local color was related to the number and thickness of the layers which varied across the wing. The colors span the visible spectrum with red, blue, and yellow/green regions on the wings. The experimental reflectance was calculated and fitted through the transfer matrix method for the structure obtained from the electron microscopy images. Measurement of the thickness and number of layers is readily achievable by electron microscopy, however it is unable to characterize the chemistry of the different layers giving rise to these natural photonic crystals.

TOF-SIMS is a well-established technique for analyzing the elemental and molecular chemistry of surfaces. TOF-SIMS can now be used to probe the 3D structure and chemistry of a wide variety of organic and inorganic materials, both synthetic and naturally occurring, due to the advent of cluster ion beams such as C_{60}^+ and large cluster Ar_n^+. We will present results of 3D TOF-SIMS analyses for both transparent and colored wings to correlate with the electron microscopy and optical results to further the understanding of these natural photonic crystals.

[1] W.W.Valeriano, Masters dissertation, UFMG, 2016. Retrieved from http://www.fisica.ufmg.br/posgrad/Dissertacoes_Mestrado/decada2010/wescley-valeriano/WescleyWalisonValeriano-diss.pdf.

Nanometer-scale Science and Technology Division
Room: 19 - Session NS+MN+MS+SS-WeA

Nanopatterning, Nanofabrication and 3D Nanomanufacturing
Moderator: Brian Borovsky, St. Olaf College

2:20pm **NS+MN+MS+SS-WeA1 Site-controlled Si Nanodot Formation for a RT-SET via Ion Beam Mixing and Phase Separation**, ***Xiaomo Xu****, *G. Hlawacek, D. Wolf, T. Prüfer, R. Hübner, L. Bischoff,* Helmholtz Zentrum Dresden-Rossendorf, Germany, *M. Perego,* Institute for Microelectronics and Microsystems (IMM-CNR), France, *A. Gharbi,* Laboratoire d'électronique des technologies de l'information (CEA-Leti), France, *H.-J. Engelmann, S. Facsko, K.-H. Heinig, J. von Borany,* Helmholtz Zentrum Dresden-Rossendorf, Germany

The increased use of personal computing devices and the Internet of Things (IoT) is accompanied by a demand for a computation unit with extra low energy dissipation. The Single Electron Transistor (SET), which uses a Coulomb island to manipulate the movement of single electrons, is a candidate device for future low-power electronics. However, so far its development is hindered by low-temperature requirements and the absence of CMOS compatibility. By combining advanced top-down lithography with bottom-up self-assembly of Si nano dots (NDs) we will overcome this barrier.

In this work, Si NDs – suitable as RT Coulomb islands – are formed via ion beam mixing followed by thermally stimulated phase separation. Broad-beam Si^+ and Ne^+ beams followed by a rapid thermal annealing (RTA) treatment were utilized to create a layer of NDs, which are subsequently visualized by Energy-Filtered Transmission Electron Microscopy (EFTEM). The conditions for ND formation, namely the dependence on ion type, primary energy, irradiation fluence, layer thickness and thermal budget during RTA, are optimized based on an extensive survey of this multidimensional parameter space. The presented work is guided by TRIDYN simulations of the Si excess in a SiO_2 layer due to ion beam mixing and 3D Kinetic Monte-Carlo (3DkMC) simulation for the phase separation during the thermal treatment. To tailor towards a single Si ND, the focused Ne+ beam from the Helium Ion Microscope (HIM) is utilized to create user defined patterns of NDs in planar layer stacks. This allows to achieve a mixing volume small enough for restricted Ostwald ripening and successful single ND formation. The existence of the formation of spatially controlled single NDs with a diameter of only 2.2 nm is confirmed by comparing the EFTEM Si plasmon-loss intensity with simulated plasmon loss images.

In the future – by combining conventional lithography, direct self-assembly (DSA) and ion beam mixing – nanopillars with a single embedded ND will be integrated in a CMOS-compatible way. EFTEM and electrical characterization techniques will be used for realizing this novel pathway towards a room-temperature SET device.

2:40pm **NS+MN+MS+SS-WeA2 Scanning Tunneling Microscope Fabrication of Atomically Precise Devices**, ***Richard Silver***, NIST, *X. Wang,* University of Maryland, College Park, *P. Namboodiri, J. Wyrick, S.W. Schmucker, M.D. Stewart, R. Murray, J.A. Hagmann, C. Richter*, NIST

Atomically precise device fabrication is a technique that enables a new class of atom-based electronic structures with applications ranging from novel low dimensional materials to devices for quantum information processing. Deterministic placement of individual dopant atoms in the Si lattice is achieved using hydrogen-based scanning probe lithography. Controlling the position and electronic or quantum state of deterministically placed atoms in a solid state environment enables novel devices such as single atom transistors and solid state qubits.

However, fabricating functional atom-based devices is particularly challenging because of the need for exceptional ultra-high vacuum, near perfect atomic order, and low temperature epitaxial silicon overgrowth. This, coupled with sensitivity of atomic positional accuracy to thermal processing, and variability in scanning tunneling microscope patterning conditions, make exquisite control of process conditions essential.

In this presentation, we will focus on measurements and characterization of ultra-thin, atomically abrupt, highly doped low-dimensional devices and strategies for contacting these devices. We will describe our methods to align and contact buried devices and address significant challenges in making robust electrical contact to buried devices. We will present low-temperature electrical measurement results from atomically abrupt wires and tunnel junctions with coplanar gates. We have studied the effects of process conditions on device dimensionality and electrical performance in the context of extensive analysis of delta layer formation with optimized locking layer epitaxial growth techniques to enhance the confinement of Phosphorus dopant atoms. Low temperature transport measurements are used to investigate materials properties, effects from atomic imperfection and quantum transport phenomena.

3:00pm **NS+MN+MS+SS-WeA3 Contacting Buried Atomic-Precision Devices in Si using Kelvin Probe and Optical Microscopy**, ***Jonathan Wyrick***, *P. Namboodiri, X. Wang, R. Murray, J.A. Hagmann, K. Li, S.W. Schmucker, M.D. Stewart, C. Richter, R.M. Silver,* NIST

STM based hydrogen lithography has proven to be a viable route to fabrication of atomic-precision planar electronic devices. These devices are realized by a patterning step followed by dopant deposition and incorporation, and ultimately encapsulation with epitaxial Si. Atomically precise tunnel junctions, SETs, and Quantum Dots are examples of components that can be fabricated using hydrogen lithography.

The strength of this technique is the ability to control the lateral placement of phosphorus atoms in a single atomic layer of Si with sub-nanometer precision. At the same time, it presents challenges that must be overcome if devices are to be interfaced to the outside world. Locating and then fabricating aligned electrical contacts to buried devices is non-trivial, and becomes easier as the size of buried features is increased, but this is done at the expense of increased writing times and exposure to potential contamination.

We present a strategy for contacting buried devices aimed at minimizing the write-times associated with STM based fabrication by maximizing the positional accuracy with which we can locate subsurface structures. This is done by employing STM fabricated fiducials, AFM topography scans, Kelvin Probe Microscopy, and dark field optical microscopy. The data from each technique can be aligned and corrected for distortions, allowing us to determine buried device locations to better than 200nm accuracy.

3:20pm **NS+MN+MS+SS-WeA4 Quantifying Liquid Transport and Patterning using Atomic Force Microscopy**, *N. Farmakidis,* ***Keith Brown***, Boston University

Atomic force microscopy (AFM) provides unique insight into the nanoscale properties of materials. It has been challenging, however, to use AFM to study soft materials such as liquids or gels because of their tendency to flow in response to stress. Here, we propose an AFM-based technique for quantitatively analyzing the transport of soft materials from an AFM probe to a surface. Specifically, we present a method for loading an AFM probe

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* **NSTD Student Award Finalist**

with a single 0.3 to 30 pL droplet of liquid, and subsequently measuring the mass of this liquid by observing the change in the vibrational resonance frequency of the cantilever. Using this approach, the mass of this liquid was detected with pg-scale precision using a commercial AFM system. Additionally, sub-fL droplets of liquid were transferred from the probe to a surface with agreement found between the real-time change in mass of the liquid-loaded probe and the volume of the feature written on the surface. To demonstrate the utility of this approach in studying nanoscale capillary and transport phenomena, we experimentally determine that the quantity of liquid transported from the tip to a surface in a given patterning operation scales as the mass of liquid on the probe to the 1.35 power. In addition to providing new avenues for studying the dynamics of soft materials on the nanoscale, this method can improve nanopatterning of soft materials by providing *in situ* feedback.

4:20pm **NS+MN+MS+SS-WeA7 Positioning and Manipulating Single Dopant Atoms Inside Silicon**, ***Andrew Lupini***, *B.M. Hudak, J. Song,* Oak Ridge National Laboratory*, H.R. Sims,* Vanderbilt University*, M.C. Troparevsky,* Oak Ridge National Laboratory*, S.T. Pantelides,* Vanderbilt University*, P.C. Snijders*, Oak Ridge National Laboratory **INVITED**

The ability to controllably position single atoms inside materials could enable production of a new generation of atomically precise artificial materials with direct relevance for many areas of technology. For example, spins from individual donors in a semiconductor comprise one of the most promising architectures for quantum computing. However, fabrication of the ‘qubits’ that would make up a quantum computer is still unreliable and many fundamental materials science questions remain unanswered. Perhaps the key technical difficulty is the task of accurately positioning single atom dopants inside a solid with control, or at least understanding, of their local environment.

Silicon is the ideal substrate to explore such ideas because of the ability to obtain isotopically purified samples (a “spin-vacuum”) and compatibility with existing electronic components and manufacturing technologies. Group V elements are promising candidates for use as single-atom qubit dopants in Si, and it has recently been argued that bismuth could be an excellent dopant for such applications, because of its anomalously high spin-orbit coupling. Bi, in particular, has a large atomic number relative to Si, making it an ideal candidate to study using *Z*-contrast scanning transmission electron microscope (STEM). However, both precise doping and the imaging of single dopant atoms present many scientific challenges. For example, Bi is not very soluble in Si, meaning that the dopant atoms tend to migrate out of position during sample growth.

Here we will show examples of sample growth including novel nanostructures and single atom dopants. We will show dopant atoms imaged inside Si samples, and demonstrate electron-beam directed movement of single dopants.

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5:00pm **NS+MN+MS+SS-WeA9 Characterization of Butyl Tin Photoresists for Nanoscale Patterning**, *J.T. Diulus, R.T. Frederick,* Oregon State University*, M. Li,* Rutgers University*, D. Hutchison, M.R. Olsen, I. Lyubinetsky, L. Árnadóttir,* Oregon State University*, E.L. Garfunkel,* Rutgers University*, M. Nyman,* Oregon State University*, H. Ogasawara,* SLAC National Accelerator Laboratory*,* ***Gregory Herman***, Oregon State University

Inorganic photoresists are of interest for nanomanufacturing due the potential for high resolution patterning with low line edge roughness, while having high sensitivity to extreme ultraviolet (EUV) radiation. The combination of high absorption coefficient elements and radiation sensitive ligands can improve inorganic photoresist sensitivity while providing high contrast. Inorganic clusters are ideal candidates for photoresists since they have nanometer particle sizes with high particle size uniformity, and the ligand chemistries can be tuned for radiation induced chemistries that control relative solubility differences. In this presentation, characterization of a promising inorganic cluster-based EUV photoresist will be presented, where the goal of the studies is to better understand patterning mechanisms. In these studies, we are investigating butyl tin Keggin cluster that has recently been synthesized, and has shown promising properties as an inorganic photoresist. Key to these clusters, for application as an EUV photoresist, are the high EUV absorption coefficient for Sn, and the radiation sensitive carbon-tin bond. Removal of the organic ligand changes the polarity of the film, which provides the necessary solubility contrast for nanopatterning. We have used temperature programed desorption, electron stimulated desorption, and ambient pressure X-ray photoelectron spectroscopy to characterize both thermal and radiation induced processes in thin films formed from these clusters. We have found that butyl group desorption occurs through both thermal and radiation induced processes, and have determined both the carbon-tin bond strength and electron desorption cross-sections. Studies performed in different ambient conditions, and photon energies, have shown large effects on the radiation induced chemistries, where a significant enhancement in carbon decay was observed for O_2 pressures up to 1 torr. These studies provide a means to better understand the radiation induced processes that result in the solubility contrast of these materials, and may guide in the development of improved EUV photoresists for nanolithography.

5:20pm **NS+MN+MS+SS-WeA10 Impact of Polymer Templated Annealing on Gold Nanowires**, ***Tyler Westover***, *R.F. Davis, B. Uptrey, J. Harb, A. Woolley, S. Noyce*, 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 or nanorods followed by electrochemical plating. 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 have found that through the use of a polymer the wires can be templated to retain their overall morphology, while improving surface roughness, throughout a low temperature anneal. We have measured these wires to have less than 1kOhm resistances by electron beam lithography, in a two point configuration. Using electron beam induced deposition we have successfully made four point contacts to measure the change in resistance due to annealing. We will present results on polymer templating, showing that the wires maintain their overall morphology with improved conductivities during low temp (200° C) annealing.

5:40pm **NS+MN+MS+SS-WeA11 Dynamic Growth of Nanopores on Graphene via Helium Ion Microscope**, *S. Kim,* ***Anton Ievlev***, *M.J. Burch, I. Vlassiouk, A. Belianinov, S.V. Kalinin, S. Jesse, O.S. Ovchinnikova*, Oak Ridge National Laboratory

Controlling atomic-to-nanoscale defect formation on graphene is of significance as defects can modify properties as well as functionality of graphene. Especially, controlled formation of nanopores in graphene can be used for energy harvesting/storage, analysis of biomolecules and the separation of gases or liquids. Nanopores can be fabricated either by using high energy focused electron beam or by focused helium ion beam with high precision. However, focused electron beam has very low throughput to form nanopores despite its superiority in pore size control. On the contrary, focused helium ion beam has much higher throughput in nanofabrication with its capability to form sub-5nm pores. In this study, we utilized the focused helium ion microscope to fabricate nanopores on graphene and demonstrated atomic scale control in growth of nanopores by helium ion irradiation. We demonstrated the size control of nanopores down to ~ 3nm in a diameter. Formation and growth kinetics of nanopores by different helium ion irradiation conditions were explored and analyzed using the image data analytics. Also, Raman spectroscopic measurements was performed to demonstrate the effect of a helium ion dose on the change of initial defect density on graphene which leads to different behaviors and growth kinetics of nanopore formation.

This work was supported by the Oak Ridge National Laboratory’s Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy, Office of Science User Facility.

Advanced Surface Engineering Division
Room: 11 - Session SE+2D+NS+SS+TF-WeA

Nanostructured Thin Films and Coatings
Moderators: Jianliang Lin, Southwest Research Institute, Matjaz Panjan, Jozef Stefan Institute, Slovenia

2:20pm **SE+2D+NS+SS+TF-WeA1 Plasma Process Development and Optimized Synthesis of TiB$_2$ Coatings from DC Magnetron Sputtering, High Power Impulse Magnetron Sputtering, and DC Vacuum Arc**, ***Johanna Rosen***, Linköping University, Sweden **INVITED**

The use of high power impulse magnetron sputtering (HiPIMS) or cathodic arc for the synthesis of TiB$_2$ coatings will drastically increase the amount of ionized species impinging on the substrate compared to regular DC magnetron sputtering. In particular for HiPIMS, it is possible to control the flux of ionized species by varying the pulse frequency, which allows exploration of the effect of ion to neutral flux ratio on the coating microstructure while keeping the substrate bias potential constant.

We show that the additional energy supplied during film growth in the HiPIMS process, compared to regular DC sputtering, results in a change from a randomly oriented polycrystalline microstructure to a 001-textured nanocolumnar structure. The change in preferred orientation also influence the hardness, which is enhanced from 36 GPa to ≥ 42 GPa. A further increase in the ion flux to the substrate leads to denser coatings with a higher residual compressive stress. Furthermore, we show that the energy supplied to the film surface is influenced by when the bias is applied relative to the HiPIMS pulse. Based on charge-state-resolved plasma analysis it is found that by applying the bias in synchronous with the HiPIMS pulse, a higher fraction of B$^+$ ions will constitute the total flux of bombarding ions. This results in a lower residual stress compared to coatings deposited under bombardment of mainly Ar$^+$ ions.

Finally, we also present results from TiB2 synthesis based on DC vacuum arc, and a route for attaining a stable, reproducible, and close to fully ionized plasma flux of Ti and B by removal of the external magnetic field. Plasma analysis shows increased ion charge states as well as ion energies compared to HiPIMS. Furthermore, while regular DC magnetron sputtering and HiPIMS typically give a B to Ti ratio above 2, the arc deposited coatings have a stoichiometry close to 2. Despite observations of macroparticle generation during synthesis, the film surface is very smooth with a negligible amount of particles.

3:00pm **SE+2D+NS+SS+TF-WeA3 Multi-technique Approach for Studying Co-sputtered M-Si-O Thin Films**, ***Lirong Sun***, General Dynamics Information Technology, *N.R. Murphy*, Air Force Research Laboratory, *J.T. Grant*, Azimuth Corporation

In this work, the M-Si-O thin films (M: Al and Ta) were prepared through reactive pulsed DC magnetron co-sputtering of M and Si targets in an O$_2$/Ar mixture. The M fraction [M/(M+Si)] of different chemical compositions ($M_xSi_yO_z$), as determined through X-ray photoelectron spectroscopy (XPS), was varied between 0 and 100% by changing sputtering power applied to the M targets. The film thickness, refractive index (n) and extinction coefficient (k) were determined by *in situ* spectroscopic ellipsometry (*i*SE). Concurrent with ellipsometry measurements, the *in situ* stress evolution of the films, as correlated to the M fraction, was investigated using a multi-beam optical sensor (MOS) system. The MOS system was used to measure both intrinsic stress resulting from the deposition process as well as thermal stress evolved during heating/cooling process. Data obtained through stress monitoring during heating and cooling was used to calculate the coefficient of thermal expansion (CTE). The density and crystallinity of the films were measured by X-ray diffraction and X-ray reflectivity, respectively. Transmission and reflectance of the films were carried out by UV-Vis-NIR spectroscopy. Finally, this study derives a process-property-microstructure relationship correlating the optical constants, CTE, intrinsic stress, and M fraction.

3:20pm **SE+2D+NS+SS+TF-WeA4 Ultra-high Vacuum Magnetron Sputter-deposition of Zr/Al$_2$O$_3$(0001): Effect of Substrate Temperature on Zr Thin Film Microstructure and Thermal Stability of Zr-Al$_2$O$_3$ Interfaces**, *K. Tanaka, J. Fankhauser,* University of California at Los Angeles, *M. Sato,* Nagoya University, Japan, *D. Yu, A. Aleman, A. Ebnonnasir, C. Li,* University of California at Los Angeles, *M. Kobashi,* Nagoya University, Japan, *M.S. Goorsky*, ***Suneel Kodambaka***, University of California at Los Angeles

Zr thin films are grown on Al$_2$O$_3$(0001) substrates in an ultra-high vacuum deposition system via dc magnetron sputtering of Zr target in Ar atmosphere at temperatures T_s between 600 ºC and 900 ºC. The as-deposited layer surface structure and composition are determined *in situ* using low-energy electron diffraction and Auger electron spectroscopy, respectively. Bulk crystallinity and microstructures of the samples are determined using x-ray diffraction, cross-sectional transmission electron microscopy along with energy dispersive spectroscopy. At 600 ºC ≤ T_s < 750 ºC, we obtain fully dense, hexagonal close-packed structured Zr(0001) thin films with smooth surfaces. At T_s ≥ 750 ºC, the Zr layers are porous, exhibit {0001} texture, and with rough surfaces. Energy dispersive x-ray spectra obtained from the Zr/Al$_2$O$_3$ interfaces reveal the formation of Zr-Al intermetallic compounds, whose thickness increases exponentially with increasing T_s. We attribute the formation of this interfacial layers to fast diffusion of Zr and reaction with the Al$_2$O$_3$ substrate.}

4:20pm **SE+2D+NS+SS+TF-WeA7 Structural, Mechanical, Optical Properties of Molybdenum Incorporated β-Ga$_2$O$_3$ Nanocrystalline Films for Extreme Environment Applications**, ***Anil Battu***, *S. Manandhar, C.V. Ramana,* University of Texas at El Paso

Recently, gallium oxide (Ga$_2$O$_3$) has been attracting the attention of researchers as a suitable material for different extreme environment applications, such as high power electronics, optoelectronics, ultraviolet transparent conductive oxides, and gas sensors. β-Ga$_2$O$_3$ exhibits the highest thermal and chemical stability, which makes the material interesting for high-temperature oxygen sensor applications. However, the response time and sensitivity must be improved. In recent years, doping Ga$_2$O$_3$ with the suitable metal ions has been considered to alter the electronic properties and to improve sensor performance. In this context, the present work was performed on using a mechanically resilient metal (Mo) to incorporate into Ga-oxide (GMO) to provide excellent physical and thermo-mechanical characteristics. The GMO nanocomposite films with variable Mo contents (0-11.23 at%) were sputter-deposited onto Si(100) by varying the sputtering power in the range of 0-100 W. The effect of Mo on the crystal structure, mechanical properties and optical properties of GMO nanocomposite films is significant. While Mo content ≤ 4 at% reatins the β-Ga$_2$O$_3$ phase, higher Mo content induces amorphization. Molybdenum incorporation into β-Ga$_2$O$_3$, reduces the grain-size leading to amorphous nature of the entire film as well as surfaces. The nanoindentation studies indicate the remarkable effect of structural evolution and Mo content on the mechanical properties of the deposited GMO thin films. While Mo incorporation increases the hardness from 25 to 36 GPa, elesatic modulus decreases. Mo-induced red-shift in the band gap is significant in GMO films. Based on the results, a structure-property relationship in established in Mo incorporated Ga$_2$O$_3$ films.

4:40pm **SE+2D+NS+SS+TF-WeA8 Investigating Mass Transport and other Events underlying Rapid, Propagating Formation Reactions in Pt/Al Multilayer Films**, ***David Adams***, *M.J. Abere, C. Sobczak, D.E. Kittell, C.D. Yarrington, C.B. Saltonstall, T.E. Beechem,* Sandia National Laboratories

Metallic thin film multilayers that undergo rapid, self-propagating exothermic reactions are of interest for several applications including advanced joining technology. Reactive multilayers, such as commercially available Ni-Al, have been developed as a heat source to locally solder or braze dissimilar materials. A local heating approach is of great benefit for joining temperature-sensitive components and metastable structures. The development of new materials for reactive joining requires an improved, detailed understanding of mass transport, chemical reactions, heat release and thermal transport processes. With this presentation, we describe recent studies of a more highly exothermic reactive multilayer system (Pt/Al). Thin Pt/Al multilayers exhibit rapid propagating reactions with flame speeds as high as 100 m/s and internal heating rates > 1x10^7 K/s. Equimolar designs are characterized by a substantial heat of formation, ~100 kJ/mol. at., which is approximately twice that of Ni/Al. Our discussion of equimolar Pt/Al multilayers will focus on the thermal and mass transport characteristics which underly their self-propagating reactions. We have utilized advanced thin film characterization techniques to probe the thermal conductivity of different Pt/Al multilayers having various periodicities. This acquired information is used within the framework of an analytical method developed by Mann et al. (J. Appl. Phys. 1997) to estimate the mass transport properties of Pt/Al multilayers subjected to high heating rates. The analytical model accounts for layer thicknesses, compositional profiles near interfaces, flame temperatures, heats of reaction, and adiabatic temperatures in order to predict reaction wavefront velocity and its variation with multilayer design.

This work was supported by a Sandia Laboratory Directed Research and Development (LDRD) program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

5:00pm **SE+2D+NS+SS+TF-WeA9 Adaptive Ceramic Coatings for Extreme Environments**, ***Samir Aouadi***, University of North Texas, *C. Muratore,* University of Dayton, *A.A. Voevodin*, University of North Texas **INVITED**

This talk will provide an overview of the latest research developments in the design and exploration of hard coatings with high temperature adaptive behavior in tribological contacts. The initial focus of the talk will be on understanding the major mechanisms that lead to a reduction in friction and/or wear in high temperature lubricious oxides. Adaptive mechanisms will also be discussed and will include metal diffusion and formation of lubricant phases at worn surfaces, thermally- and mechanically-induced phase transitions in hexagonal solids, contact surface tribo-chemical evolutions to form phases with low melting point, and formation of easy to shear solid oxides. All of these adaptive mechanisms are combined in nanocomposite coatings with synergistic self-adaptation of surface structure and chemistry to lubricate from ambient temperatures to 1000 °C and provide surface chemical and structural reversibility during temperature cycling to maintain low friction coefficients. Changes in the structural and chemical properties of these materials as a function of temperature will be correlated to their mechanical and tribological performance using a range of experimental tools in addition to simulations based on *ab initio* calculations and molecular dynamics simulation methods. This review also includes a discussion of the industrial applications of these coatings as well as of potential improvements to the coating design and other anticipated future developments.

5:40pm **SE+2D+NS+SS+TF-WeA11 Ultralow Wear of Stable Nanocrystalline Metals**, ***Nicolas Argibay***, *T.A. Furnish, T.F. Babuska, C.J. O'Brien, J.F. Curry, B.L. Nation, A.B. Kustas, P. Lu, M. Chandross, D.P. Adams, M.A. Rodriguez, M.T. Dugger, B.L. Boyce, B.G. Clark*, Sandia National Laboratories

The existence of intrinsic thermodynamically stable nanocrystalline binary metal alloys has been recently proposed and supported by demonstrations of stability through annealing of powders. There is a great deal of interest in understanding the impact of mechanical stress on this stability. In this presentation we discuss the results of an investigation on the stress and temperature dependent stability of a nanocrystalline noble-metal alloy (Pt-Au) in the form of sputtered thin films. We show that stabilization of nanocrystalline structure can impart low friction ($\mu \sim 0.2$-0.3) and remarkable wear resistance, 100x lower than any previously reported metal.

6:00pm **SE+2D+NS+SS+TF-WeA12 From Ab-Initio Design to Synthesis of Multifunctional Coatings with Enhanced Hardness and Toughness**, ***Daniel Edström***, *D. Sangiovanni, L. Hultman, I. Petrov, J. Greene, V. Chirita,* Linköping University, University of Illinois at Urbana-Champaign

Enhanced toughness in hard and superhard thin films is a primary requirement for present day ceramic hard coatings, known to be prone to brittle failure. Density Functional Theory (DFT) investigations predicted significant improvements in the toughness of several B1 structured transition-metal nitride (TMN) alloys, obtained by alloying TiN or VN with MoN and WN. The calculations reveal that the electronic mechanism responsible for toughness enhancement stems from the high valence electron concentration (VEC) of these alloys, which leads to the formation of alternating layers of high/low charge density orthogonal to the applied stress, and allows a selective response to deformations. This effect is observed for ordered and disordered ternary TMN alloys. The essential feature in the disordered alloys, as reported for ordered alloys, is the increased occupancy of electronic d-t_{2g} metallic states, which allows the selective response to tensile/shearing stresses, and explains the enhanced toughness confirmed experimentally for VMoN films.

Recently, these results have been validated experimentally. Single-crystal VMoN alloys, grown by dual-target reactive magnetron sputtering together with VN and TiN reference samples, exhibit hardness > 50% higher than that of VN, and while nanoindented VN and TiN reference samples suffer from severe cracking, the VMoN films do not crack.

New DFT calculations suggest similar toughness improvements may be obtained in pseudobinary NaCl structured transition-metal carbide (TMC) compounds by alloying TiC or VC with WC and MoC. A comprehensive electronic structure analysis, as well as stress/strain curves DFT-based calculations, carried out for the newly formed ternary TMC alloys, reveal similar trends between shear-stressed TMN and TMC compounds, and predict VMoC as the best candidate alloy with enhanced ductility.

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

Surface Science Division
Room: 25 - Session SS+HC+NS-WeA

Dynamical Processes at Surfaces
Moderators: Ashleigh Baber, James Madison University, Kathryn Perrine, Michigan Technological University

3:00pm **SS+HC+NS-WeA3 Quantum Molecular Machines**, ***Saw-Wai Hla***, Ohio University and Argonne National Laboratory **INVITED**

One of the goals of nanotechnology is the development of complex molecular machines that can be operated with atomic level control in a solid-state environment. Most biological molecular machines have the sizes from tens of nanometers to a few microns –a range where classical machine concepts hold. However, artificially designed molecular machines can be in the size range down to a few nanometers or less, which is in the range of quantum processes. In this talk, we will present various artificial molecular machines such as molecular motors and linear transport devices such as molecular cars operating in the quantum regime on materials surfaces. Fundamental operations of these synthetic molecular machines are investigated at one molecular machine-at-a-time in an atomically clean environment using low temperature scanning tunneling microscopy (STM), tunneling spectroscopy, and molecular manipulation schemes [1,2]. These investigations reveal how charge and energy transfer are taken place within single molecular machines as well as among the molecular machines in the molecular networks. Moreover by introducing dipole active components in the rotor arms of the molecular motors, communication among the molecules can be introduced via dipolar interaction. In addition to single molecule operations, synchronization of molecular motors can be achieved depending on the symmetry of the molecular assemblies on surfaces and the strength of applied electric field energy. Here, all the molecular motors can be rotated in a synchronized manner using 1V or higher electric field supplied from the STM tip. Below this bias, the rotor arms of the molecular motors can reorient into different directions. Careful analyses reveal that such reorientations of the molecular motors are not random, but they are coordinated to minimize the energy. Furthermore, individual molecular motors can be charged using the inelastic tunneling scheme with the STM tip. This introduces spin-active components within the molecular motors and enables us to investigate spintronic properties of individual molecular motors at the sub-molecular scale using tunneling spectroscopy. For the controlled linear transport at the nanoscale, we will present the latest development of molecular nanocars.This work is supported by US DOE grant DE-FG02-02ER46012.

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4:20pm **SS+HC+NS-WeA7 Collective, Multi-atom Diffusion in Epitaxially Grown Metallic Films**, ***Matt Hershberger***, *M. Hupalo, P.A. Thiel,* Iowa State University Ames Laboratory –USDOE, *M.K.L. Man, M.S. Altman,* Hong Kong University of Science and Technology, Hong Kong, *C.H. Mullet, S. Chiang,* University of California-Davis, *M.C. Tringides*, Iowa State University Ames Laboratory –USDOE

Surface diffusion is the main process controlling mass transport of many important phenomena such as nucleation, nanostructure growth, pattern formation, and chemical reactions. In practically all cases, it is described as a random walk of independently moving adatoms. Such process is inherently stochastic and therefore very slow as a route to self-organization in nature.

A series of experiments in different epitaxially grown metallic films over the last 5 years using different techniques has challenged the classical picture. The experiments have shown unusually fast, collective diffusion is present in nature, observed in a range of experiments over different length and time scales.

STM experiments show that fully completed Pb crystalline islands emerge “explosively” out of the compressed wetting layer on Si(111) after a critical coverage q_c=1.22ML is reached. The unexpectedly high island growth rates and directional correlations show that mass transport is through the correlated motion of the wetting layer.[1] Additional deposition of Pb shows island density that does not reach steady state; it shows abrupt jumps in island density with new generations of smaller islands continuing to nucleate (in contrast to classical nucleation). Real time experiments with LEEM, monitoring the refilling of an initial vacant area in Pb/Si(111), show that the initial steep profile does not disperse and that the profile propagates at constant velocity x~t. The profile follows a non-Fickian form with two moving highly correlated fronts, one inward and the other outward.[2] The formation of long anisotropic multi-height Ag islands on Ge(110) is exceedingly fast, when compared to the rates expected from random walk Ag diffusion barriers. A wetting layer is also present prior to the crystallization and is responsible for the fast growth rates, although the temperature is above room temperature.[3] Evidence for collective diffusion has been seen in Pb/Si(100), Pb/Ge(111), Pb/Ni(111), Pb/W(110), Ag/Si(110).

A better understanding of these processes can guide the search of collective transport in other systems, especially to identify the relevant growth "window" (of temperature and coverage). It can further clarify the role of stress since the compression of the non-crystalline wetting layer is critical for these effects.[4]

References:

1. M. T. Hershberger et al., .Phys. Rev. Lett. 113, 236101 (2014)

2. K. L. Man et al., Phys. Rev. Lett. 110, 036104 (2013)

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4:40pm **SS+HC+NS-WeA8 Quantitative Molecular Beam Study for CO_2 Hydrogenation on Cu (111) and Cu(100) Surfaces**, ***Jiamei Quan***, *T. Kondo, T. Kozarashi, T. Mogi, J. Nakamura*, University of Tsukuba, Japan

Catalytic conversion of CO_2 into valuable fuels and chemicals such as methanol, especially if activated by a precise energetic control, represents a potentially economic strategy for utilization of fossil feedstock and reducing CO_2 emissions and their contributions to climate changes. The formation of formate intermediates ($2CO_2 + H_2 \rightarrow 2H\ COO_a$) on Cu catalysts is an important initial step, in which the reaction probability is reported as low as 10^{-12} at 340 K.[1] Our previous reports suggested that the reaction proceeds via an Eley-Rideal type mechanism, where CO_2 directly reacts with pre-adsorbed H to form $HCOO_a$.[2] Recently, we have clarified using supersonic molecular beam apparatuses that the reaction probability is promoted up to ~10^{-3} by increasing both translational and vibrational energies, while insensitive to the Cu surface structure (Cu(111) and Cu(100)) and the surface temperature (120 - 210K). The energy efficacy on the reaction probability is found to be larger as much as 100 times for the vibrational energy compared to the translational energy, suggesting that the vibrational excitation significantly enhances the formate formation. Based on the comparison with DFT calculations, we conclude that the excitation of the bending mode of CO_2 at the transition is crucially important to form the C-H bond of HCOO via lowering LUMO level of CO_2. The small pre-exponential factor derived by the experiment is ascribed to the preferential orientation of the CO_2 molecule (C-end collision to H_a on Cu) for the reaction. The discovered thermal non-equilibrium channel in CO_2 conversion, which doesn't require the heating of catalysts, is expected to provide a prototypical surface reaction dynamics and open up novel industrial pathways of efficient CO_2 conversion into useful chemicals and fuels.

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[2] (a) J. Quan, J. Nakamrua, et al., Angew. Chem. Int. Ed. 56 (**2017**) 3496; (b) G. Wang, J. Nakamura, et al., *J. Phys. Chem. B* 110 (**2005**) 9.

5:00pm **SS+HC+NS-WeA9 A New Approach for Controlling the Rotational Orientation of a Molecule and Studying the Stereodynamics of a Molecule-Surface Collision**, ***Gil Alexandrowicz***, Technion – Israel Institute of Technology, Israel **INVITED**

The interaction between a molecule and a solid surface is fundamental to a huge variety of research fields and applications, ranging from industrial heterogeneous catalysis to ultra-cold astrochemical reactions on cosmic dust. One molecular property that affects molecule-surface interactions, but is also particularly difficult to control and resolve, is the orientation and alignment of the rotational axis of the molecule i.e. the quantum rotation projection states. The existing paradigm is that control over this molecular property can be obtained either by photo-excitation schemes and/or by deflecting experiments using strong electric or magnetic fields. Using these approaches valuable insight was obtained and the crucial role the rotation projection states have on the outcome of molecule-surface collision was demonstrated. However, the two approaches mentioned above can only be applied to a very small sub-group of systems (typically excited/paramagnetic species). In this presentation I will describe a completely different approach which utilizes the rotational magnetic moment, which is a general molecular property, to control and resolve the projection rotation states of ground-state molecules.

Our new experimental approach combines an atomic interference setup, originally built to perform ultra-fast surface diffusion measurements[1], with magnetic manipulation techniques we developed for separating quantum states of molecular beams[2]. The result is a unique setup which can both control and resolve the rotational orientation of a molecule as it collides with a solid surface. In this presentation I will show some recent experiments where we controlled the rotational orientation of a ground state hydrogen molecule, and correspondingly modified the outcome of a collision event with flat and stepped copper surfaces[3].The possibilities this new technique opens for studying the stereodynamic nature of molecule-surface interactions as well as ultra-fast surface dynamics will be briefly discussed.

[1] Progress in Surface Science, 84, 323 (2009).

[2] Science, 331, 319 (2011).

[3] Nature communications, (DOI: 10.1038/ncomms15357), in press (2017).

5:40pm **SS+HC+NS-WeA11 Surface Temperature Effects in CH_4 Dissociation on Flat and Stepped Nickel Single Crystals**, ***Eric High***, *E.K. Dombrowski, A.L. Utz*, Tufts University

A modified King and Wells molecular beam reflectivity method was used to obtain thermal and quantum state resolved initial sticking probabilities (S_0) for CH_4 on nickel single crystals at elevated surface temperatures (500 to 1000K). We recorded the reactivity of a supersonic molecular beam of methane with and without laser excitation to v=1 of the v_3 antisymmetric C-H stretching vibration. Square wave modulation of the laser source during CH_4 deposition provided simultaneous real-time measurement of $S_0^{LaserOff}$ and S_0^{v3}, resulting in a dramatic reduction in data acquisition time, a significant reduction in experimental error, and the opportunity to measure S as a function of accumulating surface coverage. On a Ni(111) surface, both laser-off and vibrational state-resolved measurements of S_0 were essentially independent of surface temperature, within error, from 1000 to 800K and then decreased linearly as T_{surf} dropped from 800 to 500K. These findings are consistent with the predictions of Reaction Path Hamiltonian calculations by Jackson and Guo over a wide range of incident kinetic energies (96 to 167 kJ/mol). The calculations suggest that at low incident energies, reactivity occurs predominantly at on-top sites, but as energy increases, reactions begin to occur at bridge sites as well. We will also present more recent measurements on the low step density Ni(997) surface that provide insight into the role of step-edge nickel atoms at these industrially relevant surface temperatures.

6:00pm **SS+HC+NS-WeA12 Experimental and Theoretical Study of Rotationally Inelastic Diffraction of $H_2(D_2)$ from Methyl-Terminated Si(111)**, ***Kevin Nihill****, *Z.M. Hund,* University of Chicago, *A. Muzas, C. Diaz, M. del Cueto,* Universidad Autónoma de Madrid, Spain, *T. Frankcombe,* University of New South Wales, Australia, *N. Plymale, N.S. Lewis,* California Institute of Technology, *F. Martin,* Universidad Autónoma de Madrid, Spain, *S.J. Sibener*, University of Chicago

Fundamental details concerning the interaction between H_2 and CH_3-Si(111) have been elucidated by the combination of diffractive scattering experiments and electronic structure and scattering calculations. Rotationally inelastic diffraction (RID) of H_2 and D_2 from this model hydrocarbon-decorated semiconductor interface has been confirmed for the first time *via* both time-of-flight and diffraction measurements, with modest $j = 0 \rightarrow 2$ RID intensities for H_2 compared to the strong RID features observed for D_2 over a large range of kinematic scattering conditions along two high-symmetry azimuthal directions. The Debye-Waller model was applied to the thermal attenuation of diffraction peaks, allowing for precise determination of the RID probabilities by accounting for incoherent motion of the CH_3-Si(111) surface atoms. The probabilities of rotationally inelastic diffraction of H_2 and D_2 have been quantitatively evaluated as a function of beam energy and scattering angle, and have been compared with complementary electronic structure and scattering calculations to provide insight into the interaction potential between H_2 (D_2) and hence the surface charge density distribution. Specifically, a six-dimensional potential energy surface (PES), describing the electronic structure of the $H_2(D_2)/CH_3$-Si(111) system, has been computed based on interpolation of density functional theory (DFT) energies. Quantum and classical dynamics simulations have allowed for an assessment of the accuracy of the PES, and subsequently for identification of the features of the PES that serve as classical turning points. A close scrutiny of the PES reveals the highly anisotropic character of the interaction potential at these turning points. This combination of experiment and theory provides new and important details about the interaction of H_2 with a hybrid organic-semiconductor interface, which can be used to further investigate energy flow in technologically relevant systems.

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* **Morton S. Traum Award Finalist**

Tribology Focus Topic
Room: 10 - Session TR+AS+HI+NS+SS-WeA

Molecular Origins of Friction
Moderators: J. David Schall, Oakland University, Paul Sheehan, US Naval Research Laboratory

2:20pm **TR+AS+HI+NS+SS-WeA1 On the Stochastic Nature of Bonding in Contact: Simulations of Indentation and Sliding of DLC Tips on Diamond Surfaces**, ***J. David Schall***, Oakland University, *R.A. Bernal*, University of Texas at Dallas, *Z. Miline*, University of Pennsylvania, *P. Chen*, *P. Tsai*, *Y.-R. Jeng*, National Chung Cheng University, Taiwan, Republic of China, *K.T. Turner*, *R.W. Carpick*, University of Pennsylvania, *J.A. Harrison*, United States Naval Academy

Contact at the nanoscale has important implications in the use of tip-based nanomanufacturing, data storage, and imaging with scanning probes. Tip wear reduces predictability in manufacturing and image quality such scanning probe applications. As a means to reduce wear, hard wear-resistant materials such as diamond-like carbon (DLC), ultra nanocrystalline diamond (UNCD) and amorphous carbon (a-C:H) have been used to coat scanning probe tips. Understanding of the behavior of these materials in contact is critically important towards their successful application. Recent studies using a TEM nanoindenter showed significant variation in both pull-in and pull-off forces obtained during the repeated indentation of a DLC tip on to a diamond surface. Furthermore, the pull-in and pull-off forces do not appear to be correlated. In this presentation, results from molecular dynamics simulations of a DLC tip on hydrogen terminated diamond surfaces will presented. The tip was constructed with a structure and geometry similar to that of the tip used in experiment. The resulting simulations show that the pull-in force appears to be dominated by long range dispersion forces while the pull-off force is determined by the number of covalent bonds formed during the contact. For a given surface, the formation of bonds during indention appears to be a stochastic process with multiple indents of the same tip at the surface same location showing a widely varying number of bonds formed. It is therefore hypothesized that the variation in pull-off forces observed in experiment are also related to the number of bonds formed across the tip-surface interface.

Supported by **The National Science Foundation and the Air Force Office of Scientific Research

2:40pm **TR+AS+HI+NS+SS-WeA2 New Insights about the Fundamental Mechanisms of Friction of MoS$_2$**, ***John Curry***, Lehigh University, *M. Wilson*, *T.F. Babuska*, *M. Chandross*, Sandia National Laboratories, *H. Luftman*, *N.C. Strandwitz*, *B.A. Krick*, Lehigh University, *N. Argibay*, Sandia National Laboratories

Molybdenum Disulfide (MoS$_2$) is a solid lubricant used widely in aerospace applications, capable of providing ultralow friction (coefficients, $\mu < 0.01$) in inert environments such as the vacuum found in outer space. Research over the years has led to the development of MoS$_2$ nanocomposites that are less susceptible to the effects of environment and aging. Yet, the fundamental mechanisms responsible for environmental sensitivity and degraded friction behavior remain highly debated. Tribological experiments and molecular dynamics (MD) simulations were used to understand the evolution of friction behavior for MoS$_2$ coatings as a function of temperature, lattice commensurability and defect density. The oxidative resistance of MoS$_2$ coatings prepared with differing degrees of defect density and basal orientation was also assessed via high-sensitivity low-energy ion scattering (HS-LEIS) depth profiling, X-ray photoelectron spectroscopy (XPS), tribological experiments and MD. Through these findings, we discuss new connections between atomic-scale mechanisms and macro-scale friction behavior of this class of lubricant in a wide range of environments.

3:00pm **TR+AS+HI+NS+SS-WeA3 The Influence of Environmental Exposure and the Substrate on the Lubricating Properties of Two-Dimensional Materials**, *P. Gong*, University of Calgary, Canada, *Z. Ye*, Miami University, *L. Yuan*, ***Philip Egberts***, University of Calgary, Canada **INVITED**

The friction reducing properties of graphene has been shown to have a number of interesting properties, such as a dependence on the number of layers of the lubricant present, an exceptional dependence on the surface adhesion properties of the underlying substrate, and environmental stability. These properties have been attributed to its low mechanical strength to out-of-plane deformation, its innate thinness, and the influence of the environment on the surface energy. In this work, the friction reducing properties of graphene are examined using experiments and simulation. In particular, the influence of surface energy and associated wettability of graphene are explored as a property that can influence the lubrication properties of graphene, but also friction hysteresis. While little to no variation in pull-off forces have been observed on varying numbers of graphene covering the surfaces in experiments, the impact of the variance of surface energy on friction, and in particular friction under humid environments, suggests that surface energy may have a stronger influence on graphene's friction reducing ability than suggested in previous work.

4:20pm **TR+AS+HI+NS+SS-WeA7 Fundamental Understanding of Interfacial Adhesion and Tribochemistry by Ab Initio Calculations**, ***M.Clelia Righi***, University of Modena and Reggio Emilia, Italy **INVITED**

Tribologically-induced chemical modifications of surfaces interacting with lubricant additives or other molecules present in the environment surrounding the sliding media can substantially change the adhesion and friction of materials in contact. Therefore, is highly desirable to understand how they take place. However, tribochemical reactions are difficult to monitor in real-time by experiments, which leaves a gap in the atomistic understanding required for their control.

We apply *ab initio* molecular dynamics to monitor chemical reactions involving common solid lubricants, namely molybdenum disulfide, graphene/graphite and carbon-based films, interacting with water molecules in the presence of mechanical stresses. Our simulations elucidate atomistic mechanisms relevant to understand the effects humidity on the lubricating properties of these materials.[1,2]

As second issue, we investigate the tribochemistry of sulfur, phosphorus and graphene on iron and discuss the role of metal passivation in reducing the interfacial adhesion and shear strength. We generalize the result by establishing a connection between the tribological and the electronic properties of interfaces. This adds a new piece of information for the ultimate understanding of the fundamental nature of frictional forces. [3,4]

[1] P. Restuccia, G. Levita and M. C. Righi *Graphene and MoS2 interacting with water: a comparison by ab initio calculations* Carbon 107, 878 (2016).

[2] S. Kajita and M. C. Righi *A fundamental mechanism for carbon-film lubricity identified by means of ab initio molecular dynamics*, Carbon 103, 193 (2016).

[3] M. C. Righi, S. Loehlé, M. I. De Barros Bouchet, S. Mambingo-Doumbeand J. M. Martin *A comparative study on the functionality of S- and P-based lubricant additives by combined first principles and experimental analysis* RSC Advances, 6, 47753 (2016).

[4] P. Restuccia and M. C. Righi *Tribochemistry of graphene on iron and its possible role in lubrication of steel* Carbon 106, 118 (2016).

5:00pm **TR+AS+HI+NS+SS-WeA9 Friction Between 2D Solids during Lattice Directed Sliding**, ***Paul Sheehan***, US Naval Research Laboratory, *CM. Lieber*, Harvard University

Nanometer-scale crystals of the 2D oxide molybdenum trioxide (MoO$_3$) were formed atop the transition metal dichalcogenides MoS$_2$ and MoSe$_2$. The MoO$_3$ nanocrystals are partially commensurate with the dichalcogenide substrates, being aligned only along one of the substrate's crystallographic axes. These nanocrystals can be slid only along the aligned direction and maintain their alignment with the substrate during motion. Using an AFM probe to oscillate the nanocrystals, it was found that the lateral force required to move them increased linearly with nanocrystal area. The slope of this curve, the interfacial shear strength, was significantly lower than for macroscale systems. It also depended strongly on the duration and the velocity of sliding of the crystal, suggesting a thermal activation model for the system. Finally, it was found that lower commensuration between the nanocrystal and the substrate increased the interfacial shear, a trend opposite that predicted theoretically.

5:40pm **TR+AS+HI+NS+SS-WeA11 Single Molecule Force Measurement: Mechanic and Symmetry Dependent Lateral Force**, ***Yuan Zhang***, Argonne National Laboratory, *S. Khadka*, Ohio University, *B. Narayanan*, *A. Ngo*, Argonne National Laboratory, *Y. Li*, Ohio University, *B. Fisher*, *L. Curtiss*, *S. Sankaranarayanan*, *S.W. Hla*, Argonne National Laboratory

Mechanical properties of molecules adsorbed on materials surfaces are increasingly vital for the applications of molecular thin films as well as for the fundamental understanding of quantum friction. Here, we employ atomic/molecular manipulation schemes to investigate mechanic and symmetry dependent lateral diffusion processes of individual molecules on various substrates using a combined scanning tunneling microscope (STM) and q+ atomic force microscopy system at low temperature and in ultrahigh vacuum environment. Lateral force measurements of individual sexiphenyl, an oligomer type molecule, exhibits an interesting friction behavior originated from the symmetry of the molecule-substrate system. We found ~160% increase in the lateral force during the diffusion of the molecule across a Ag(111) surface depending on the long molecular axis alignment on the surface. A comparison of the shape and symmetry dependent molecular diffusion process is realized by manipulating cobalt-porphyrin molecules on aAu(111) surface. The results are in full agreement with molecular dynamic simulations. In addition, we will also discuss atomic and molecular level force measurement using an STM tip, which opens simultaneous electronic, structural and force measurements at the single atom and molecule level.

Electronic Materials and Photonics Division
Room: 14 - Session EM+MI+NS+SP+SS-ThM

Photonics, Optoelectronics, and Light Manipulation

Moderators: Yohannes Abate, Georgia State University, Nikolaus Dietz, Georgia State University

8:00am **EM+MI+NS+SP+SS-ThM1 Evolutionary Design of Multi-functional Optical Metasurfaces**, ***Teri Odom***, Northwestern University **INVITED**

Metasurfaces are an emerging class of flat optics that can manipulate light via subwavelength phase elements. Their 2D structures are usually determined by (1) calculating the phase change required at each location to obtain far-field properties from analytical equations and (2) structuring each building block to produce that wavefront change. However, computational or digital approaches to design metasurfaces based on search heuristics offer advantages in targeting and realizing properties not possible by analytical expressions. This talk will describe an evolutionary approach to design flat lenses based on subwavelength plasmonic building blocks. Our lattice evolution algorithm can achieve desired optical responses by tuning the arrangement of the phase units on a discrete square lattice. We will discuss two different systems with different classes of building units—holes and particles—to realize achromatic lattice lenses at up to three wavelengths and flat lenses in semiconductor plasmonic materials such as titanium nitride. We will describe prospects for scaling the production of these lenses as well as their ability to achieve dynamic optical responses.

8:40am **EM+MI+NS+SP+SS-ThM3 Dielectric Freeform Metasurfaces for Optical Sensing**, ***Arka Majumdar***, University of Washington, Seattle **INVITED**

The macroscopic volume of optical sensors, such as cameras, often originates from the requirement of having multiple optical elements and thick spherical geometries. In recent years, researchers have made subwavelength optical elements, commonly known as metasurfaces, with an ultra-thin form factor using well-developed semiconductor nano-fabrication technology. In parallel with the progress in such nano-photonic devices, researchers have also made vast improvements in the field of freeform optics. Freeform optics aim to expand the toolkit of optical elements beyond those exhibiting rotational symmetry. Most conventional optical elements have rotational symmetry for manufacturing reasons, but freeform optics emphasizes complex surface geometries, which are difficult to manufacture by traditional means. While both metasurface and freeform optics have progressed substantially in recent years, they have developed independently of one another as their respective research communities are disconnected.

In our work, we demonstrated how metasurface technology can be used for the realization of subwavelength scale freefrom optics, with applications in implantable bio-sensing and potentially in augmented reality systems. I will present some of our recent results on metasurface freeform optics that enable a large depth of focus and a tunable focal length lens. I will also show how these metasurfaces can be used to perform truly colored imaging, by virtue of the extended depth of focus. Finally, I will talk about our ongoing work on metasurface based cavity engineering.

9:20am **EM+MI+NS+SP+SS-ThM5 Moth eye-based, graded index surface treatments to control reflection and light extraction**, *L. Chan, C. Pynn, P. Shapturenka, R. Ley, S. Denbaars, D. Morse,* ***Michael Gordon***, University of California at Santa Barbara

This talk will highlight our recent work on bio-inspired surface treatments to control reflection and enhance light extraction at interfaces. An easy, scalable and defect-tolerant surface modification protocol, based on colloidal lithography and plasma etching, was developed to create synthetic 'moth-eye' (ME) anti-reflective structures in different material platforms for photonics and energy applications. Large increases in transmission, bandwidth, and omni-directional response were obtained in Si, Ge, GaAs, ZnS/ZnSe, and CdTe platforms for IR (2-50+ um), with performance better than commercial, interference-based coatings. Effective medium theory, finite difference time domain (FDTD) simulations, and quantitative measurements of transmission, reflection and diffuse scattering were used to understand the ‘photon balance’ of ME films to investigate how optical behavior depends on moth-eye geometry, (dis)order, and pattern fidelity. ME coatings were also implemented in blue-green InGaN/GaN quantum well LED structures on c-plane and semi-polar substrates to enhance light extraction and device efficiency. A 4.8-fold overall enhancement in light extraction (9-fold at normal incidence) compared to a flat surface was achieved using a feature pitch of 2530 nm—performance on par with current photoelectrochemical (PEC) roughening methods. The colloidal lithography roughening technique presented herein is independent of GaN crystal orientation and is therefore applicable to roughening semipolar and nonpolar GaN devices, on which PEC roughening is ineffective.

9:40am **EM+MI+NS+SP+SS-ThM6 Infrared Surface Plasmon-influenced Interfacial Chemistry of Semiconductor Nanocrystals**, *W. Hu,* ***Michael Filler***, Georgia Institute of Technology

Localized surface plasmon resonances (LSPRs) present exciting opportunities to improve the spatial and temporal control of chemistry at semiconductor surfaces. While the ultraviolet and visible LSPRs supported by metallic nanoparticles are known to impact surface chemistry, heavily-doped semiconductor nanocrystals promise similar capabilities in the near and mid-infrared. Here, we use time-resolved *in situ* infrared spectroscopy to study the influence of mid-infrared LSPRs on a model interfacial process: desorption. We find that the molecular desorption rate for a range of "beacon" molecules (e.g., indole, benzoic acid) on indium tin oxide (ITO) nanocrystals is enhanced by as much as 2x upon illumination with mid-infrared light (~0.6-0.1 eV) at room temperature. The desorption rate is linearly dependent on light intensity, indicating a single photon process. Experiments as a function of LSPR energy, nanocrystal film thickness, and adsorbate concentration provide clues as to the mechanism of the enhancement. Our findings open new avenues to leverage low energy photons for manipulating chemical reactions on the surfaces of heavily-doped semiconductors.

11:00am **EM+MI+NS+SP+SS-ThM10 Dynamically Tunable Polarization Response in a Si/Au Metamaterial**, ***Nicole Pfiester***, Tufts University, *C. Shemelya,* Technische Universität Kaiserslautern, Germany, *D. DeMeo, E. Carlson, T.E. Vandervelde*, Tufts University

Polarimetry is utilized across many fields, from chemical characterization to classification of astronomical objects to the detection of man-made items. Present technology requires a different filter for each polarization of light you wish to measure. This requires either a cluster of four pixels to differentiate between the polarizations incident on an area, reducing the final image resolution compared to a non-polarized image, or a filter wheel that adds weight and mechanical reliability issues. Metamaterials can be leveraged to design materials with a polarization sensitive response. Application of a bias voltage can further alter the material’s interaction with incident light, resulting in a metamaterial whose response can be tuned dynamically. This technique can be used to create a filter that can be turned on and off for a given polarization. An integrated stack of these filters would allow the measurement of any polarization direction at the full resolution capacity of the detector with the advantages of on-chip integration.

We designed a metamaterial structure that generates a polarization-dependent response in the mid-infrared wavelength range. Off-setting the absorption and transmission peaks for the two polarizations allows equal transmission while the filter is in a static state, or without a bias voltage. The application of a bias changes the metamaterial response and blocks polarized waves parallel to one axis. A thin film semiconductor layer is required to achieve this effect. Previous work utilized thin film gallium arsenide, but poor film quality of the epitaxial layer, with surface roughness on the order of the metamaterial feature size, did not provide sufficient conductivity for an applied bias to impact the light interactions. We will present new results using thin film silicon with a gold nanostructure pattern. A static filter, one that does not require an applied voltage to operate as a polarizing filter, was fabricated to demonstrate the design suitability. We will report on our progress toward a dynamic filter and compare to previous results with III-V films.

11:20am **EM+MI+NS+SP+SS-ThM11 Imaging Stress Induced Lateral Quantum Barrier Manipulation of Indium Gallium Arsenide Quantum Wells, using Micro-Photoluminescence Spectroscopy**, ***Brian Rummel***, *M. Rimada, S. Addamane, G. Balakrishnan,* University of New Mexico, *T. Sinno,* University of Pennsylvania, *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 epitaxial compound semiconductor films.[1] This compositional patterning laterally manipulates quantum barriers within the film in a press-and-print manner, completely eliminating the need for Stranski-Krastanov growth. For the proof-of-concept, the said mechanism was used to diffuse Ge in a SiGe substrate to form regions of Ge-depleted, pure Si surrounded by SiGe. This result opened the door to thermo-mechanically triggered, rewritable circuitry for a wide variety of applications. For the current effort on InGaAs quantum well systems, an array of Si pillars is pressed against a GaAs/In$_{.20}$Ga$_{.80}$As/GaAs substrate in a mechanical press, and the assembly is heated to elevated temperatures. The applied elastic stress field promotes the diffusion of larger In atoms away from the compressed regions, leaving In-depleted GaAs in localized regions of the quantum well. Careful assembly and design of the Si nanopillar array would controllably define GaAs and InGaAs regions, producing laterally organized quantum structures. Photoluminescence spectroscopy is used to confirm the diffusion of In and compositional variation, based on the wavelength shift of the emission line from the InGaAs quantum well. In this presentation, we will further discuss how micro-photoluminescence imaging can be used to directly image regions of In-enriched regions as well as In-depleted regions found under the elastically compressed areas. This method may allow us to register the compositionally altered regions for addressable circuitry.

[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," *Appl. Phys. Lett.***107,** 072106-1:5 (2015).

11:40am **EM+MI+NS+SP+SS-ThM12 Silicon-Based Infrared Photodetectors Enabled by Hot Electrons**, ***Seok-Jun Han***, *S.M. Han, S.E. Han*, University of New Mexico

Infrared (IR) detectors typically employ low band gap materials, such as InGaAs, InSb, or HgCdTe. However, these materials include elements that are rare, expensive, or toxic. Past research indicates that low-cost, abundant crystalline Si (c-Si) could be used for IR detection when metal electrodes are appropriately nanostructured. In this type of photodetection, the IR with energies below the Si band gap is strongly absorbed by the metal structures. The photoexcited electrons in the metal can then be injected into the conduction band of c-Si before being thermalized, and electric current can be generated. These non-thermalized hot electrons enable the detection of IR light with energies below the c-Si band gap. For efficient transport of electrons in the metal before thermalization, the metal layer should be as thin as approximately the electron mean free path. To induce strong optical absorption in such a thin metal layer, surface plasmon polaritons (SPPs) can be excited at the metal surface. Previous studies on hot electron photodetection utilized small-scale metamaterials or deep trench resonators to have strong resonant absorption of SPPs in thin metal films on c-Si at the desired frequencies. However, these structures had to be fabricated with high precision (e.g., e-beam lithography) because the metal structure size determines resonance. In this study, we pursue a low-cost, manufacturable path, which can tolerate practical fabrication errors. We make use of metal metasurfaces that can be fabricated by scalable, inexpensive techniques and achieve a broad-band IR absorption of over 95% in 15-nm-thick metal films. This unprecedented strong and broad-band absorption is enabled by a new scheme which uses multiple modes of SPPs while the light takes multiple passes within the c-Si substrate. During the passage, light is preferentially absorbed by the thin metal layer that is on one side of the substrate. Absorption on the other side is efficiently eliminated by using a dielectric layer. In our effort, the surface of the c-Si substrate where thin meal film is deposited is structured by a simple optical lithography. The structured surface admits the incident light into the substrate and prevents the light from leaking out of the substrate. In our scheme of multiple light passes, extremely strong resonances are not necessary and fabrication errors would not destroy the optical properties appreciably. In this talk, we will discuss the details of the optical absorption in our scheme. We will also present our experimental results on the electronic characteristics of our hot electron devices.

12:00pm **EM+MI+NS+SP+SS-ThM13 Low Temperature Wafer Bonding of LTG-GaAs to $Si_3N_4$for Terahertz Photoconductive Switch Application**, *X. Fu,* Illinois Institute of Technology and Argonne National Laboratory, *M. Haji-Sheikh, G. Westberg, S. Ross,* Northern Illinois University, *E. Landahl,* DePaul University, *K. Attenkofer,* Brookhaven National Laboratory, ***Thomas Wong***, Illinois Institute of Technology

Integrating GaAs optoelectronic devices with Si- based platforms has attracted much attention and efforts in recent years, as a thin layer of GaAs can exhibitsuperior bulk quality. Wafer bonding, an emerging approach of monolithic integration of GaAs on Si-based substrate, overcomes the lattice mismatch in heterogeneous growth. Several techniques with a post-bonding annealing at temperature exceeding 800°C have been demonstrated to achieve high-energy covalent bonds between III-V compound semiconductors and Si/SiO_2systems. However, the elevated temperature bonding process may create not only an inevitable thermal mismatch barrier but also damage the bonding materials. Thus, there is a need for improved technique to integrate GaAs with silicon based devices.

Low temperature grown (LTG) GaAs, which is typically obtained by molecular beam epitaxy (MBE) at temperatures as low as 200°C, offers very attractiveproperties such as ultra-short carrier lifetime, high electron mobility and high resistivity. It is verydesirable for applications such as ultrafast photoconductive switch, high efficiency solar cells and infrared LEDs. Pioneering work has demonstrated techniques to bond LTG-GaAs to Si/ SiO_2 at temperature as low as room temperature by means of plasma activation and by wafer bonding under vacuum. However, very few techniques have been developed to bond LTG-GaAs layer to Si_3N_4 substrate, mainly because Si_3N_4 is naturally hydrophobic and bonding has been considered unachievable10. The existing Si_3N_4 bonding techniques employ high temperature fusion of Si_3N_4 layers or apply a layer of bonding agent such as SiO_2.

In this paper, we report a room temperature approach to directly bond LTG-GaAs to Si_3N_4 by activating the surface of Si_3N_4 using weak HF acid solution. This method can be implemented on Si_3N_4 deposited over wide temperature range. Procedures to reduce the bonding voids and improve the bond strength are also described. In an application to utilize the developed method, we implemented this approach to fabricate a photoconductive switch on Si_3N_4 substrate bonded with LTG-GaAs and validated that the bonded LTG-GaAs retained the electro-optical properties. A THz opticalcross correlation test showed that the photoconductive switch responded swiftly to a femtosecond Ti-Sapphire laser pulse with a resolution of approximately 0.25ps. This wafer bonding method can be integrated with a wide range of microelectronic device fabrication thatrequires the bonding of LTG-GaAs layer with Si_3N_4.

Advanced Ion Microscopy Focus Topic
Room: 7 & 8 - Session HI+BI+NS+TR-ThM

Advanced Ion Microscopy Applications

Moderators: Armin Golzhauser, Bielefeld University, Germany, Olga Ovchinikova, Oak Ridge National Laboratory

8:00am **HI+BI+NS+TR-ThM1 Scanning Helium Atom Microscopy: Imaging with a Deft Touch**, ***Paul Dastoor***, University of Newcastle, Australia **INVITED**

Delicate structures (such as biological samples, organic films for polymer electronics and adsorbate layers) suffer degradation under the energetic probes of traditional microscopies. Furthermore, the charged nature of these probes presents difficulties when imaging with electric or magnetic fields, or for insulating materials where the addition of a conductive coating is not desirable. Scanning helium microscopy is able to image such structures completely non-destructively by taking advantage of a neutral helium beam as a chemically, electrically, and magnetically inert probe of the sample surface. Here, we present scanning helium micrographs demonstrating image contrast arising from a range of mechanisms including, for the first time, chemical contrast observed from a series of metal-semiconductor interfaces [1]. The ability of neutral helium microscopy to distinguish between materials without the risk of damage makes it ideal for investigating a wide range of systems.

1. M. Barr, A. Fahy, J. Martens, A.P. Jardine, D.J. Ward, J. Ellis, W. Allison & P.C. Dastoor, "Unlocking new contrast in a scanning helium microscope", *Nature Communications*, **7**, 10189, (2016).

8:40am **HI+BI+NS+TR-ThM3 Biofilm Structure of Geobacter Sulfurreducens by Helium Ion Microscopy**, ***Alex Belianinov***, Oak Ridge National Laboratory, *M. Halsted, M.J. Burch,* Oak Ridge National Laboratory, *S. Kim, S. Retterer*, Oak Ridge National Laboratory

Microbial communities form biofilms on material surfaces in a multitude of ecosystems, from the root hairs of a plant to the human gut. The hallmarks of an established biofilm include (1) the attachment of microbial cells to a surface, (2) production of extracellular polymeric substance, (EPS) (3) a complex structure or "architecture," and (4) the ability to exchange genetic information between cells. [1] Geobacter sulfurreducens forms unique, electrically conductive biofilms, a property that can be exploited in production and design of microbial fuel cells. In this work, examine biofilm formation, and biofilm properties of Geobacter sulfurreducens using a Scanning Electron Microscope (SEM) as well as a Helium Ion Microscope (HIM).

SEM is a high-resolution imaging technique used for characterization of a broad variety of materials. However, in order to image highly insulating, soft biological materials, the samples must be coated for charge compensation. These (typically) metallic coatings create a homogenous surface and may cloak true biological behavior and material contrast in the micrograph. In the case of Geobacter sulfurreducens, metal coating precludes detailed investigation of microbial attachment, presence of EPS, and fine surface details that may elucidate the mechanisms behind architecture formation and genetic material exchange.

Recently introduced HIM, offers more flexibility in investigating biological samples, as highly insulating sample can be imaged sui generis, without the use of a conductive coating. [2] This opens new pathways to capturing high resolution spatial details of biofilm formation and biofilm properties. Furthermore, high-resolution HIM imaging reveals true surface details of Geobacter sulfurreducens, such as flagella or pilin typically inaccessible by

SEM. Finally, the effects of different sample preparation strategies for SEM and HIM will be illustrated and discussed.

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Acknowledgements:

This research was supported by Oak Ridge National Laboratory’s Center for Nanophase Materials Sciences (CNMS), which is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

9:00am **HI+BI+NS+TR-ThM4 Channeling via Transmission He Ion Microscopy**, ***Christoph Herrmann***, Simon Fraser University, Canada, *S.A. Scott, M. Lagally*, University of Wisconsin-Madison, *K. Kavanagh*, Simon Fraser University, Canada

The spatial coherence of focussed helium (He) ion beams is significant. The He ion source is atomic size (W filament tip) and the resolution from scanning probe, ion-induced secondary electron images is sub 1 nm. Scanning transmission images with atomic resolution are theoretically predicted. We have been experimenting with a digital camera located underneath the sample stage and tilt cradle of our instrument (Zeiss Nanofab). The camera consists of an array of Si p-i-n diodes (55 μm square pixels) that allow direct detection of single He ions and atoms (20 keV - 40 keV). We have previously reported that the beam intensity profiles are uniformly distributed, as expected from the small de Broglie wavelength (80 fm), with a half angle convergence of 2 mrad.[1] At beam currents in the pA range the detector count rate was consistent with one count per He ion or atom. In this talk, we will present results that indicate planar channeling in single crystalline Si (100) membranes (25 nm - 75 nm thick). The transmission intensity as a function of position depends on the beam incidence angle, and beam energy, with random incidence profiles consistent with monte carlo scattering and range calculations (SRIM). The peak in transmission as a function of incidence angle has a half angle width of 1° at 25 kV. These results will be compared with theoretical calculations based on impact factors at low energies. Channeling experiments with other thin crystalline materials including graphite and MgO will be discussed. **Acknowledgements**: We thank Norcada Inc. (Edmonton) for supplying Si (100) 50 nm thick membranes; NSERC, CFI/BCKDF, 4DLABs for funding. [1] K.L. Kavanagh and C. Herrmann, Direct He Detection for Transmission Helium Ion Microscopy, Microsc. Microanal. submitted 2017.

9:20am **HI+BI+NS+TR-ThM5 Rapid Imaging of Nano-Porous Catalyst Particles Via Helium Ion Microscopy**, *M.J. Burch, A.V. Ievlev,* ***Holland Hysmith***, Oak Ridge National Laboratory, *K. Mahady, P.D. Rack*, University of Tennessee, *L. Luo*, ExxonMobil Chemical Company, *A. Belianinov*, Oak Ridge National Laboratory, *S. Yakovlev*, ExxonMobil Chemical Company, *O.S. Ovchinikova*, Oak Ridge National Laboratory

Porous materials are some of the most important modern day material systems, as the pore structure defines many materials applications and functionality. The pore structure of catalyst precursor particles, in particular, is of great importance to the catalyst community, as this pore structure dictates the efficiency and efficacy of grown polymers. However, despite the importance of these materials systems, there are few techniques to analyze pore size and structure. The most common technique is gas absorption, where the amount of gas absorbed and desorbed from a known amount of material is tracked and the average pore volume and size can be extracted. However, the technique is heavily dependent on sample quality and which fitting model is used to calculate volume and size. In addition, the technique is quite slow, where generally at most a single sample can be analyzed a day.

In this work, we demonstrate a novel technique to directly image and quantify pore size in nano-porous catalyst precursor particles via helium ion microscopy. We demonstrate the technique by directly imaging the surface pore structure of SiO_2 precursor catalyst particles with helium ion microscopy. Using modern day data analytics, we created an automated routine to extract pore size and distributions. We show that our HIM based technique shows comparable data to the industry standard gas absorption technique, within a 5 percent difference between the techniques of a known porous samples.

Further, to determine the effect of the helium beam on the surface of the SiO_2 particles, we simulate the beam interaction between porous SiO_2 particles and the helium beam. At low ion doses the surface modification by the ion beam is quite negligible, where at higher ion doses, significant surface modification is observed.

In conclusion, we’ve demonstrated a novel technique to directly visualize and quantify nano-pore size and structure in SiO_2 that yields complimentary data to gas absorption.

Acknowledgements

This work was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy (DOE) Office of Science User Facility. The users acknowledge the ExxonMobil Chemical Company for funding.

9:40am **HI+BI+NS+TR-ThM6 Ion Beam Induced Current Measurements of Solar Cells with Helium Ion Microscopy**, *A. Belianinov, S. Kim,* ***Ryan Cannon***, *M.J. Burch, S. Jesse, O.S. Ovchinnikova*, Oak Ridge National Laboratory

The scanning electron microscope (SEM) is a versatile high-resolution microscopy tool, and perhaps the most widely used imaging platform across many engineering and scientific fields [1]. Within the last decade, another microscopy technique based on a gaseous field ionization source, utilizing Helium and Neon ions has been introduced [2]. While the popularity of the SEM is hardly challenged by the Helium Ion Microscopy (HIM), there are instances when imaging with ions offers significant advantage as opposed to imaging with electrons. In principle, both HIM and the SEM share many similarities, for example, a HIM operating at 40 keV will generate ions with velocity comparable to SEM operating at 5 keV. However, due to much higher stopping power of ions, as compared to electrons, ion based secondary electron (iSE) will be higher. Also, as a result, there is little ion backscattering, and consequently, the concentration of the ion-generated iSE2 (additional secondary electron generated by SE interaction within the material) is usually insignificant.

In this work, we exploit small interaction volumes in the HIM, and take advantage of the lower iSE2 yield, and positively charged helium ions to map ion beam induced current (IBIC) in solar cell materials. Similar studies, using electrons, have visualized induced current profiles at grain profiles in polycrystalline solar cells, and in silicon [3, 4]. Furthermore, broad ion sources have been utilized in conjunction with scanning probe systems in the past to map out current changes in FinFETs [5]. We are interested in utilizing the HIM to map current at the nanoscale near p-n junctions in CdTe to elucidate differences in contrast captured by the ion beam induced current, as opposed to the electron beam induced current. These findings will illustrate the peculiarities of ionic transport in these solar cell materials, and will evaluate the HIM technology as a potential quality control tool.

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11:00am **HI+BI+NS+TR-ThM10 Writing Magnetic Domains with a Helium Ion Microscope**, ***Daniel Emmrich***, Bielefeld University, Germany, *A. Gaul, D. Holzinger, A. Ehresmann*, University of Kassel, Germany, *F. Karimian, M. Klug, J. McCord*, Kiel University, Germany, *A. Beyer, A. Gölzhäuser*, Bielefeld University, Germany

Microscopes based on gas field ion sources offer surface-sensitive, high resolution imaging and state of the art nano-machining.[1] It was further shown that light ions like helium or neon enable a modification of the magnetic properties, e.g., turning thin films from paramagnetic to ferromagnetic state, without significant sputtering.[2]

In this work, two-dimensional ion bombardment induced magnetic patterning (IBMP)[3] is demonstrated with a helium ion microscope to create magnetic domains in an exchange biased thin film system. Such a system consists of a thin ferromagnetic layer coupled to an underlying antiferromagnet. Low dose helium ion irradiation at an energy of 15 keV in an external magnetic field leads to a new, remanent magnetization direction, determined by the external magnetic field. By subsequently patterning the sample in differently orientated external magnetic fields, complex magnetic domain patterns such as chiral structures can be written. Based on magnetic force microscopy and optical Kerr microscopy, we will discuss the achievable resolution as well as the shapes of different artificial magnetic domains.

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11:20am **HI+BI+NS+TR-ThM11 Characterisation of Nanomaterials on the Helium Ion Microscope using Correlative Secondary Electron and Mass Filtered Secondary Ion Imaging**, *J.-N. Audinot, D.M.F. Dowsett, F. Vollnhals, T. Wirtz*, Luxembourg Institute of Science and Technology (LIST), Luxembourg, ***John A. Notte***, Carl Zeiss Microscopy, LLC

In order to add nano-analytical capabilities to the Helium Ion Microscope, we have developed a Secondary Ion Mass Spectrometry (SIMS) system specifically designed for the Zeiss ORION NanoFab [1-3]. SIMS is based on the generation and identification of characteristic secondary ions by irradiation with a primary ion beam (in this case helium or neon). It is an extremely powerful technique for analysing surfaces owing in particular to its excellent sensitivity (detection limits down to the ppb are possible, so that SIMS can be used to detect both major and trace elements), high dynamic range (a same signal can be followed over several orders of magnitude), high mass resolution and ability to differentiate between isotopes.

In SIMS, the typical interaction volume between the impinging ion beam and the sample is around 10 nm in the lateral direction. As the probe size in the HIM is substantially smaller (both for He and Ne), the lateral resolution on the integrated HIM-SIMS is limited only by fundamental considerations and not, as is currently the case on commercial SIMS instruments, the probe size [4,5]. We have demonstrated that our instrument is capable of producing elemental SIMS maps with lateral resolutions down to 12 nm [3-5].

Furthermore, HIM-SIMS opens the way for in-situ correlative imaging combining high resolution SE images with elemental and isotopic ratio maps from SIMS [4,5]. This approach allows SE images of exactly the same zone analysed with SIMS to be acquired easily and rapidly, followed by a fusion between the SE and SIMS data sets.

In this talk, we will present a number of examples taken from various fields of materials science (battery materials, solar cells, micro-electronics, coatings) and life science (nanoparticles in creams and biological tissues) to show the powerful correlative microscopy possibilities enabled by the integrated HIM-SIMS instrument.

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Nanometer-scale Science and Technology Division
Room: 19 - Session NS+AS+EM+MI+SP+SS-ThM

Nanoscale Imaging and Characterization

Moderators: Stephane Evoy, University of Alberta, Canada, Indira Seshadri, IBM Research Division, Albany, NY

8:00am **NS+AS+EM+MI+SP+SS-ThM1 Characterizing Optoelectronically-Active Molecules via STM Imaging and Advanced Raman Spectroscopy Techniques**, *J. Schultz, P. Whiteman, Z. Porach, **Nan Jiang***, University of Illinois at Chicago

In response to the ever increasing demand for cleaner, cheaper energy generation, significant efforts have been made to fabricate and characterize materials that can be used for optoelectronic devices. Porphyrins, phthalocyanines, and their derivatives have been involved in many surface studies to investigate their optoelectronic properties for use in organic photovoltaics and other optoelectronic devices, such as organic light-emitting diodes (OLED). Our research take place in a commercial ultrahigh vacuum (UHV) scanning tunneling microscopy (STM) chamber. Molecules were evaporated onto various single crystal substrates at a base pressure of 10^{-10} torr. Different surface-supported structures were imaged via STM at sub-molecular resolution, allowing the competition of molecule-substrate and molecule-molecule interactions to be investigated.

In addition to imaging via STM, we also performed spectroscopy experiments in the forms of UHV Tip Enhanced Raman Spectroscopy (TERS), supplementing vital vibrational information at single-molecule spatial resolution. These tools provide a complete picture of the system in question, allowing our lab to answer previously unknown questions regarding the molecule-molecule interactions in order to characterize the molecule's exciton-generating and electron-transferring properties at a fundamental level.

8:20am **NS+AS+EM+MI+SP+SS-ThM2 BCC to FCC Phase Transition of Pd_xCu_{1-x} at Nanoscale**, ***Xiaoxiao Yu***, Carnegie Mellon University, *A. Gellman*, Carnegie Mellon University, W.E. Scott Institute for Energy Innovation

One of the most interesting characteristics of alloy nanoparticles (NPs) is that they can have different phases from those of the bulk. In the bulk phase diagram of Pd_xCu_{1-x}, there exists a composition range, $0.35 < x < 0.55$, over which a B2 phase (ordered body centered cubic, CsCl structure) is formed at T < 873 K, in spite of the fact that pure Pd and Cu both have face centered cubic (FCC) bulk crystal structures. An experimental methodology has been developed for determining the phase behavior of Pd_xCu_{1-x} size and composition spread nanoparticle (SCSNP) libraries. Spatially resolved X-ray photoemission spectroscopy (XPS) was used to map the Cu $2p_{3/2}$ core level shifts (CLS) with respect to the value for pure Cu across composition space on the bulk Pd_xCu_{1-x} alloy. The result has shown that the Cu $2p_{3/2}$ binding energy decreases monotonically with increasing Pd at.% in the FCC phase. There is additional discontinuous CLS over the composition range from 0.35 to 0.55 Pd at.%, where the B2 phase forms. Therefore, the Cu $2p_{3/2}$ core level binding energy measured by XPS can be used to distinguish between the ordered B2 phase and disordered FCC phase. The Pd_xCu_{1-x} SCSNP library on a Mo substrate was prepared using a rotatable shadow mask deposition tool previously developed by our group. After annealing the Pd_xCu_{1-x} alloy thin film to 700 K, the additional CLS over the composition range, $0.35 < x < 0.55$, has been observed at a film thickness > 6 nm, which suggests the formation of B2 phase. However, at a film thickness between 4 – 6 nm, the Cu $2p_{3/2}$ binding energy decreases monotonically across composition space which suggests that only FCC phase exists for alloy films in this thickness range. Because the FCC phase is more densely packed than the B2 phase, the surface tension in this thickness regime can drive a conversion from the ordered B2 phase back to the randomly distributed FCC solid solution. More interestingly, the additional CLS over the composition range from 0.35 to 0.55 Pd at.% reoccurs at a film thickness < 4 nm, which suggests the formation of B2 phase. This observation is the result of dewetting of the Pd_xCu_{1-x} NPs after heating at 700 K for 30 mins, and the size of dewetting NPs exceeds 6 nm where the close-packed FCC phase is stabilized. Dewetting of Pd_xCu_{1-x} NPs is validated by the appearance of the substrate Mo XPS signal at a film thickness < 4 nm. This comprehensive experimental study of the phase behavior for Pd_xCu_{1-x} alloy NPs will be correlated with their catalytic activity across composition and size spaces to accelerate the development of alloy NPs for catalytic applications.

8:40am **NS+AS+EM+MI+SP+SS-ThM3 Hybrid Environmental Transmission Electron Microscope: An Integrated Platform for In situ Imaging and Spectroscopies**, ***Renu Sharma***, NIST **INVITED**

Environmental transmission electron microscopes (ETEM) and TEM holders with windowed reaction cells, enable in situ measurements of the dynamic changes occurring during gas-solid and/or liquid-solid interactions. The combination of atomic-resolution images and high spatial and energy resolution has successfully revealed the nucleation and growth mechanisms for nanoparticles, nanowires, carbon nanotubes and the functioning of catalyst nanoparticles. While TEM-based techniques are ideally suited to distinguish between active and inactive catalyst particles and identify active surfaces for gas adsorption, we still must answer the following questions: (1) Are our observations, made from an area a few hundred nanometers in extent, sufficiently representative to determine the mechanism for a specific reaction? (2) Is the reaction initiated by the incident electron beam? (3) Can we determine the sample temperature accurately enough to extract quantitative kinetic information? And (4), can we find efficient ways to make atomic-scale measurements from the thousands of images collected using a high-speed camera. The lack of global information available from TEM measurements is generally compensated by using other, ensemble measurement techniques such as x-ray or neutron diffraction, x-ray photoelectron spectroscopy, infrared spectroscopy, Raman spectroscopy etc. However, it is almost impossible to create identical experimental conditions in two separate instruments to make measurements that can be directly compared.

We have designed and built a unique platform that allows us to concurrently measure atomic-scale and micro-scale changes occurring in samples subjected to identical reactive environmental conditions by incorporating a Raman Spectrometer into the ESTEM. We have used this correlative microscopy platform i) to measure the temperature from a 60 μm^2 area using

Raman shifts, ii) to investigate light/matter interactions in plasmonic particles iii) to act as a heating source, iii) to perform concurrent optical and electron spectroscopies such as cathodoluminescence, electron energy-loss spectroscopy and Raman. We have developed an automatic image-processing scheme to measure atomic positions, within 0.015 nm uncertainty, from high-resolution images, to follow dynamic structural changes using a combination of algorithms publicly available and developed at NIST. This method has been proven to capture the crystal structure fluctuations in a catalyst nanoparticle during growth of single-walled carbon nanotube (SWCNT). Details of the design, function, and capabilities of the optical spectrum collection platform and image processing scheme will be presented.

9:20am **NS+AS+EM+MI+SP+SS-ThM5 Critical Dimension Metrology by Localization Optical Microscopy**, *C.R. Copeland, C.D. McGray, J.C. Geist, J.A. Liddle, B.R. Ilic,* ***Samuel Stavis***, NIST

Optical microscopy methods of localizing subresolution emitters are broadly useful in many fields from biology to nanofabrication. Precision and accuracy are fundamental for localization measurements. Subnanometer precision is readily achievable for many emitters and can elucidate structure and motion at atomic scales, but is potentially false precision in the absence of calibrations that enable corresponding accuracy, particularly over a wide field for imaging and tracking. Whereas improving localization precision generally requires counting more photons by increasing emitter intensity and stability, improving localization accuracy presents diverse challenges in the calibration of an optical microscope as a measurement system. This involves not only its discrete components but also their interaction during a measurement. Such calibration is complex, motivating the development of practical devices and methods to facilitate the process, which we present here.

First, we characterize a complementary metal oxide semiconductor (CMOS) camera, enabling full use of its dynamic range and megapixel array. Next, we fabricate aperture arrays by electron-beam lithography and test them as calibration devices, exploiting their uniformity and stability. Then, we refine localization analysis, presenting a novel estimator and accommodating saturation. Finally, we evaluate aberrations of our optical system, including field curvature, distortion, and others that break the symmetry of the point spread function. After calibrating our system in this way, we validate our widefield measurements and demonstrate critical dimension localization microscopy (CDLM) of aperture arrays, and answer open questions about the apparent motion of nanoparticle fiducials. Our study casts new light on localization microscopy at subnanometer scales.

Our study also highlights the importance of nanoscale fabrication and metrology in achieving localization accuracy. Previous studies have applied aperture arrays for lens evaluation but have not quantified their critical dimensions, in particular the array pitch. This is essential to ensure that electron-optical aberrations do not propagate as errors through the calibration and correction of photon-optical aberrations. Moreover, the application of CDLM to aperture arrays provides useful information on the effects of dose delivery and beam scanning to optimize the future nanofabrication of reference materials.

9:40am **NS+AS+EM+MI+SP+SS-ThM6 Tunable Emission from Nanophotonic Structures in a Modified SEM: Characterizing Smith Purcell Radiation Generation from the VUV to the Near IR**, ***Steven Kooi***, *I. Kaminer, A. Massuda, M. Soljačić, C. Roques-Carmes*, MIT

We present theoretical predictions and experimental results of multiple order Smith-Purcell radiation in a variety of samples from periodic high aspect ratio silicon nanowire structures to engineered metasurfaces using low-energy electrons (2.5 -20 keV) in a modified scanning electron microscope. The samples emit photons in a controlled way and we demonstrate optical emission from the VUV to the near IR, opening a pathway to building a fully tunable optical source that we intend to extend into the soft X-Ray regime.

11:00am **NS+AS+EM+MI+SP+SS-ThM10 Ultrafast Optical Response of Graphene/$LaAlO_3/SrTiO_3$ Heterostructure**, *L. Chen, E. Sutton, J. Li, M. Huang, J.F. Hsu, B. D'Urso,* University of Pittsburgh, *J.W. Lee, H. Lee, C.B. Eom,* University of Wisconsin-Madison, *P. Irvin,* ***Jeremy Levy***, University of Pittsburgh **INVITED**

The unique electronic and optical properties of graphene make it a promising device in terahertz(THz) regime. Another 2D electron system, the complex-oxide heterostructure $LaAlO_3/SrTiO_3$, has been shown to exhibit great promise for control and detection of broadband THz emission at extreme nanoscale dimensions[1]. Recently, we have successfully integrated these two platforms: we have created graphene/$LaAlO_3/SrTiO_3$ structures with (1) high mobility in the graphene channel[2] and (2) oxide nanostructures patterned directly underneath the graphene layer[3]. Here we describe new experiments that probe graphene with this nanoscale THz spectrometer using ultrafast optical techniques. This unprecedented control of THz radiation at 10 nm length scales creates a pathway toward hybrid THz functionality in graphene/$LaAlO_3/SrTiO_3$ heterostructures.

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11:40am **NS+AS+EM+MI+SP+SS-ThM12 Single-Molecules Fluorescence Spectroscopy and Lifetime with Simultaneous Super-resolution Imaging for Materials Science Applications**, ***James Marr***, CNST/NIST and University of Maryland, *M. Davanço,* CNST/NIST, *S.J. Stranick,* NIST, *B.R. Ilic, J.A. Liddle*, CNST/NIST

We have developed a widefield imaging system that measures single-molecule position, orientation, lifetime and fluorescence spectra. We achieve this by combining conventional super-resolution imaging using an sCMOS detector with a unique, photon-counting, wide-field, high-temporal, high-spatial resolution, high-throughput, three-dimensional detector (H33D). The use of dual-objectives maximizes the fluorescent photon flux to each camera. Individual fluorophore point-spread functions collected by the sCMOS detector provide position and orientation information, while the 100 ps timing resolution of the H33D detector enables us to make precise lifetime measurements of the same fluorophore. By incorporating a diffraction grating into the beam path of the sCMOS camera we can simultaneously record both a zero-order image of each fluorophore for position and orientation measurement, and a wavelength-dispersed image that provides single-molecule spectroscopic data. The sensitivity of fluorophore lifetime, spectroscopic behavior, orientation, and position to dynamic processes in soft materials with nanosecond, millisecond, and second timescales, respectively, enables us to collect three-dimensional, local structure-property information that would otherwise be impossible to obtain. We have fabricated unique structures that enable us to accurately determine the influence of metallic and high-refractive index materials on fluorophore lifetime and point-spread function shape. Our far-field system, combined with these nanoengineered structures, permit minimally-perturbative measurements to be made on individual fluorophores. We apply our imaging system to probe the nanoscale behavior of polymers in nanocomposite materials and to investigate fluorophore response to structured samples consisting of thin, high-refractive index materials.

12:00pm **NS+AS+EM+MI+SP+SS-ThM13 Atomic Scale Surface Effects of Controlled Crystal Structure in III-V Semiconductor Nanowires: Preferential Surface Alloying and Local Electronic Properties.**, *J. Knutsson, M. Hjort,* Lund University, Sweden, *P. Kratzer,* University Duisburg-Essen, Germany, *J. Webb, S. Lehmann, K.D. Thelander,* Lund University, Sweden, *C.J. Palmstrom,* UCSB, *R. Timm,* ***Anders Mikkelsen***, Lund University, Sweden

Despite the many III-V nanowire (NW) technologies under current development, be it solar cells and light emitting diodes or high speed/low power electronics, there are still only few studies of their surfaces. The atomic scale structure and morphology of NW surfaces are however central in determining their functionality, due to the inherently large surface to bulk ratio. In addition, III-V NWs can be tailored with segments of both the cubic zinc blende (ZB) and hexagonal wurtzite (WZ) structures and in a variety of materials combinations. This allow experimental access to nanocrystallite surfaces and interfaces not found in the bulk. We have demonstrated atomically resolved Scanning Tunneling Microscopy/Spectroscopy (STM/S) on a wide variety of these III-V NWs and on operational NW devices [1-5]. We now use these methods for studying atomic scale surface structural changes and impact on local electronic properties on both GaAs and InAs NWs at room temperature and at 5K.

We explore the surface diffusion and alloying of Sb into GaAs NWs with controlled axial stacking of Wz and Zb crystal phases. We find that Sb preferentially incorporates into the surface layer of the -terminated Zb segments rather than the -terminated Wz segments. Density functional theory calculations verify the higher surface incorporation rate into the Zb phase and find that it is related to differences in the energy barrier of the Sb-for-As exchange reaction on the two surfaces. These findings demonstrate a simple processing-free route to compositional engineering at the monolayer level along NWs.

Using low temperature STM/S we measure local density of states of atomic scale tailored Zb segments in Wz InAs nanowires down to the smallest possible crystal lattice change. We find that Zb crystal phase signatures can be seen in the density of states both on the conduction and valence band sides as well as in the band positions down to the smallest possible Zb segment. Additionally we find indications of confined state effects due to the difference in bandgap between Wz and Zb. Finally we explore the stability of InAs NWs with atomic scale STM during the application of voltages through the NWs in a device configuration. We observe that applying realistic voltages to InAs NWs results in removal of atomic scale defects and smoothening of the morphology.

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Plasma Science and Technology Division
Room: 23 - Session PS+NS+SS+TF-ThM

Atomic Layer Etching I
Moderators: Andrew Gibson, University of York, UK, Saravanapriyan Sriraman, Lam Research Corporation

8:00am **PS+NS+SS+TF-ThM1 Strategies to Control the Etch per Cycle During Atomic Layer Etching of SiO_2 and SiN_x**, ***Ryan Gasvoda***, Colorado School of Mines, *S. Wang, E.A. Hudson,* Lam Research Corporation, *S. Agarwal*, Colorado School of Mines

Decreasing device dimensions and the incorporation of increasingly complex 3D architectures place new constraints on conventional plasma processing techniques. One method to address the limitations of conventional etching is atomic layer etching (ALE) which can provide low damage and atomic-scale etch control. ALE has been extensively studied for a variety of materials, including Al_2O_3, HfO_2, Si, and Si-based dielectrics. In this study, we have explored the atomistic-level details of an SiO_2 and SiN_x ALE process consisting of a hydrocarbon-containing precursor dose, CF_x deposition from a C_4F_8/Ar plasma, and an Ar plasma activation step in which the CF_x film is activated and the underlying substrates are etched. In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and *in situ* four-wavelength ellipsometry during ALE to monitor the surface reactions and film composition as well as the net film thickness during the deposition and etching steps.

Sequential cycles of ALE of SiO_2 show a drift in the etch per cycle (EPC) with increasing cycle number. We attribute the drift in EPC is from excess CF_x that is liberated from the reactor walls in the Ar plasma step. This increase in the EPC occurs even though the infrared spectra confirm that the CF_x deposition onto the SiO_2 film is reproducible from cycle to cycle. To minimize the drift in EPC, Ar plasma half-cycles of twice the length are employed, which allows for the removal of CF_x from the reactor walls during each cycle, thus creating more reproducible chamber wall conditions.

To further control the EPC, a hydrocarbon precursor prior to the start of ALE retards the EPC. A broad feature centered at ~1,400 cm^{-1} builds up on the surface with increasing hydrocarbon dose frequency and cycle number, which is assigned to a carbonaceous film of CH_xF_y. The film acts as a blocking layer which prevents the activation of CF_x at the CF_x/SiO_2 interface and thus limits SiO_2 etching. No graphitic carbon buildup is observed. However, increasing the Ar plasma half-cycle length limits the buildup of the CH_xF_y film and increases the EPC. Using the same baseline processing conditions as ALE of SiO_2, ALE of SiN_x leads to a carbonaceous film buildup of both CH_xF_y and nitrile species at ~2,225 cm^{-1} which accumulates over cycle number and eventually leads to an etch stop. A longer Ar plasma half-cycle limits the accumulation of the CH_xF_y film and the EPC drift. The addition of a hydrocarbon precursor retards the EPC in a similar fashion as observed on the SiO_2 film.

8:20am **PS+NS+SS+TF-ThM2 Enabling Atomic Layer Etching of Magnetic and Noble Metal Alloys**, ***Nicholas Altieri****, *E. Chen*, University of California, Los Angeles, *J.K. Chen*, Lam Research Corporation, *J.P. Chang*, University of California, Los Angeles

Etching of magnetic and noble metals alloys utilized in ferromagnetic thin films crucial to the operation of magnetic memory has created a processing bottleneck, due to their chemically resistant nature. Widely-used etch techniques, including noble ion sputtering, exhibit limited success at patterning high aspect ratio features as well as a lack of selectivity. Furthermore, as feature sizes shrink, the demand for atomic level precision in patterning increases. A generalized strategy has been developed to enable dry etch processes shown to be effective for patterning elemental and alloyed metal thin films through the use of surface modification. Controlling the thickness of the modified layer allowed for direct control of the amount of material removed, indicating that this process would be viable for achieving atomic layer etch.

The etch of Co and Pt, elements commonly used in the magnetic memory stack, as well as ferromagnetic alloys CoPt and $Co_{30}Fe_{45}B_{25}$ were studied in this work. Inductively coupled oxygen plasma was utilized for surface modification, and organics including oxalic acid, formic acid, acetylacetone, and hexafluoroacetylacetone were investigated as chemical etchants.

Pt, Co, CoPt, and CoFeB thin films were first studied using continuous exposure to organic solutions. Pt showed no etch beyond the removal of a thin layer of native oxide. CoPt and CoFeB were shown to etch at rates up to 10 nm/min in formic acid solutions without plasma modification. Upon translation to the gas phase, where the concentration of organics was substantially lower, no etch was observed across all materials when continuously exposed to organic acid vapor.

Plasma oxidation was then utilized to chemically modify the surface through generation of directional metal-oxide bonding prior to treatment with organics. Subsequent exposure to formic acid solution indicated preferential and complete removal of metal oxides. A dual-step dry etch process consisting of plasma oxidation and organic vapor dosing was then developed which exhibited etch rates of 0.5, 2.8, 1.1, and 1.8 nm/cycle for Pt, Co, CoPt and CoFeB, respectively, and removing metallic oxides.

In formic acid solution, PtO_2 exhibited infinite selectivity to Pt, while oxidized CoPt and CoFeB were observed to have selectivities of 6.4 and 3.1, respectively, compared to their unoxidized counterparts. In the vapor phase, each oxidized material exhibited nearly infinite selectivity to each corresponding metallic film. Coercivity values (H_c) of 20 and 3.5 Oe were measured for Co and CoFeB before processing conserved to up to 99% of their original pre-processing values.

8:40am **PS+NS+SS+TF-ThM3 Directional Atomic Layer Etching: First Principles, Modelling and Applications**, ***Thorsten Lill***, *K. Kanarik, I.L. Berry, S. Tan, Y. Pan, V. Vahedi, R.A. Gottscho*, Lam Research Corporation **INVITED**

Atomic layer etching (ALE) has recently been introduced into manufacturing to produce 10 nm logic devices. ALE is an etching technology that deploys time or space separated and self-limited steps. In directional ALE, at least one of the two steps has to be directional, i.e., has to transfer momentum to the surface and/or be sensitive to line of sight. Ion bombardment is most commonly used to realize directional ALE. ALE exhibits the same ion-neutral synergy as RIE but the removal amount is not flux dependent due to the separation of the neutral (chemical) and ion fluxes /1,2/. Flux independence gives ALE its most prominent property: inherent uniformity across all length scales – across wafer, loading, ARDE and surface smoothness.

As compared to conventional plasma etching, step separation in ALE also offers a simplified system in which to study the etching mechanisms based on first principles. For example, recently, the process window of ALE was shown to be predictable based on the energy barriers relevant to the substrate-reactant combination, such as the surface binding energies of the chemically modified and bulk material /3/. The separate and independent steps make it particularly suitable to modelling efforts. Here we present the latest results in feature scale modelling of new material systems amenable to the ALE approach as well as experimental results.

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* **Coburn & Winters Student Award Finalist**

9:20am **PS+NS+SS+TF-ThM5 Thermal Atomic Layer Etching of VO_2 Using Sequential Exposures of SF_4 and Either Sn(acac)$_2$ or BCl_3**, ***Jonas Gertsch***, *V.M. Bright, S.M. George*, University of Colorado Boulder

Thermal atomic layer etching (ALE) is based on sequential self-limiting thermal reactions [1]. Thermal ALE offers a precise and gentle etching procedure and has been demonstrated for many materials including Al_2O_3, HfO_2, ZnO, ZrO_2, SiO_2 and AlN [1,2]. This study developed thermal ALE processes for vanadium oxide (VO_2). VO_2 has a metal-insulator transition at ~68 °C and is useful for thermochromic films and heat-switching devices. The initial VO_2 films were deposited using VO_2 atomic layer deposition (ALD) with tetrakis(ethylmethylamino) vanadium(IV) (TEMAV) and H_2O as the co-reactants at 150 °C.

The VO_2 films were etched using sequential exposures of sulfur tetrafluoride (SF_4) and either tin(II) acetylacetonate (Sn(acac)$_2$) or boron trichloride (BCl_3) at temperatures ranging from 150-250 °C. *In situ* quartz crystal microbalance studies were used to monitor film growth and etching during the ALD and ALE reactions. The VO_2 etching mechanism using SF_4 and Sn(acac)$_2$ is observed to occur by fluorination and ligand-exchange reactions [1]. The SF_4 exposures yielded mass gains that were consistent with fluorination of VO_2 to VF_4. The Sn(acac)$_2$ exposures then led to mass losses that were attributed to ligand-exchange reactions that produced volatile acetylacetonate reaction products. VO_2 ALE etch rates increased with temperature from 0.04 Å/cycle at 150 °C to 0.27 Å/cycle at 225 °C.

A different reaction mechanism was observed for VO_2 ALE using SF_4 and BCl_3. The SF_4 exposures yielded mass losses at all temperatures that were not consistent with simple fluorination of VO_2 to VF_4. The BCl_3 exposures produced mass losses at higher temperatures and slight mass gains at 150 °C. The etching of VO_2 by SF_4 and BCl_3 is believed to occur by a “conversion-etch” mechanism [2]. In the “conversion-etch” mechanism, BCl_3 converts the surface of VO_2 to a thin B_2O_3 layer. SF_4 can then remove the B_2O_3 layer to produce volatile BF_3 and SO_2. The VO_2 etch rates increased with temperature from 0.06 Å/cycle at 150 °C to 1.9 Å/cycle at 250 °C.

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9:40am **PS+NS+SS+TF-ThM6 Atomic Layer Etching of MoS_2 for Nanodevices**, ***KiSeok Kim***, *K.H. Kim, Y.J. Ji, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Among the layered transition metal dichalcogenides (TMDs) that can form stable two-dimensional (2-D) crystal structures, molybdenum disulfide (MoS_2) has been intensively investigated due to its unique properties in various electronic and optoelectronic applications with different band gap energies from 1.29 to 1.9 eV as the number of layers is decreased. To control the MoS_2 layers, atomic layer etching (ALE) (which is a cyclic etching consisting of a radical-adsorption step such as Cl adsorption and a reacted-compound desorption step via a low-energy Ar^+-ion exposure) can be a highly effective technique to avoid inducing damage and contamination that occur during the cyclic steps. In this study, for the MoS_2 ALE, the Cl radical is used as the adsorption species and a low-energy Ar^+ ion is used as the desorption species. A MoS_2-ALE mechanism (by which the $S_{(top)}$, $Mo_{(mid)}$, and $S_{(bottom)}$ atoms are sequentially removed from the MoS_2 crystal structure due to the trapped Cl atoms between the $S_{(top)}$ layer and the $Mo_{(mid)}$ layer) is reported with the results of an experiment and a simulation. A monolayer MoS_2 field effect transistor (FET) fabricated after one-cycle of ALE of a bilayer MoS_2 FET exhibited electrical characteristics similar to a pristine monolayer MoS_2 FET indicating no electrical damage on the monolayer MoS_2 surface after the ALE.

11:00am **PS+NS+SS+TF-ThM10 Ge Atomic Layer Etching for High Performance FinFET**, *W. Mizubayashi,* AIST, Japan*, S. Noda,* Tohoku University, Japan*, Y. Ishikawa, T. Nishi,* AIST, Japan*, A. Kikuchi,* Tohoku University, Japan*, H. Ota,* AIST, Japan*, P.-H. Su, Y. Li,* National Chiao Tung University, Taiwan*, S. Samukawa,* Tohoku University, AIST, Japan, ***Kazuhiko Endo***, AIST, Japan **INVITED**

Ge is a promising material for use as high mobility channel in future CMOS. For 5-nm-node CMOS and smaller, to attain electrostatic controllability of the gate electrode, a multichannel fin structure is utilized. Fin structure formation in Ge FinFETs on GeOI substrates is mainly performed by ICP etchings. However, ICP etching causes plasma induced damages owing to the ultraviolet (UV) light generated from the ICP and charge up by ionized atoms. A concern is that such etching damage reduces the performance and reliability of Ge-channel CMOS. In this work, to break-through these plasma induced damages, we demonstrated defect-free and highly anisotropic Ge etching for Ge FinFET fabricated by Cl neutral beam etching.

There are two advantages in the neutral beam etching process. 1) The wafer is not exposed by the UV light generated from the plasma through the high-aspect-ratio carbon aperture plate. 2) Ions are efficiently neutralized by collision with the carbon aperture plate. Thus, in neutral beam etching, the influences of the UV light and charge-up can be perfectly eliminated and defect-free etching can be realized.

In the ICP etching, the Ge fin is formed but has a trapezoidal shape. On the other hand, the Ge fin in the case of neutral beam etching can be vertically formed as compared with that in the case of the ICP etching. A channel surface with atomic-level smoothness was confirmed in neutral beam etching while some roughness was observed in the ICP etching. In neutral beam etching without UV light irradiation, the Ge surface is not damaged, and a surface dangling bond is formed only on the atomic layer and it undergoes a chemical reaction with the reactive species [1]. Thus, atomic layer etching can be realized by neutral beam etching.

The $|I_d|–V_d$ and $|I_d|–V_g$ characteristics of the Ge FinFET fabricated by neutral beam etching are markedly improved as compared with those of the FinFETs fabricated by ICP etching, in n- and p-type FinFETs. $g_{m\,max}$ for the Ge FinFET fabricated by neutral beam etching is two times higher for the nFinFET and 10% higher for the pFinFET than those of the FinFETs fabricated by ICP etching, regardless of the fin thickness. In the case of neutral beam etching, since there is no etching damage in the Ge fin, the interface state and surface roughness are drastically lowered. This is the reason for the improved $g_{m\,max}$ for the n- and p-type Ge FinFETs fabricated by neutral beam etching. Thus, the atomic-level flatness and damage-free etching in the Ge fin formation are essential to high performance Ge FinFETs, which can be realized by neutral beam etching.

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11:40am **PS+NS+SS+TF-ThM12 Numerical Simulations of Atomic-Layer Etching (ALE) for SiO_2 and SiN**, ***Yuki Okada***, Osaka University, Japan, *R. Sugano*, Hitachi, Ltd., Japan, *M. Isobe, T. Ito, H. Li, K. Karahashi, S. Hamaguchi*, Osaka University, Japan

As the sizes of modern semiconductor devices approach near-atomic scales, processing to create such devices in mass production scale also requires atomic-scale precisions. Recent technological advancement for atomic-scale processing includes the development of atomic-layer deposition (ALD) and atomic-layer etching (ALE), in which deposition or etching processes take place layer by layer with each step having self-limiting chemical reactions. In such a process, self-limiting reactions result in not only atomic-scale accuracy of processed structures but also process uniformity over a large area regardless of structure densities. In this study we have examined mechanisms of ALE processes of SiO2 and SiN based on digital or pulsed application of fluorocarbon or hydrofluorocarbon plasmas, using molecular dynamics (MD) simulations. In MD simulations, chemically reactive species and low-energy incident ions are supplied to a SiO2 or SiN surface alternatively. A supply of a certain amount of chemically reactive species to the surface does not spontaneously induce etching reactions. However, when the surface with such reactive species is subject to ion bombardment, energy and momentum supplied to the surface by incident ions activate surface reactions and etching reactions take place. If the ion bombardment energy is sufficiently low, this etching process stops when reactive species are depleted from the surface. In this study, we have examined various combinations of reactive species and ion bombardment. For example, in the case of SiO2, reactive species and ions used in this study are fluorocarbon radicals and low-energy (e.g., 40 eV) Ar+ ions. In the case of SiN, reactive species and ions are hydrogen radicals and low-energy (e.g., 10 eV) Ar+ ions. Also in the case of SiN, we have used simultaneous injection of hydrogen radicals with low energy CF3+ ion bombardment as a radical supply process and low-energy (e.g., 50 eV) Ar+ ion injections as a process to remove excess fluorocarbon deposited on the surface. In the last case, etching self limit occurs because of accumulation of a fluorocarbon layer, rather than the removal of it. It has been found that, in most cases, the complete removal of reactive species from the surface is not easy and the control of remaining reactive species on the surface after each digital process step is the key for the success of ALE process development.

12:00pm **PS+NS+SS+TF-ThM13 Organometallic Etching Chemistry for Thermal Atomic Level Etching of Lanthanum Oxide**, ***Yoshihide Yamaguchi***, *K. Shinoda*, Hitachi, Japan, *Y. Kouzuma, S. Sakai, M. Izawa*, Hitachi High-Technologies Corp., Japan

The demand for thermal atomic level etching (ALEt) of a wide variety of materials including silicon-based materials, metals, and high-k materials is increasing as semiconductor device geometries continue to shrink. To meet the increased demand, remarkable progress into ALEt research has been made in the last few years. One example is the pioneering research on the thermal ALEt of hafnium oxide emerged [1], where hafnium oxide sequentially reacted with HF and a stannous organometallic compound (Sn(acac)2). Thermal ALEt of SiN is another example [2][3], where sequential reactions of a plasma-assisted self-limiting surface modification and a thermal desorption of the self-limiting layer was employed.

In this work, we present our challenge for the thermal ALEt of lanthanum oxide by using surface modification followed by thermal desorption. A key technology of this ALEt is the novel organometallic chemistry for the one-step surface modification of lanthanum oxide. A lanthanum oxide sample exposed to gas of fluorine-containing ketone together with a stabilizer led to the formation of volatile organic species on the sample surface, while a SiO2 sample remained unchanged under the same process condition. The gas-exposed lanthanum oxide sample was then annealed at elevated temperatures under vacuum to remove the volatile species from the surface. After these consecutive processes, the volatile organic species from the lanthanum oxide sample were collected and identified by nuclear magnetic resonance (NMR) spectroscopy and infrared (IR) spectroscopy. These results indicated that the volatile species was an organo-lanthanum complex bearing the fluorine-containing ketone moiety as the ligand. On the basis of these results, a novel selective dry-chemical removal of lanthanum oxide was successfully demonstrated.

Several results on selective dry-chemical removal of lanthanum oxide with respect to TiN, metal oxide, and some other material will also be disclosed.

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Electronic Materials and Photonics Division
Room: 14 - Session EM+NS-ThA

Wide and Ultra-wide Band Gap Materials for Electronic Devices: Growth, Modeling, and Properties

Moderators: Michael Filler, Georgia Institute of Technology, Rachael Myers-Ward, U.S. Naval Research Laboratory

2:20pm **EM+NS-ThA1 Synthesis of β-Ga2O3 Thin Films on SiC by Molecular Beam Epitaxy**, ***Neeraj Nepal****, D.S. Katzer, D.F. Storm, M.T. Hardy, B.P. Downey, D.J. Meyer*, U.S. Naval Research Laboratory

Recently, there has been great interest in β-Ga2O3 as a next generation ultra-wide bandgap semiconductor (UWBGS) for high-power/temperature electronics devices. However, it has low thermal conductivity of β-Ga2O3 may limit device performance. One strategy to improve performance of Ga2O3 based devices is through heterostructure design on high thermal conductivity substrate. In this paper, we report growth and characterization of 100 nm thick β-Ga2O3 on SiC by molecular beam epitaxy (MBE) at 650 °C. First, the growth parameter space such thermocouple measured growth temperature, relative Ga flux, and oxygen plasma were varied to grow β-Ga2O3 films on c-plane sapphire substrates. For an O2 plasma flow of 1 sccm (2.5x10-5 torr) X-ray diffraction shows weak facets of β-Ga2O3 appear regardless of the Ga flux and temperature, however for <0.6 sccm O2 flow, smooth β-Ga2O3 [(-201)||(0001)] grows on c-plane sapphire. Optimized MBE growth conditions on sapphire substrate were used to grow β-Ga2O3 on SiC. Single phase MBE β-Ga2O3 film on SiC grown at 650 °C are insulating, have rocking curve full-width-at-half-maximum of 720 arc-sec with root mean square surface roughness of less than 2 nm. In this paper we will discuss MBE growth parameter space of β-Ga2O3 on sapphire and the structural, morphological, and electrical properties of MBE grown β-Ga2O3 thin films on SiC.

2:40pm **EM+NS-ThA2 Growth and Characterization of *α*-, *β*-, and *ε*-Ga_2O_3 Epitaxial Layers**, ***Lisa Porter****, Y. Yao, L.A.M. Lyle,* Carnegie Mellon University*, S. Okur, G.S. Tompa, T. Salagaj, N. Sbrockey*, Structured Materials Industries, Inc.

Increasing global demand for energy makes urgent the need for highly efficient high-power electronics for energy conversion and transport. Although silicon devices have been traditionally used for high-power electronics, wide bandgap semiconductors (e.g., SiC and GaN) are much more efficient for these applications, because they can withstand higher electric fields with less material and reduced energy loss. However, the substrates of both materials are still very expensive. A very promising alternative to SiC and GaN is gallium oxide, Ga_2O_3, which has an even larger bandgap than the former two materials. The availability of this material presents new possibilities for disruptive devices and technologies that could translate to even greater energy efficiencies at lower cost than predicted for SiC and GaN. Polished 2-in diameter, single-crystal wafers of the monoclinic *β*-phase can be grown using melt-growth methods and are commercially available. However, there is increasing interest in the other Ga_2O_3 phases, particularly the metastable corundum-structured *α*- and hexagonal-structured *ε*-Ga_2O_3 phases because of their higher symmetry and simpler epitaxial relations to c-plane sapphire, in addition to the possibility of producing functional heterostructures or tunable bandgaps through alloying. We have successfully grown epitaxial films of *α*-, *β*- and *ε*-phases on c-plane sapphire using different precursors and growth conditions. The *α*- and *ε*-phases have generally been reported in the literature to form at lower growth temperatures than the *β*-phase. However, we observed a change in phase formation at the same growth temperature by changing our growth technique and Ga precursor from metalorganic chemical vapor deposition (MOCVD) and trimethlygallium to halide vapor phase epitaxy (HVPE) and gallium chloride. Data from x-ray diffraction, scanning electron microscopy and high-resolution transmission electron microscopy will be presented to illustrate the different epitaxial films and orientation relationships. The results of secondary ion mass spectrometry depth profiles, which showed compositional differences within the different phases, will also be presented. The authors wish to acknowledge the Office of Naval Research under contract no. N00014-16-P2059.

3:00pm **EM+NS-ThA3 Ultra-wide-bandgap Ga_2O_3 Material and Electronic Device Technologies**, ***Masataka Higashiwaki****, M.H. Wong,* National Institute of Information and Communications Technology, Japan, *K. Konishi*, Tokyo University of Agriculture and Technology, Japan, *Y. Nakata, T. Kamimura*, National Institute of Information and Communications Technology, Japan, *K. Sasaki, K. Goto,* Tamura Corporation, Japan, *A. Takeyama, T. Makino, T. Ohshima,* National Institutes for Quantum and Radiological Science and Technology, Japan, *H. Murakami, Y. Kumagai*, Tokyo University of Agriculture and Technology, Japan, *A. Kuramata, S. Yamakoshi*, Tamura Corporation, Japan **INVITED**

Recently, gallium oxide (Ga_2O_3) has attracted much attention as a candidate for future power and harsh environment electronics due to its extremely large bandgap of 4.5 eV and the availability of economical melt-grown native substrates. In this talk, following a short introduction of the material properties of Ga_2O_3, we will discuss our recent progress in the development of Ga_2O_3 metal-oxide-semiconductor field-effect transistors (MOSFETs) and Schottky barrier diodes (SBDs), including Ga_2O_3 thin-film epitaxial growth technologies by molecular beam epitaxy (MBE) and halide vapor phase epitaxy (HVPE).

State-of-the-art Ga_2O_3 MOSFETs with a gate-connected field plate (FP) were fabricated using MBE-grown Ga_2O_3 homoepitaxial layers. The devices showed excellent room-temperature (RT) characteristics such as a record high off-state breakdown voltage (V_{br}) of 755 V, a large drain current on/off ratio of over nine orders of magnitude, and DC-RF dispersion-free output characteristics [1]. Furthermore, the MOSFETs demonstrated strong prospects of Ga_2O_3 devices for extreme environment electronics by virtue of their stable high-temperature operation up to 300°C and strong radiation hardness against gamma-ray irradiation [2].

We have also fabricated and characterized Ga_2O_3 FP-SBDs on n^--Ga_2O_3 drift layers grown by HVPE [3-5]. The illustrative device with a net donor concentration of 1.8×10^{16} cm^{-3} exhibited a specific on-resistance of 5.1 $m\Omega\cdot cm^2$ and an ideality factor of 1.05 at RT. Successful FP engineering resulted in a high V_{br} of 1076 V. Note that this was the first demonstration of V_{br} of over 1 kV in any Ga_2O_3 power device. The maximum electric field in the Ga_2O_3 drift layer at the condition of destructive breakdown was estimated to be 5.1 MV/cm by device simulation, which is about two times larger than the theoretical limits for SiC and GaN.

This work was partially supported by Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), "Next-generation power electronics" (funding agency: NEDO).

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4:00pm **EM+NS-ThA6 Reactive Magnetron Sputtering of Titanium Nitride and Titanium Aluminum Nitride on Lithium Niobate for Electronic and Opto-Electronic Applications**, ***Amber Reed****, H.A. Smith, D.C. Abeysinghe, P.J. Shah, L. Grazulis, M.J. Hill, M.E. McConney, B.M. Howe, A.M. Urbas*, Air Force Research Laboratory

High temperature stability, hardness, abrasion resistance, chemical stability and potential complimentary metal-oxide semiconductor process compatibility, combined with a high electrical conductivity make titanium nitride (TiN) an important material for electronic and opto-electronic applications. TiN is particularly important as an electrode material due to its oxidation resistance, which can be improved by alloying it with aluminum nitride to form titanium aluminum nitride ($Ti_{1-x}Al_xN$). In addition to its use as an electrode, TiN is also a promising plasmonic material because, similar gold, it possesses a zero crossover wavelength in the visible region. The ability to synthesize high quality TiN crystals on different electronic substrates would greatly facilitate its incorporation in electronic and opto-electronic devices. One particular material of interest is lithium niobate ($LiNbO_3$), which possesses unique piezoelectric, opto-electronic and nonlinear optical properties. Synthesis of high quality TiN on $LiNbO_3$ would allow for integration of TiN into acoustic devices (i.e. SAWs and BAWs), optical modulators, and other electronic and opto-electronic devices.

In this work, we demonstrate the synthesis of high quality epitaxial TiN crystals on Z-cut $LiNbO_3$ substrates. We also discuss the growth of TiN and $Ti_{1-x}Al_xN$ on Y-cut $LiNbO_3$. While the (001) plane of Z-cut $LiNbO_3$ creates a template for epitaxial growth of (111)-oriented TiN crystals, similar to growth on (001)-oriented sapphire, the (010) plane of Y-cut $LiNbO_3$ is equally lattice matched to the TiN (001) and (101) planes which results in competitive growth of those two orientations. Alloying the TiN with AlN exacerbates this issue as the lattice constant shrinks with increased AlN content. We investigate the role of deposition power, nitrogen gas fraction, and substrate temperature and ion flux impingement on the competitive growth to determine the optimal growth conditions to promote epitaxy. Films are characterized using x-ray diffraction (XRD), atomic force microscopy (AFM), transmission electron microscopy, ellipsometry and electrical measurements. XRD and AFM of TiN on Z-cut $LiNbO_3$ show remarkably smooth (< 220 pm RMS roughness) epitaxial films. Ellipsometry measurements of the TiN on Z-cut $LiNbO_3$ reveal carrier concentrations up to $4.0\ x10^{22}$ cm^{-3}, mobilities of ~3.2 cm^2/(V s) and a $\varepsilon_1/\ \varepsilon_2$ of 1.00 to 3.34 at a wavelength of 1550 nm.

4:20pm **EM+NS-ThA7 Growth and Property Analysis of Doped GaN-GaAlN Heterostructures on Low- and High-temperature AlN/Sapphire Templates**, ***Nikolaus Dietz***, *B.G. Cross, M. Vernon,* Georgia State University, *R. Collazo, R. Kirste, S. Mita, Z. Sitar,* North Carolina State University

The developing of radiation-hard UV solid state avalanche photodiodes (APD's) based on group III-Nitride wide band gap materials have a wide application area from solar blind detector to wavelength specific PMT based detector devices that can be tuned in the 220 nm to 450 nm wavelength range, tailored to specific scintillators of interest. This contribution focuses on closely lattice-matched, high-quality GaN a substrate technologies using metalorganic chemical vapor deposition (MOCVD) technique, which provide sufficient high-quality AlGaN layers and heterostructures with high phase uniformity and low dislocation density for low leakage currents, to enable avalanche mechanisms, low leakage currents, high performance characteristics and reliability of the devices.

We will present results on the growth and doping of GaN/GaAlN heterostructures deposited on low- and high-temperature AlN/Sapphire template structures, using a customized D125 Veeco MOCVD reactor system. The structural quality of the initial GaN layer grown on various AlN-/GaN-sapphire template structure has been analyzed and is accessed regarding its resulting dislocation and defect densities, using XRD, Raman and FTIR spectroscopy. The influence of Silicon n-doping in GaN and $Ga_{0.9}Al_{0.1}N$ epilayers on the defect density was analyzed XRD and the dopant incorporation by SIMS analysis.

4:40pm **EM+NS-ThA8 A Thermodynamic Supersaturation model for the Growth of AlGaN by MOCVD**, ***Ramón Collazo***, *S. Washiyama, I. Bryan,* North Carolina State University, *P. Reddy, S. Mita,* Adroit Materials Inc., *Z. Sitar,* North Carolina State University **INVITED**

AlGaN have been considered to be essential for the development of optoelectronic and electronic devices such as deep UV LEDs and other power devices. However, even under well-controlled growth conditions it is difficult to precisely predict the behavior of AlGaN growth with regards to Al-concentration and related defect incorporation. We have developed a thermodynamic model for the calculation of the Ga supersaturation during the growth of GaN by metalorganic chemical vapor deposition (MOCVD), which was successfully used to predict incorporation of impurities such as carbon as well as the surface morphology (Mita et al., JAP 104, 13521). This model was extended to evaluate the supersaturation of Al and Ga in AlGaN growth and to allow for the prediction of the properties of MOCVD grown AlGaN layers. Non-linear equations for Al and Ga equilibrium vapor pressure calculation describe the process under the following assumptions: (1) under low total pressure, gas phase reactions between the metalorganics and NH_3 are negligible; the III metal precursors are irreversibly cracked on the growth surface, thus, Al, Ga, NH_3, H_2 and N_2 are analyzed; (2) number of moles of growing species are conserved; (3) at least some NH_3 molecules are thermally cracked in the gas phase. Using the resulting model, the influence of growth parameters such as V/III and flow rate on AlGaN growth was determined through the dependence of the Ga and Al supersaturation. The independent parameters for the calculations included the growth conditions that were set by typical conditions for AlGaN MOCVD growth. Calculation showed a significantly lower equilibrium vapor pressure for Al (10^{-12}-10^{-16} Torr) than for Ga (10^{-4}-10^{-6} Torr). The Ga equilibrium pressure monotonously decreased with increasing V/III ratio, while NH_3 thermal cracking was more significant on the equilibrium pressure, as expected from Le Chatelier`s principle. The significant difference in the supersaturation between Ga and Al has a significant influence on the growth of ternary AlGaN compounds and need to be considered for finding appropriate and robust growth conditions at high temperatures, exceeding 1150 ºC. A processing AlGaN compositional phase diagram dependent on the typical growth conditions will be presented. In addition, experimental validation of this model with respect to Al composition, process stability and robustness will be discussed. This validation will be presented in terms of temperature and V/III ratio.

5:20pm **EM+NS-ThA10 Anomalous Hall Effect in MOCVD-grown Gadolinium-doped Gallium Nitride**, *V.G. Saravade, P. Patel, C. Ferguson, K. Yunghans, A. Ghods, C. Zhou,* ***Ian Ferguson***, Missouri University of Science and Technology

Dilute Magnetic Semiconductor (DMS) materials for spintronics applications have the potential to reduce power consumption while increasing the processing speed, integration densities and non-volatile memory, compared to the conventional semiconductor devices. While Gd-doped GaN has exhibited room temperature (RT) ferromagnetism, the Anomalous Hall Effect (AHE) has not been reported in relation to the observed magnetic properties [1, 2].

In this work, we study the AHE in MOCVD-grown Gd-doped GaN with different Gd concentrations and precursors, and investigate their magnetic properties. RT AHE along with XRD helps in determining the mechanisms responsible for the observed ferromagnetism. Our preliminary measurements showed residual R_{xy}/R_{xx} up to 10 and residual coercive field up to 50 Oe. These hysteresis curves can be caused by the ferromagnetic properties of MOCVD-grown Gd-doped GaN. Additionally, GaN (002) peak had been identified in the initial Ω-2θ XRD scans. XRD rocking curve scans with varying Ω will be performed to study, the defects that are induced by doping GaN with Gd, and their potential contribution towards ferromagnetism. AHE and XRD results of Gd-doped GaN will be compared to those of un-doped GaN to verify that the ferromagnetism is caused by Gd doping. Furthermore, the effect of temperature on the magnetic behavior of Gd-doped GaN will be analyzed using variable temperature AHE.

To our knowledge, we are the first to report the AHE in MOCVD-grown Gd-doped GaN. We consider this work to contribute towards the investigation of DMS for RT ferromagnetism and further for spintronics applications.

References

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5:40pm **EM+NS-ThA11 Valence and Conduction Band Offsets of Al_2O_3, $LaAl_2O_3$, AZO and ITO with Ga_2O_3**, ***Patrick Carey IV***, *F. Ren, D. Hays, B. Gila, S.J. Pearton,* University of Florida, *S. Jang,* Dankook University, South Korea, *A. Kuramata,* Tamura Corporation, Japan

Band alignments for Al_2O_3, $LaAl_2O_3$ (LAO), Aluminum Zinc Oxide (AZO), and Indium Tin Oxide (ITO) with bulk β-Ga_2O_3 were determined by X-ray Photoelectron Spectroscopy. β-Ga_2O_3 is a direct band gap, ~4.9 eV, semiconductor, it has a very high theoretical breakdown electric field (~8 MV/cm), and is suitable for high power electronics in industrial, military applications, deep-UV photodetectors for a cut-off wavelength of 280 nm, and high temperature gas sensors. Ohmic contact with low contact resistance and gate oxides with low leakage current are essential for fabricating high performance base Ga_2O_3 electronic and optical devices. Since Ga_2O_3 has a wide energy bandgap, it is difficult to form low resistance Ohmic contact with conventional metal contact. ITO and AZO were found to have a conduction band offset of gap of -0.32 and -0.79 eV, respectively, which can be used as an intermediate layers between the metal contact and Ga_2O_3 to reduce contact resistance on Ga_2O_3-based devices. For wider energy band oxides, for use as gate oxides, sputtered LAO, atomic layer deposited (ALD) and rf-magnetron sputtered Al_2O_3 were employed. LAO was found to have a bandgap of 6.5 eV, a valence band offset of -0.21 eV, and a conduction band offset of 2.01 eV. LAO has a type II alignment and would provide excellent electron confinement, but no barrier for hole transport. Al_2O_3 was found to have a bandgap of 6.9 eV regardless of preparation method. However, the deposition method affected the band alignment. For ALD Al_2O_3, it has a has a nested (type I) gap alignment with a valence band offset of 0.07eV and a conduction band offset of 2.23 eV. While for sputtered Al_2O_3 on the same Ga_2O_3, there is a type II alignment with a valence band offset of -0.86 eV and a conduction band offset of 3.16 eV. The conduction band offsets in either case are large and provide excellent electron confinement, but the valence band offsets are smaller than desirable for limiting hole transport.

6:00pm **EM+NS-ThA12 *In Situ* Plasma Emission Spectroscopy of InN/GaN Heterostructures Grown by MEPA-MOCVD**, ***Daniel Seidlitz***, *B.G. Cross, Y. Abate,* Georgia State University, *A. Hoffmann,* Technical University of Berlin, Germany, *N. Dietz,* Georgia State University

In this study, we will present results of the in-situ plasma emission spectroscopy (PES) of the plasma activated nitrogen species during the growth of GaN/InN heterostructures by MEPA-MOCVD in correlation to their optical and structural characteristics.

Indium-rich InGaN semiconductors are of high interest due to the high electron mobility which enables ultrafast electronics operating in the THz regime. In conventional MOCVD, indium incorporation above 25 % is a challenge due to the vastly different partial pressures between InN and GaN and the lattice mismatch between the binaries. Migration enhanced plasma-assisted MOCVD is a kinetic stabilized growth surface approach to reduce the partial pressure difference between the InN and GaN. It also replaces the traditional ammonia precursor source for nitrogen through energetically controlled ionized nitrogen species (N*/NH*/NHx*), generated by a radio-frequency hollow cathode (13.56 MHz) with an output power between 50-600 W. The plasma-excited species are tailored in the gas phase and directed to the growth surface in the afterglow regime of the remote plasma utilizing the kinetic energies of the active nitrogen species to achieve a stable growth surface. Altering the process parameters like reactor pressure and nitrogen flux allows variation of the kinetic energies. A grid between the plasma source and the growth surface enables the control of the charged species reaching the growth surface and with it the electrostatic interactions in the InN/GaN growth process and the resulting layer properties. In-situ real-time plasma emission spectroscopy (PES) is used to monitor and identify the active nitrogen species close to the hollow cathode as well as near the growth surface. Comparison of the spectra could help to determine which nitrogen species promote the growth of group III- nitride materials.

Optoelectronic and structural qualities such as free carrier concentration as well as crystallinity, growth rate, the surface morphology of the GaN and InGaN films are examined using ex-situ characterization techniques (Raman, AFM, FTIR). We will present a correlation of the in-situ and ex-situ results as a function of the explored growth parameters like growth temperature, plasma power, and reactor pressure.

Advanced Ion Microscopy Focus Topic
Room: 7 & 8 - Session HI+NS+TR-ThA

Novel Beam Induced Surface Analysis and Nano-Patterning

Moderators: Anne Delobbe, Orsay Physics, Shinichi Ogawa, National Institute of Advanced Industrial Science and Technology (AIST)

2:20pm **HI+NS+TR-ThA1 Multimodal Chemical Imaging of Nanoscale Interfacial Phenomena on a Combined HIM-SIMS Platform**, ***Olga Ovchinnikova***, Oak Ridge National Laboratory **INVITED**

The key to advancing energy materials is to understand and control the structure and chemistry at interfaces. However, significant gaps hamper chemical characterization available to study and fully comprehend interfaces and dynamic processes; partly due to the lack of breadth of necessary information, as well as its scattered nature among a multitude of necessary measurement platforms. Multimodal chemical imaging transcends existing analytical capabilities for nanometer scale spatially resolved interfacial studies, through a unique merger of advanced helium ion microscopy (HIM) and secondary ion mass spectrometry (SIMS) techniques. In this talk I will discuss how to visualize material transformations at interfaces, to correlate these changes with chemical composition, and to distil key performance-centric material parameters using a multimodal chemical imaging approach on a combined HIM-SIMS system. Particular attention will be focused on how to use the HIM-SIMS to study the role of ionic migration on the photovoltaic performance, or alternatively whether the ionic migration plays a positive or negative role in determining superior photovoltaic performance in organic-inorganic perovskites (HOIPs). I will discuss how synthesizing perovskite on custom substrates effect active chemical agents in materials and understand how interfaces in materials affect the local chemistry, specifically, key energy related parameters such as electron and ion motion and their re-distribution. Overall, multimodal chemical imaging on a combined HIM-SIMS platform offers the potential to unlock the mystery of active interface formation through intertwining data analytics, nanoscale elemental characterization, with imaging; to better grasp the physical properties of materials and the mechanistic physics-chemistry interplay behind their properties.

Acknowledgements

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

3:00pm **HI+NS+TR-ThA3 Characterizing Surface Immobilized Antibodies using ToF-SIMS and Multivariate Analysis**, *N.G. Welch,* CSIRO Manufacturing, Australia, *R.M.T. Madiona,* La Trobe University, Australia, *J.A. Scoble, B.W. Muir,* CSIRO Manufacturing, Australia, ***Paul Pigram***, La Trobe University, Australia

Antibody attachment, orientation and function at the solid interface are critical for the sensitive detection of biomolecules during immunoassays. Correctly oriented antibodies with solution-facing antigen binding regions have improved antigen capture in comparison with randomly oriented antibodies. Direct characterization of oriented proteins with surface analysis methods still remains a challenge. Surface sensitive techniques, however, such as Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) provide information-rich data that can be used to probe antibody attachment, orientation, denaturation and related characteristics.

Diethylene glycol dimethyl ether plasma polymers (DGpp) functionalized with chromium (DGpp+Cr) have improved immunoassay performance that is indicative of preferential antibody orientation. ToF-SIMS data from proteolytic fragments of anti-EGFR antibody bound to DGpp and DGpp+Cr have been used to construct artificial neural network (ANN) and principal component analysis (PCA) models indicative of correctly oriented systems. Whole antibody samples (IgG) tested against each of the models indicate preferential antibody orientation on DGpp+Cr. Cross-reference between ANN and PCA models yield 20 mass fragments associated with $F(ab')_2$ region representing correct orientation, and 23 mass fragments associated with the Fc region representing incorrect orientation. The mass fragments have been compared with amino acid fragments and amino acid composition in $F(ab')_2$ and Fc regions. A ratio of the sum of the ToF-SIMS ion intensities from the $F(ab')_2$ fragments to the Fc fragments demonstrated a 50% increase in intensity for IgG on DGpp+Cr as compared to DGpp.

This systematic data analysis methodology offers new opportunities for the investigation of antibody orientation on a range of substrates. It also yields good results for the characterization of antibody denaturation and for determining limits of detection.

4:00pm **HI+NS+TR-ThA6 Single-nanometer Functional Graphene Devices Patterned with Helium Ion Beam**, ***Hiroshi Mizuta***, *M.E. Schmidt, T. Kanzaki,* Japan Advanced Institute of Science and Technology (JAIST), Japan, *S. Ogawa,* National Institute of Advanced Industrial Science and Technology (AIST), Japan, *M. Muruganathan*, Japan Advanced Institute of Science and Technology (JAIST), Japan **INVITED**

The bombardment of specimen by accelerated ions causes implantation and surface sputtering. The latter can be employed to create structures with sub-10 nm dimensions. This precision is demonstrated in electrically contacted and suspended graphene layers by a Helium ion microscope (HIM). 5 nm wide monolayer graphene, suspended above a pore and milled by HIM, had been demonstrated [1]. However, the physical properties of such a ribbon cannot be investigated in such a device architecture due to lack of electrical contacts. Recently, we demonstrated a ~6 nm wide suspended GNR and reported on the room temperature electrical characteristics. A wide range of drain current, at which current suppression occurs, has been observed [2]. However, that device was based on exfoliated grapheme, which makes it necessary to individually design the structures, and the yield is typically small.

Here, we report on the large-array processing of 100 nm wide monolayer CVD based suspended graphene structures by HIM. The structures are prepared by electron-beam lithography and thin-film processing. Before HIM milling, the graphene is released by buffered hydrofluoric acid etching and critical point drying. Annealing in H_2/Ar atmosphere is used to remove the resist contamination.

We will first discuss results of fabricating suspended GNRs with constriction milled with HIM (30 keV acceleration voltage, 1.1x10^{18} ion/cm^2). The GNRs with sub-10-nm constriction are successfully patterned, and the electrical conduction is measured as function of temperature. We will discuss the milling results and electrical characterization in detail along with their potential impact on the performance of graphene-NEMS-based single-molecular detection [3]. We will then report on the recent progress in preparing arrays of nanopores in graphene by HIM. 9x9 arrays with pitch of ~9 nm are successfully realized with a dose of 6.5x10^{18} ions/cm^2. Arrays of pores spanning a complete suspended ribbon with a pitch of ~18 nm are demonstrated as well, and we will discuss the impact of such periodic structure on the electrical and thermal (phononic) transport for nanoscale heat phonon engineering.

Acknowledgements: T. Iijima is acknowledged for the usage of the HIM at AIST SCR Station**.** This research was supported through the Grant-in-Aid for Scientific Research KAKENHI 25220904, 16K13650, 16K18090 from JSPS and COI program of the Japan Science Technology Agency.

References [1] D. Pickard and L. Scipioni, “Graphene Nano-Ribbon Patterning in the ORION® PLUS,” Zeiss application note, 2009. [2] M. E.

Schmidt *et al*., 63rd JSAP Spring Meeting (2016) [3] J. Sun *et al*., Science Advances **2**(4), e1501518 (2016)

5:00pm **HI+NS+TR-ThA9 Monte Carlo Simulation Study of Gas Assisted Focused Ion Beam Induced Etching**, ***Kyle Mahady***, *P.D. Rack,* University of Tennessee, *S. Tan,* Intel Corporation, *Y. Greenzweig,* Intel Corporation, Israel, *R.H. Livengood,* Intel Corporation, *A. Raveh*, Intel Corporation, Israel

We present a simulation study of focused ion beam etching using a gas assist. The use of a precursor gas greatly enhances material removal rate when compared to ion beam sputtering, enabling features such as valleys to be etched with lower ion doses, and consequently less damage to the substrate. The basis of our study is a Monte Carlo based code for focused ion beam milling, which simulates the cumulative removal of material due to sputtering, and secondary electron emission, for various target compositions and structures. In this talk, we describe the gas assisted etching portion of the code, which simulates monolayer adsorption of XeF_2 to a SiO_2 substrate, and the reactions between adsorbed gas and surface atoms which lead to volatilization and material removal. We study the effect of etching parameters such as beam current and gas flux on the shape of etched valleys, and the influence of ion species such as Ne^+ and Ga^+, to characterize the underlying limitations on etching resolution. Simulations are compared against experimental results, for validation and to understand experimentally observed features.

5:20pm **HI+NS+TR-ThA10 Direct Write of Complex 3-Dimensional Structures with Helium Ion Microscopy**, ***Matthew Burch***, *A.V. Ievlev,* Oak Ridge National Laboratory, *M.G. Stanford, B. Lewis,* University of Tennessee, *X. Sang, S. Kim, J. Fowlkes,* Oak Ridge National Laboratory, *P.D. Rack*, University of Tennessee, *R.R. Unocic, A. Belianinov, O.S. Ovchinikova*, Oak Ridge National Laboratory

The next generation of computing, the generation which will follow the end of Moore's law, will need materials processing and interconnects that exist in 3-dimensions. This need has led to multiple investigations into the fabrication of complex free standing 3-dimensional structures onto any substrate at the nano-scale. Several techniques are currently being developed to fabricate free-standing micro- and nano- level structures including two-beam photon lithography and focused electron beam induced deposition (FEBID). Recent advancements in FEBID has led to the ability to simulate and subsequently fabricate complex 3D-platinum structures from an organometallic precursor.

In this work, we demonstrate the ability of the helium ion microscope (HIM) to fabricate complex 3-dimensional structures using focused ion beam deposition (FIBID) at scales smaller than previously demonstrated with FEBID. Using modern day image analytics we demonstrate a method we've successfully utilize to investigate and understand some of the most important structure-growth parameters with FIBID and how that parameter space impacts the size and morphology of created structures. These parameters include beam current, organometallic gas volume, dwell time, etc., and how these impact a grown structures length, width, and possible growth angles.

We further investigate the composition and crystalline nature utilizing scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) in the prescence of different carrier gasses of nitrogen and oxygen. We show, that in general the morphology and chemistry is nearly identical between the two gasses, that there is a slight difference in the apparent crystalline nature between the two flow gasses.

Finally, we demonstrate the minimum size structures currently grown with FIBID and the complex nature of the way these structures can be grown. We also demonstrate the HIM's unique ability to direct write structures repeatedly and reliably on non-conductive using the HIM's unique charge compensation mechanisms.

Acknowledgements

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

Nanometer-scale Science and Technology Division
Room: 19 - Session NS+SP+SS-ThA

Advances in Scanning Probe Microscopy
Moderator: Sergei Kalinin, Oak Ridge National Laboratory

2:20pm **NS+SP+SS-ThA1 Mapping Stress in Polycrystals with sub-10 nm Spatial Resolution**, ***Celia Polop***, Universidad Autónoma de Madrid, Spain, *E. Vasco, A. Perrino, R. Garcia*, Instituto de Ciencia de Materiales de Madrid, CSIC, Spain

From aircraft to electronic devices, and even in Formula One cars, stress is the main cause of degraded material performance and mechanical failure in applications incorporating thin films and coatings. Over the last two decades, the mechanisms responsible for stress generation during film deposition and processing have generated intense conjecture and scientific activity. However, no consensus has been reached so far. The main difficulty is that current models of stress generation, most of which are atomistic in nature, are only supported by data with at best sub-micron resolutions. For example, techniques such as curvature-based measurements, Raman spectroscopy, and x-ray diffraction cannot reveal the stress distribution in films on nanometer scales.

Here, we present a novel method for mapping the stress at the surface of polycrystals with sub-10 nm spatial resolution. This method consists of transforming elastic modulus maps measured by atomic force microscopy (AFM) techniques, such as force modulation method and bimodal AFM, into stress maps via the local stress-stiffening effect. The validity of this approach is supported by Finite Element Modeling simulations. By applying the method to Au polycrystalline films, we show that the intrinsic stress is heterogeneously distributed along the grain diameter, being concentrated in narrow strips adjacent and parallel to the grain boundaries (not directed inside the grain boundary, as is usually assumed). Stress gradients as intense as 100 MPa/nm are detected in these regions. Note that these gradients, which are undetectable by the standard techniques and tests used for stress analysis, are in the order of magnitude of the mechanical strengths required for many applications. The heterogeneous spatial distribution of the intrinsic stress along the grain diameter is the result of the Mullins-type surface diffusion towards the grain boundaries, and would be the probable cause of the kinetic compression that appears in polycrystals under conditions of high atomic mobility. Consequently, we demonstrate that the nanoscale stress mapping has great potential to disclose the nature and origin of the stress in solids.

[1] C. Polop, E. Vasco, A. P. Perrino and R. Garcia, "Mapping stress in polycrystals with sub-10 nm spatial resolution", submitted.

[2] E. Vasco, C. Polop, "The compressive intrinsic stress in polycrystals is not inside the grain boundary", submitted.

3:00pm **NS+SP+SS-ThA3 XTIP – A Dedicated Beamline for Synchrotron X-ray Scanning Tunneling Microscopy**, *N. Shirato, M. Fisher, R. Reininger, S.W. Hla,* ***Volker Rose***, Argonne National Laboratory

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 500-1600 eV energy range.

The dedicated XTIP beamline will provide researchers access to a one-of-a-kind instrument. Among the potential breakthroughs are "designer" materials created from controlled assembly of atoms and molecules, and the emergence of entirely new phenomena in chemistry and physics.

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.

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

[2] H. Yan et al., J. Nanomaterials 2015, 492657 (2015).

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

3:20pm **NS+SP+SS-ThA4 Kelvin Probe Force Microscopy for High-Resolution Imaging of Hydrogen in Steel Alloys**, ***Joy McNamara***, *P. Korinko, M. Morgan, A. Duncan*, Savannah River National Laboratory

Understanding the mechanism of hydrogen interactions in metals is continually a topic of interest for those exploring the use of hydrogen as an alternative fuel source and for other applications which involve the long term storage of hydrogen. Atomic hydrogen in stainless steel alloys segregates to regions of extended defects, such as grain and phase boundaries, and can cause stress and premature cracking in a process known as hydrogen embrittlement. The presence of hydrogen can have serious consequences on the structural integrity and lifetime of hydrogen containers and piping, making it essential to understand the effect of hydrogen on the microstructural properties of stainless steel alloys. The migration of hydrogen through the crystal structure depends on the diffusion rate and solubility of hydrogen in a given phase which gives rise to varying hydrogen concentrations between phases. Hydrogen segregated at the surface of stainless steel specimens and particularly at defect sites changes the local work function of the material and can be measured by Kelvin probe force microscopy (KPFM). By co-locating the presence of hydrogen with extended defects at the surface using KPFM, it may be possible to predict the long term storage properties of a container. KPFM produces nanoscale surface potential (i.e., voltage) images, and is capable of measuring the local change in work function of materials with very high spacial resolution compared to current methods of optically imaging the microstructures of stainless steel. In this work, stainless steel specimens were fabricated by forging techniques and laser engineered net shaping (LENS), a directed energy deposition method of additive manufacturing, and were hydrogen charged at high pressure and temperature for approximately 2 weeks. The samples were then cut and polished to produce smooth surfaces and were imaged using KPFM. The resulting surface potential images show concentration differences of hydrogen at twin boundaries, phase boundaries and other defects as evidenced by a reduction in the local contact potential difference (CPD). Differences in CPD between the forged and LENS samples were observed and will be discussed. This work has potential to elucidate the effects of hydrogen on stainless steel components.

4:00pm **NS+SP+SS-ThA6 Video-Rate Atomic Force Microscopy**, ***Roger Proksch***, Asylum Research **INVITED**

We present results from a new, video rate AFM (Cypher VRS) capable of imaging delicate samples in air and fluid up to 625 lines/second (or >10 frames per second). This is about 300x faster than typical AFMs and 10x faster than current "fast scanning" AFMs. We will describe the architecture of this new AFM, and demonstrate the advantages of its unique design. Some recent specific examples are shown, including: (1) real time observation of the cleavage of a DNA molecule with the DNase1 enzyme. (2) a variety of high resolution examples including Bacteriorhodopsin molecules, the DNA double helix and single atomic point defects, all acquired at frame rates in excess of 1 frame per second, (3) the self-assembly of type I Collagen molecule into fibrils. Collagen molecules were injected on a bare mica surface and let spontaneously polymerize to form fibrils in a phosphate buffer. The typical banding pattern of 67 nm appeared as early as 1 min after introduction of the molecules, and, finally, (4) the dynamics of CTAB hemi-micelles at the solid-liquid interface (HOPG and aqueous buffer). These long molecules spontaneously form micelles in aqueous solutions and hemicylindrical structures upon adsorption onto HOPG. AFM can image these structures with high resolution but with the VRS the kinetics of the formation can now be followed in real time.

4:40pm **NS+SP+SS-ThA8 Novel AFM Probes Enable Highly Sensitive Chemical and Thermal Characterisation at the Nano Scale**, ***Georg Ramer***, *J. Chae, S. An*, NIST Center for Nanoscale Science and Technology / University of Maryland, *V.A. Aksyuk, A. Centrone*, NIST Center for Nanoscale Science and Technology

Photothermal induced resonance (PTIR) - a hyphenated technique of optical spectroscopy and scanning probe microscopy - allows to perform chemical imaging at nanoscale resolution [1,2]. The signal generation in PTIR consists of illuminating the sample with a pulsed tunable laser and transducing the local thermal expansion using a conventional AFM tip. The rapid expansion of the sample induces a ring down motion in the cantilever with amplitudes proportional to the absorption coefficient. Absorption images can be collected by moving the AFM tip across the sample, local absorption spectra can be collected by keeping the tip still and tuning the laser. PTIR works at ambient conditions and is non-destructive, making for a wide range of possible applications.

PTIR has been successfully applied to range of different samples, from life sciences, to photonics, material science and quality control [1,2]. Recently, PTIR sensitivity down to a monolayer has been demonstrated by using optical field enhancement between a gold tip and gold substrate as well as a mechanical enhancement by resonant excitation of the AFM cantilever.

Here, we present latest advances in improving the sensitivity of PTIR. Our novel AFM tips based on a nanosized picogram scale micromechanical cantilever as a displacement sensor and an optical resonator based near field read out achieve a thermal noise limited deflection measurement in the low fm Hz$^{-0.5}$ range. Through the high sensitivity and low noise detection of these new probes we obtain PTIR spectra of monolayer samples with high signal to noise ratio, without the need for optical field enhancement or resonant excitation.

Furthermore, low detection noise across the large bandwidth achieved by these probes enables the direct measurement of the sample thermal expansion dynamics after each laser pulse. Leveraging a simple model, the fitting of the thermal expansion dynamics yields the local thermal conductivity at unprecedented, nanoscale lateral resolution.

1 Centrone, A.: 'Infrared Imaging and Spectroscopy Beyond the Diffraction Limit', Annual Review of Analytical Chemistry, 2015, 8, pp. 101-126

2 Dazzi, A., and Prater, C.B.: 'AFM-IR: Technology and Applications in Nanoscale Infrared Spectroscopy and Chemical Imaging', Chem Rev, 2016

5:00pm **NS+SP+SS-ThA9 Photoinduced Thermal Desorption Coupled with Atmospheric Pressure Chemical Ionization Mass Spectrometry for Multimodal Imaging**, ***Matthias Lorenz***, *C.C. Brown*, University of Tennessee, *R. Proksch, M. Viani, A. Labuda*, Oxford Instruments, *S. Jesse, O.S. Ovchinnikova*, Oak Ridge National Laboratory

The key to advancing materials is to understand and control their structure and chemistry. However, thorough chemical characterization is challenging since existing techniques characterize only a few properties of the specimen, thereby necessitating multiple measurement platforms to acquire the necessary information. The multimodal combination of atomic force microscopy (AFM) and mass spectrometry (MS) transcends existing analytical capabilities for nanometer scale spatially resolved correlation of the chemical and physical properties of a sample surface. The combination of AFM and MS using resistively heated cantilever tips for thermal desorption has been demonstrated as a promising pathway for multimodal imaging. However, the nano-TA heated probes limit the ability to carry out more standard AFM measurements such as PFM, KPFM and cAFM. To enable a more general application of chemical imaging into an AFM platform we have developed a novel closed cell sampling on an Oxford Instruments Cypher ES for in situ surface sampling/imaging analysis using photothermal heating of the AFM tip for thermal desorption (TD) coupled to a Thermo Orbitrap Velos Pro with inline ionization by atmospheric pressure chemical ionization (APCI). This approach takes advantage of the blueTherm cantilever heating technology developed by Oxford Instruments for localized thermal desorption, and demonstrates its applicability to multimodal chemical imaging using mass spectrometry. The ability to use photothermal heating of an AFM probe versus conventional resistive heating nano-TA technology opens up the possibility for carrying out multiple AFM measurement approaches on a single AFM cantilever, for a true multimodal imaging approach to link chemical composition with material functionality. We show the use of photothermal heating as a means for thermal desorption surface sampling mass spectrometry. We illustrate the application of the AFM-MS coupling for the analysis of small molecules, i.e. pigment yellow 74 as a test substrate to show 500 nm achievable lateral resolution as well as show the application to pharmaceuticals and polymer films. Additionally, the ability to introduce fast heating rates for the TD through ps laser pulsing reduces the melting of sample material and improves the access to intact molecules.

5:40pm **NS+SP+SS-ThA11 Synchrotron X-ray Scanning Tunneling Microscopy Investigations of Magnetic and Electronic Properties of Nanoscale Metal-Clusters**, ***Hao Chang***, Ohio University and Argonne National Laboratory, *N. Shirato, M. Cummings*, Argonne National Laboratory, *H. Kersell*, Ohio University and Argonne National Laboratory, *D. Rosenmann, J.W. Freeland, V. Rose*, Argonne National Laboratory, *S.W. Hla*, Ohio University and Argonne National Laboratory

Synchrotron X-ray scanning tunneling microscope (SX-STM) [1,2] combines two of the most powerful materials characterization techniques, synchrotron X-rays and scanning tunneling microscopy. SX-STM has a great potential revolutionize material characterizations with simultaneous elemental, magnetic and topological contrast down to the atomic scale. Here, we will present our recent SX-STM results of nanoscale materials measured at the Advanced Photon Source of Argonne National Laboratory. Using SX-STM X-rays absorption spectroscopy (XAS) technique, we are able to determine the X-ray absorption cross-section of a single nickel and cobalt nanoclusters on a Cu(111) surface. By employing circular polarized synchrotron X-rays, we are also able to demonstrate X-ray magnetic circular dichroism (XMCD) of the Fe L_2 and L_3 edges of a thin iron film deposited on Cu(111) [3] as well as LSMO/LNO superlattices in room and lower temperatures. Here, polarization dependent x-ray absorption spectra have been obtained through a specially fabricated tip that captures photo-electrons. Unlike conventional spin-polarized STM, x-ray excitations provide magnetic contrast even with a non-magnetic tip. Intensity variations in the photo-excited current indicate chemical variations within a single magnetic Fe domain. Moreover, using a hard X-ray nanoprobe beamline, we have successfully detected element specific X-ray induced electron emissions from a single cobalt nanocluster at room temperature. Here, varying the incident x-ray energy across the Co electron binding K-edge enables the detection of elementally sensitive electrons. As the tip scans across the single Co nanocluster- Au(111) surface boundary, atomic spatial dependent changes in the x-ray absorption cross section are directly measured by taking the x-ray induced current as a function of x-ray energy. In addition to presenting the recent results, we will also discuss potential future research directions using SX-STM.

[1] V. Rose, K. Wang, T.U. Chien, J. Hiller, D. Rosenmann, J.W. Freeland, C. Preissner, and S.-W. Hla. ***Adv. Funct. Mater.*****23**, 2646-2652 (2013).

[2] N. Shirato, M. Cummings, H. Kersell, Y. Li, B. Stripe, D. Rosenmann, S.-W. Hla, and V. Rose. ***Nano Lett.*****14**, 6499-6504 (2014).

[3] A. Dilullo, N. Shirato, M. Cummings, H. Kersell, H. Chang, D. Rosenmann, D. Miller, J.W. Freeland, S.-W. Hla, and V. Rose. ***J. Synchrotron. Rad.*****23**, 574-578 (2016).

Thin Films Division
Room: 21 - Session TF+MI+NS-ThA

ALD and Nanostructures
Moderators: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, France, Richard Vanfleet, Brigham Young University

2:20pm **TF+MI+NS-ThA1 Coating and Infilling 3D Geometries by Low-T CVD : HfB$_2$ throughout 0.5 mm Thick CNT Forests**, ***John Abelson***, University of Illinois at Urbana-Champaign **INVITED**

We describe the use of extremely conformal chemical vapor deposition to coat carbon nanotube forests throughout their depth with a film of HfB$_2$, a mechanically hard, electrically conductive and highly refractory alloy. CVD uses the precursor Hf(BH$_4$)$_4$ at partial pressures $\leq$ 15 Torr at substrate temperatures $\leq$ 200°C. The CNT forests are up to 500 µm thick and can be shaped by pre-depositing patterns of seed metal on the underlying substrate prior to their synthesis.

Coating CNT forests affords a new class of composite foams with adjustable mechanical properties : the HfB$_2$ coating both stiffens individual tubes and “welds” them together wherever they touch, whereas in the uncoated forest the tubes can slide relative to one another. We fabricate cylindrical pillar structures with HfB$_2$ thicknesses from 3-50 nm. As measured by nanoindentation using a flat punch, the Young’s modulus varies over three orders of magnitude as $E \sim \rho^{1.7}$, where the mass density ρ is dominated by the HfB$_2$ coating. The maximum stiffness and strength are 56 and 1.9 GPa, respectively.

A major question is how CVD can achieve a nearly uniform coating in such a deep structure. The challenge is inherent in the diffusion-reaction kinetics : the transport of reactants occurs by molecular diffusion, which is slow in narrow cross-sections; while at the same time the reaction (consumption) rate must be high enough to be useful. In combination, these factors imply that the partial pressure (flux) of reactants must diminish with depth; if the film growth rate varies monotonically with flux, then the coating thickness must decline with depth in the structure.

The solution is to (i) employ a precursor that exhibits a hard saturation in the growth rate vs. partial pressure, (ii) use a high partial pressure above the sample, and (iii) grow at low temperature to limit the reaction rate. Under these conditions, even though the partial pressure of precursor drops considerably from the top to the bottom of the sample, the growth rate remains almost constant. To achieve the high precursor pressure, we employ a static (unpumped) reaction tube apparatus. We previously derived a master relationship [1] that predicts the precursor pressure (*p*) necessary to achieve a desired step coverage (*SC*) and growth rate (*GR*) in a given aspect ratio (*AR*) given knowledge of the atomic density (r), growth rate coefficient (*K*) and molecular diffusivity (D_0): $p = (GR\ AR) * ((c\ r\ kT) / (2\ D\ K) * (1 - SC))$^0.5

We will discuss extension of this method to other thin film systems and substrate geometries.

1. A. Yanguas-Gil, Y. Yang, N. Kumar, and J. R. Abelson, JVST A **27,** 1235 (2009) [DOI: 10.1116/1.3207745]

3:00pm **TF+MI+NS-ThA3 Varying Penetration Depths in ALD on High Aspect Ratio Carbon Nanotube Forests**, ***David Kane***, *RC. Kane, R.R. Vanfleet*, Brigham Young University

We have observed steps in the penetration depth in atomic layer deposition on tall vertically aligned multiwall carbon nanotube (MWCNT) forests. The deposition thickness at the top of the forest is greater than that at the bottom and varies in distinct steps. The MWCNT forests used were 200 µm tall with an aspect ratio of about 2000. In the thermal TMA/water process on MWCNTs, precursor pulse times ranged from 0.5s to 2s. We propose a model for banding where Al2O3 nuclei grow in each cycle, thus the number of TMA adsorption sites increases. Due to the confined geometry, Knudsen diffusion and adsorption site density determine the relationship between precursor penetration depth and exposure time. The penetration depth is inversely proportional to the square root of the precursor adsorption site density and proportional to the square root of the exposure time. We have measured the penetration depth for different bands and a good fit to our model is shown.

3:20pm **TF+MI+NS-ThA4 NiOx Decorated Platinum Nanoparticles Via Atomic Layer Deposition for Enhanced Sintering Resistance**, ***Jiaming Cai***, *K. Cao, M. Gong, B. Shan, R. Chen*, Huazhong University of Science and Technology, PR China

Platinum nanoparticles (NPs) play an important role in the catalytic applications such as conversion of automotive exhaust, fuel cells, nano sensing and so on. For most catalytic applications, sintering of Pt NPs is undesired since the coalescence decreases the number of active sites of the catalyst. Herein we report the utilization of active oxide layers to encapsulate Pt NPs to enhance sintering resistance at high working temperature. The active oxide coated catalysts have additional metal-oxide interfaces which may further improve the catalytic activity besides good sintering resistance. Nickel oxide coating layer is prepared via atomic layer deposition (ALD) method. The effect of layer thickness towards catalytic properties and thermal stability for CO oxidation are investigated. The thickness of nickel oxide coating layer was controlled accurately by varying the ALD cycles. Characterizations including TEM, XPS, FTIR and XAFS were undertaken to explore the origin of the CO oxidation catalytic activity enhancement. *In-situ* AFM test is carried out to explore the mechanism of nanoparticles migration and sintering phenomenon in different environment by controlling the calcination temperature and oxygen partial pressure. Nickel oxide anchors Pt NPs with a strong metal oxide interaction, and coating structure around Pt NPs provide physical blocking that suppresses NP particle migration and coalescence. The catalysts show both enhanced CO conversion activity and improved sintering resistance up to 700 °C under oxidative atmospheric conditions.

4:00pm **TF+MI+NS-ThA6 Atomic Layer Deposition of HfO$_2$/Al$_2$O$_3$ Nanolaminates on Single-crystal GaN and Ga$_2$O$_3$: Investigation of Device Degradation in Power Semiconductor Devices**, ***David Mandia***, *A. Yanguas-Gil, J.A. Libera, J.W. Elam*, Argonne National Laboratory

The search for adequate binary metal oxide dielectric nanolaminates (NLs) to prevent degradation of power semiconductor devices is ongoing and involves the atomic layer deposition (ALD)-growth of a variety of binary metal oxide combinations. In the present work, we explore the ALD growth of amorphous (x)HfO$_2$/(y)Al$_2$O$_3$ NLs on Si (with native SiO$_2$ layer) substrates and then on both GaN and Ga$_2$O$_3$ single crystals. A variety of samples ranging from their homogeneous mixtures to HfO$_2$ or Al$_2$O$_3$-rich NLs are assessed before and after a thermal annealing by spectroscopic ellipsometry (SE), X-ray reflectometry (XRR), X-ray photoelectron spectroscopy (XPS) and 4-point probe resistivity measurements in order to elucidate the structural evolution of the NL at the GaN (or Ga$_2$O$_3$)-NL interface. By quantifying the HfO$_2$ incorporation throughout the Al$_2$O$_3$ layer and using the programmable nature of ALD to alternate layers of the HfO$_2$ and Al$_2$O$_3$ in an $(AB)_x$-$(CD)_y$ fashion, the influence of HfO$_2$ mobility within Al$_2$O$_3$ layer on the NL dielectric constant can be verified unequivocally. Moreover, combined X-ray absorption near-edge (XANES) and X-ray absorption fine structure (XAFS) spectroscopy data obtained at the Advanced Photon Source will confirm the local coordination environment of the Ga at the GaN (or Ga$_2$O$_3$)-HfO$_2$ interface and, at low super-cycle numbers (sub-nm scale), the ultimate stability of the NLs can be probed and optimized such that the bulk material properties are retained.

4:20pm **TF+MI+NS-ThA7 Atomic Layer Deposition Enabled Synthesis of Multiferroic Composite Nanostructures**, ***Jeffrey Chang****, University of California at Los Angeles, *A. Rosenberg,* Stanford University, *A. Buditama,* University of California at Los Angeles, *E. Jin, L. Kornblum, C. Ahn,* Yale University, *S.H. Tolbert,* University of California at Los Angeles, *K.A. Moler,* Stanford University, *J.P. Chang*, University of California at Los Angeles

Multiferroic materials, which exhibit the coexistence and coupling between ferroelectricity and magnetism, are of great interest due to their potential for enabling next-generation memories. To overcome the scarcity and weak responses of single-phase multiferroics, composite strategies were proposed for a robust multiferroic behavior by coupling the functional properties through the interface. By interfacing magnetostrictive and piezoelectric materials, the strain-mediated coupling strategy holds great promise, while both the interfacial-area-per-volume and the quality of interfaces play important roles in attainable functional properties. To obtain applicable magnetoelectric (ME) coupling under such scheme, lead-free multiferroic $BiFeO_3$ (BFO) and ferrimagnetic $CoFe_2O_4$ (CFO) were used in this study due to their robust functionality.

With the aim of enhancing the coupling by nanostructuring, atomic layer deposition (ALD), with its high quality and conformal film growth, was employed to achieve BFO/CFO composites with closely coupled interfaces and industrial scalability. BFO and CFO with were synthesized by radical enhanced ALD on $SrTiO_3$ (001) substrates using tmhd-based organometallic precursors(tmhd=2,2,6,6-tetramethylheptane-3,5 dione). The use of oxygen radicals as the oxidant provides a low temperature processing capability at 200°C. Post-deposition thermal treatments promotes the crystallization of both the BFO and CFO films and thus comparable functional properties were obtained. 2D-2D BFO/CFO composites were then synthesized by combining the ALD processes, with an optimized functionality obtained by nanolayering. ME behaviors comparable to previously studied multiferroic composites were observed, and the scaling of materials leads to an enhancement in the coupling coefficient (≈64 Oe cm/kV). The change in magnetic domains upon electrical poling was characterized using scanning SQUID. The 2D-2D BFO/CFO on $SrTiO_3$-buffered Si substrates exhibited comparable ME behaviors to the case on $SrTiO_3$, illustrating a path to integrate multiferroic materials into current industrial processes by ALD.

0D-3D BFO/CFO was realized by incorporating ALD-grown $BiFeO_3$ and mesoporous CFO substrates. Composite functionality as well as ME coupling were studied as a function of residual porosity after ALD filling. Higher BFO incorporation increases the overall ferroelectricity but limits the strain interaction due to a decreased mechanical flexibility. The strain interaction was verified by the change in lattice parameters observed using high-resolution XRD measurements. The results showed that the residual porosity is the key for ME coupling in a strain-mediated scheme.

4:40pm **TF+MI+NS-ThA8 Recent Developments in the Analysis of ALD/CVD Thin Film Conformality**, ***Riikka Puurunen***, Aalto University, School of Chemical Engineering, Finland **INVITED**

The downscaling of future semiconductor devices with increasing 3D character has lead to increasing demand of highly conformal thin films. Atomic layer deposition (ALD), based on the use of repeated, self-terminating reactions of typically at least two compatible reactants on a solid substrate, is often the only technique that can meet the conformality specifications. Conformal films made by ALD are also needed in other fields with intrinsic three-dimensionality requirements such as microelectromechanical systems (MEMS) and porous particle based applications (e.g., catalysis).

This work overviews recent progress in thin film conformality analysis made with the microscopic lateral high-aspect-ratio (LHAR), especially the “PillarHall” structures developed at VTT. Significant progress has taken place during the past year in the design and fabrication of the structures, conformality testing by academic and industrial partners, as well as modelling. The key feature of VTT’s PillarHall structures is the existence in silicon of a lateral gap of controlled height, typically 500 nm (can be varied from wafer to wafer, 100 to 2000 nm demonstrated), and controlled length up to 5 mm (several variations inside one chip, starting from 1 µm). Test structures with aspect ratio (AR) up to 50 000 : 1 ("hole-equivalent AR (EAR)" up to 25 000 : 1) have been fabricated this way. Growth of thin film inside the controlled 3-D gap and analysis of the film thereafter, often after removing the top part of the test structure by applying an adhesive, reveals the film thickness and composition profile. As compared to conventional vertical trenches etched into silicon, with VTT’s lateral PillarHall test structures, one can in a significantly shorter time obtain more detailed information on the conformality, which can be used for optimising processes, designing new processes, and investigating the fundamental mechanisms behind the deposition processes. Three scientific publications [1-3] report on the use of PillarHall 1st generation prototypes. At the time of writing this abstract, we work with 3rd generation prototypes and design the 4th generation.

Acknowledgements: Funding for the development of the conformality test structures has come from the Academy of Finland’s Finnish Centre of Excellence in Atomic Layer Deposition and the Tekes PillarHall project.

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5:20pm **TF+MI+NS-ThA10 Spatial Atomic Layer Deposition Reactor Design for Nano-laminates**, *X.L. Wang*, ***Yun Li***, *J.L. Lin*, *J.M. Cai*, *R. Chen*, Huazhong University of Science and Technology, PR China

Atomic layer deposition (ALD) is commonly a vacuum based technique for ultrathin film fabrication with precise control of film thickness, uniformity and conformity. In contrast to conventional temporal ALD (T-ALD) that precursors and purging gases are introduced into reactor sequentially, the separation mode of spatially-separately ALD (S-ALD) between reactive precursors is in space instead of in time, thus the process is continuous. In S-ALD process, the inert gas serves as a flow gas barrier to separate the precursors’ zones, which prevents the cross contamination and atmosphere perturbation. With the alternating arrangements of oxidizer gas channels, metal source channels, and gas barriers of inert gas, the deposition rate of S-ALD could reach 1-3 order of magnitude higher than T-ALD. Moreover, the atmospheric pressure in S-ALD system enables this technique in a continuous form without vacuum. As the continuing development of S-ALD, it has found many potential high through-put and large scale applications. Here we present an S-ALD system design for fabricating binary oxides and their nano-laminates. The design of S-ALD reactor is based on motion structure of linear track and injector with a multiple slit gas source channel. By optimizing the structure of precursor channel based on the flow field simulation, a tree-branch-like gas feed structure is obtained, and the uniformity of the precursor distribution is enhanced significantly. The T-curve motion profile is replaced by the S-curve t o control the movement of substrate which can avoid abrupt change of acceleration and jerk in the acceleration and deceleration process, stabilizing the distance between injector and substrate precisely. The growth of thin film at different moving speeds has good linearity and uniformity. By integrating different reaction units, nano-laminates with tunable optical and electrical properties can be obtained.

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* **TFD James Harper Award Finalist**

Nanometer-scale Science and Technology Division
Room: Central Hall - Session NS-ThP

Nanometer-scale Science and Technology Poster Session

NS-ThP1 Co-deposition of Nanoparticle – Diamond-Like Carbon Composite Thin Films

***Ajai Iyer**, J. Etula, N. Wester, J. Koskinen*, Aalto University, School of Chemical Engineering, Finland

Nanoparticles have been proven to have properties very different from bulk materials and extensive research is undertaken to ascertain application based nanoparticle functional properties. One of the most elegant solutions for nanoparticle usage is to form a composite thin film with desired nanoparticles embedded in a matrix. Such composite films are generally fabricated in one of two ways. Either the nanoparticles are synthesized in-situ during the film growth process or the nanoparticles are seeded prior to film growth process. We propose a unique method of using physical vapour deposition methods to co-deposit pre-processed nanoparticles in tandem with the matrix material forming a composite thin film. These composite films could be deposited as single or multi-layer bulk films or as films with nanoparticle concentration gradient throughout the film thickness. The matrix material is chosen to be diamond-like carbon (DLC) with controllable sp^3 to sp^2 bonded carbon ratio, allowing the film to have a wide range of mechanical, optical and electrical properties. Co-deposition of nanoparticles with DLC results in composite films where nanoparticles are embedded into a DLC matrix. The effect of the type and concentration of nanoparticles on the mechanical, optical and electrical properties of the composite film are currently under study with possible application fields related to sensors, electrically conductive coatings, thin film optical waveguides and energy storage. In this work we demonstrate detonation nanodiamonds (DNDs) co-deposited with high quality DLC using a pulsed filtered cathodic vacuum arc (p-FCVA) method to form DND-DLC composite film. Transmission electron microscopy (TEM) has been used to verify the presence of DND agglomerates (sized few tens of nm) in the composite film as well as the crystallinity of the embedded DND nanoparticles. The DND nanoparticle concentration has been estimated to be of the order of 0.1 vol% in the composite film. The DND-DLC composite film has been measured to have around 16% enhancement in hardness and 40% reduction in wear in comparison to DLC film. Preliminary tests indicate that the composite film has potential as an electrochemical sensor and further tests are in progress. Results of co-deposition of other nanoparticles with DLC to form composite film are also discussed.

NS-ThP2 Atmospheric Pressure Plasma Functionalization of Diamond Particles

***Gary McGuire**, O.A. Shenderova, N.J. Nunn*, Adamas Nanotechnologies, Inc.

Dielectric barrier discharges are non-equilibrium plasmas which may operate at atmospheric-pressure avoiding the necessity of generating vacuum conditions. Operation at atmospheric pressure facilitates the introduction and surface functionalization of gram quantities of nanoparticles within minutes at room temperature as an alternative means to high temperature processes which typically takes hours. In this study nanodiamond particles of detonation origin were fluorinated using CF_4. Surface analysis using x-ray photoelectron spectroscopy confirmed a fluorine concentration of up to ~4.5 at% of the nanodiamond particles surface. Fourier transform infrared spectroscopy revealed the presence of F-bands, related to CF_3 - (CF_2) stretching vibrations and symmetric and asymmetric CF_2 vibrations. Fluorine surface functional groups can serve as a means for further chemical substitution reactions so that other, more complex functional groups such as amino acids, oligonucleotides, peptides, etc. can bond to the surface, facilitating material applications for biosensors. It has been demonstrated that an atmospheric pressure dielectric barrier glow discharge is a highly effective means to rapidly fluorinate, oxidize and aminate diamond surfaces.

NS-ThP3 Nanometer-scale Etch Characteristics of TiN Thin Films using Inductively Coupled Plasma of $Cl_2/C_2F_6/Ar$

***JaeSang Choi**, J.Y. Lee, D.H. Cho, C.W. Chung*, Inha university, Republic of Korea

As the information era has come, high performance semiconductor memory devices which have the characteristics containing high density, fast process time, lower power consumption for faster mass data transfer has been required. To satisfy these demands, scaling down to nanometer scale for etching process has been important in fabricating semiconductor devices. Titanium nitride (TiN) thin film has been widely employed as a hard mask due to its fine property such as good thermal and chemical stability, and good adhesion than conventional inorganic masks. In the past, there were some studies on TiN films using Cl_2, BCl_3, NF_3, CF_4, and SF_6 gases [1-3]. However, the etching process of nanometer-sized TiN films was rarely investigated.

In this study, nanometer-scaled e-beam resists were patterned on TiN thin films and inductively coupled plasma reactive ion etching using $Cl_2/C_2F_6/Ar$ gas mixtures was applied to investigate the characteristics of TiN thin films. First, a variety of gas ratio was examined to find out best etch profile using micro-patterned TiN thin films. Then, based on these results, the nanometer-patterned TiN thin films using $Cl_2/C_2F_6/Ar$ gas mixtures were investigate in terms of etch selectivity and etch profile. Finally, energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy will be performed on the etched TiN films to elucidate the etch mechanism.

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J. Tonotani, T. Iwamoto, F. Sato, K. Hattori, S. Ohmi, H. Iwai, Dry etching characteristics of TiN film using Ar/CHF_3, Ar/Cl_2, and Ar/BCl_3 gas chemistries in an inductively coupled plasma, J. Vac. Sci. Technol. B 21 5 (2003) 2163-2168.

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NS-ThP4 Etch Characteristics of Magnetic Tunnel Junction Stacks using Pulse-modulated RF Source Plasma

***JaeYong Lee**, J.S. Choi, D.H. Cho, C.W. Chung*, Inha University, Republic of Korea

The source/bias pulse-time modulated RF plasma has been introduced to progress further in convoluted challenges from conventional continuous wave (CW) plasma such as fatal etch damage, low etch selectivity, and etch residues. This modulated plasma means the plasma condition modified by a specific matching system which can change on-off duty ratio of 13.56MHz RF power and frequency on the specific duty ratio. Especially, since the magnetic materials used for magnetic random access memory (MRAM), which is a promising candidate for next generation semiconductor, have less reaction with even corrosive gases, this process can offer a prospective approach. Some researches on etch characteristics of magnetic materials using bias-pulse time modulated plasma has been reported, resulting in improved etch profiles compared to CW plasma . However, few studies on the magnetic materials using source-pulsed plasma can be found.

In this study, etch characteristics of nanometer-scale patterned magnetic tunnel junction stacks (MTJs), which is a critical component of MRAM, using the pulsed modulated RF source plasma were investigated. The MTJs consisted of TiN/Ta/CoFeB/MgO/CoFeB/Ta on the SiO_2 substrate and E-beam resists of 70×70 nm^2 were patterned on the TiN hardmasked MTJ stacks. In the plasma process, the non-corrosive gas mixture of $CH_4/O_2/Ar$ was used. The effects of on-off duty ratio and frequency of pulsed plasma on the etch characteristics of MTJ stacks were examined.

NS-ThP5 Dry Etching of Nanometer-scale Patterned CoFeB Thin Films under Pulse Modulated Plasma

***DooHyeon Cho**, J.S. Choi, J.Y. Lee, C.W. Chung*, Inha University, Republic of Korea

Dynamic random access memory device has been commercially sucessful. However this device has disadvantages such as volatility and scaling problem. Spin transfer torque magnetic random access memory(STT-MRAM) has been recieved a great attention as the next-generation memory device owing to the advantages such as non-volatility, high density, unlimited endurance and low operating voltage[1]. The STT-MRAM devices are composed of magnetic tunnel junction stacks (MTJs) and CMOS. As the dimension of MTJs is decreased, perpendicular magnetic anisotropy (PMA) is necessary for high density MRAM. Therefore, the MTJs comprised of multilayers incluing CoFeB thin films should be fabricated in nanometer-scale dimension for PMA [2]. In order to realize this demand for high density MRAMs, the magnetic thin films such as CoFeB, CoPt, PtMn and so on should be patterned in nanometer-scale.

In the previous studies, micrometer-scale patterned CoFeB thin films showed relatively good etch profiles using CH_3OH, CH_3COOH and $CH_4/O_2/Ar$ [3,4,5]. In this study, the etch characteristics of nanometer-scale patterned CoFeB thin films using $CH_4/O_2/Ar$ gas mixture under pulse-modulated plasma were investigated. The main parameters in pulsed-modulated plasma, which are on-off duty ratio and pulse frequency, were applied to investigate the etch characterisitic of CoFeB thin films. Finally, high degree of anisotropy of the etched CoFeB films with 70 x 70 nm^2 patterns were obtained and the etch mechanism also was examined using optical emission spectroscopy, X-ray photoelectron spectroscopy and TEM micrographs.

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NS-ThP6 The Formation of Stable GeO_2 Oxide using the High Pressure Oxidation, ***Juhyun Bae***, *I.S. Chung*, Sungkyunkwan University, Republic of Korea

Thermal oxidation of Ge has been investigated under high pressure ambient to suppress GeO vaporization. Ge oxide was grown in the temperature range of 450 °C to 550 °C in dry O_2 ambience at three different pressures such 10, 30, and 50 atm. The physical property of GeO_2 is analyzed using the transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Additionally, C-V characteristics were obtained from GeO_2/Ge MOS capacitors. The hysteresis in C-V characteristics and the interface trap density (D_{it}) are significantly reduced as the pressure increases. Consequently, the properties of both GeO_2 film and GeO_2/Ge interface are successfully improved by suppressing GeO volatilization utilizing high pressure.

NS-ThP8 Controlling Kondo Resonances of Magnetic Molecules on Au(111) by Binding of Metal Atoms, ***MinHui Chang***, Korea University, Republic of Korea, *Y.H. Chang,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea, *H. Kim, S.H. Lee*, Korea University, Republic of Korea, *Y.H. Kim*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea, *S.-J. Kahng*, Korea University, Republic of Korea

Controlling and sensing spin states of magnetic molecules at the single molecule level is essential for spintronic molecular device applications. The exchange coupling between magnetic-molecules and metallic substrates has been actively studied by measuring Kondo resonances at Fermi level. The resonances have been controlled by small molecule bindings, but not by adsorption of metal atoms to magnetic-molecules. Here, we demonstrate that Kondo resonances of Co-porphyrin on Au(111) can be controlled by adsorption of metal atoms, 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 resonances in STS, whereas Co-porphyrin adsorbed metal atoms showed modified zero-bias resonances, 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-orbitals of Co-porphyrin by the adsorption of metal atoms. Our study shows that the spin-state of metallo-porphyrin can be modified in multiple ways by the adsorption of additional metal atoms, and be probed through Kondo resonances with STS.

NS-ThP9 Nanolithography Toolbox: Design Solutions for Nanoscale Devices, ***Roberto De Alba***, *K.C. Balram, D.A. Westly, M. Davanco, K.E. Grutter, Q. Li,* NIST, *T. Michels,* GenISys GmbH, *C.H. Ray, L. Yu, R.J. Kasica, C.B. Wallin,* NIST, *D.A. Czaplewski, L.E. Ocola,* Argonne National Laboratory, *S. Krylov,* Tel Aviv University, Israel, *P. Neuzil,* Brno University of Technology, Czech Republic, *K. Srinivasan, S.M. Stavis, V.A. Aksyuk, J.A. Liddle, B.R. Ilic*, NIST

Various lithography patterning technologies can be used to define structures with nanometer-scale lateral dimensions. The first step in any lithographic process consists of device design. There are a number of available design packages that output semiconductor-standard graphic database system (GDSII) files, which is a binary format representing planar geometric shapes. The predominance of IC devices in manufacturing has led to the development of software packages that are ideal for designing and laying out integrated circuits, which typically have rectilinear geometries, where shape edges are parallel to the *x* and *y* axes. Consequently, many of these software packages are not ideal for designing curved geometries with aggressively-scaled dimensions for nanophotonic, nanoplasmonic, nanofluidic, and nanomechanical devices. To solve this design problem, we have developed a computer-aided design (CAD) software package for streaming complex shapes to GDSII. The platform-independent Nanolithography Toolbox runs on Linux, Windows and MacOS, and is free for users to download from the Center for Nanoscale Science and Technology at the National Institute of Standards and Technology (CNST) website (http://www.nist.gov/cnst/).

The CNST developed the Toolbox to help users of the CNST NanoFab to design their nanoscale devices, particularly those with curved features and small dimensions. The Toolbox offers design features that are difficult to implement in software optimized for IC design, and allows users to rapidly customize nanoscale shapes of arbitrary complexity. The Nanolithography Toolbox offers hundreds of parameterized shapes that are useful in a variety of applications spanning nanoscale photonics, mechanics, fluidics, electronics, and other disparate fields of scientific endeavor. Furthermore, the Toolbox allows users to precisely define the number of vertices for each shape or to create vectorized shapes using Bezier curves. In the former case, the Toolbox constructs the resulting shapes with a uniform vertex distribution along the periphery, rendering symmetric objects. A shape-rendering parameter controls the number of vertices for vectorized objects. The parameter is set globally for all shapes, or individually for each shape. In the latter case, the resulting rendered shapes have an increased vertex density at higher curvatures. A full description of the all the capabilities of the Toolbox can be found in the manual.

NS-ThP10 Visualizing Silicide Formation via Interface Electrostatics with BEEM, ***Westly Nolting***, SUNY Polytechnic Institute, *C. Durcan*, SUNY College of Nanoscale Science and Engineering, *V. LaBella*, SUNY Polytechnic Institute

Nanoscale fluctuations in the electrostatics of a metal semiconductor interface impact performance and are important to understand and measure, which can be accomplished with ballistic electron emission microscopy (BEEM), an STM based technique. In this work, we perform BEEM on Cr/Si Schottky contacts to visualize the interface electrostatics to nanoscale dimensions to understand the effects of silicide formation. This is accomplished by acquiring tens of thousands of spectra on a regularly spaced grid and fitting the results to determine the local Schottky barrier height. Monte-Carlo modeling is utilized to calculate the barrier height distributions that includes scattering of the electrons that traverse the metal layer and a distribution of electrostatic barriers at the interface. Improved agreement between the model and the data is achieved when specifying more than one barrier height, providing a signature of silicide formation. This, and recent work extended this method to the W/Si interface will be presented.

NS-ThP11 Dimensionality Effects in $FeGe_2$ Nanowires: Enhanced Anisotropic Magnetization and Anomalous Electrical Transport, ***Ivan Kravchenko***, Oak Ridge National Laboratory, *S. Tang*, Central South University, PR China, *T.Z. Ward, Q. Zou,* Oak Ridge National Laboratory, *J. Yi,* University of Tennessee, *C. Ma, M. Chi, G. Cao, A.-P. Li, D.G. Mandrus, Z. Gai*, Oak Ridge National Laboratory

We report the synthesis of single-crystal iron germanium nanowires via chemical vapor deposition without the assistance of any catalysts. The assembly of single-crystal $FeGe_2$ nanowires with tetragonal C16 crystal structure shows anisotropic magnetic behavior which is ferromagnetically coupled perpendicular to the wires and antiferromagnetically coupled parallel to the wires' long axis. Single $FeGe_2$ nanowire devices were fabricated using e-beam lithography. Transport in these devices show two resistivity anomalies near 250 K and 200 K which are likely signatures of the two spin density wave states in $FeGe_2$.

NS-ThP12 A High Coherence Package for Quantum Circuits Containing Topologically Isolated Qubits, ***Vivekananda Adiga***, *N.T. Bronn, S.B. Olivadese*, IBM Research Division, T.J. Watson Research Center, *X. Wu, D.P. Pappas,* NIST Boulder, *J.M. Chow*, IBM Research Division, T.J. Watson Research Center

We demonstrate a package containing a superconducting quantum processor wherein we use Pogo pins (50 Ohm) to access the topologically isolated qubits. This allows us to enclose our quantum processor in a non-magnetic environment where we can maintain RF-Hygiene and the entire assembly is compatible with low temperature operation. Self-alignment of the parts allows for rapid testing and scalable integration. We demonstrate low energy loss and high phase coherence comparable to the standard packages involving wirebonds. Single and two-qubit gate fidelities are on par with standard packaging schemes with cross talk less than -40 db at the frequencies of operation. Results are promising for integration with extensible qubit architectures.

NS-ThP16 Few-Wall Carbon Nanotube Coils, ***Dekel Nakar***, *R. Popovitz-Biro, K. Rechav, E. Joselevich*, Weizmann Institute of Science, Israel

Various electronic components based on carbon nanotubes (CNTs) have been produced, but an induction coil has not been demonstrated yet. Our group previously created defect-free single-wall CNT coils, but short-circuiting between turns prevents the coils from acting as inductors. To overcome this limitation, here we explore the use of few-wall CNTs, in which the outer walls may act as sheathing for the inner walls. We show the successful formation of the first few-wall CNT coils from individual CNTs and thin bundles.We characterized the structural properties of the coils using optical microscopy, SEM, AFM, top-view TEM and cross-sectional TEM. We also characterized their electrical properties. The coils comprised CNTs of two, three and four walls without observable defects. The coils had up to 163 turns and diameters between 1 and 5 µm. Based on the structural results, we suggest a mechanism for the formation of the coils. These ordered coils extend the known repertoire of self-organized structures of 1D nanomaterials. They are also promising candidates for inductive devices, and for manifesting other interesting properties, such as electromagnetism and superconductivity.

Nakar, D.; Popovitz-Biro, R.; Rechav, K.; Joselevich, E., “Few-Wall Carbon Nanotube Coils”, *in preparation*.

2D Materials Focus Topic
Room: 15 - Session 2D+MI+NS+SS+TF-FrM

Nanostructures including Heterostructures and Patterning of 2D Materials

Moderators: Huamin Li, University of Buffalo, SUNY, Arkady Krasheninnikov, Helmholtz Zentrum Dresden-Rossendorf, Germany

8:20am **2D+MI+NS+SS+TF-FrM1 Electro-optics with 2D Semiconductors and Heterostructures**, ***Goki Eda***, National University of Singapore, Singapore **INVITED**

Despite being only a few atoms thick, two-dimensional (2D) semiconductors such as monolayer MoS_2 and phosphorene exhibit distinctly strong light-matter interaction compared to their bulk counterparts. Excitons and their complexes with giant oscillator strength play a fundamental role in mediating the strong coupling between light and a 2D semiconductor. These excitons are stable at room temperature and make 2D semiconductors attractive for a number of photonic devices including ultra-fast photo-detectors, optical modulators, on-chip photonic circuits, flexible photovoltaic devices, chiral light emitters, single photon sources, and ultra-low threshold lasers[1]. In order for these devices to be integrated for photonic devices, practical schemes for electrical generation, manipulation, and detection of excitons need to be developed. We create artificial quantum wells based on van der Waal heterostructures and investigate the dynamics of 2D excitons under various conditions to achieve the desired photonic functionalities. In this talk, I will start by discussing our findings on the ultrafast dipole-dipole energy transfer processes involving 2D excitons. I will show that exciton-exciton energy transfer in hetero-bilayers is among the fastest measured in nanomaterials[2]. Peculiar optical effects arising from strong exciton-plasmon coupling in 2D semiconductors hybridized with metal nanoparticles will also be discussed[3]. Finally, our recent efforts in realizing electro-optical (electroluminescence, electro-absorption, and Pockels effect) devices will be discussed. I will share our views on the potential advantages of 2D semiconductors over other materials and discuss our outlook for further studies.

References:

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9:00am **2D+MI+NS+SS+TF-FrM3 Understanding Variations in Circularly Polarized Photoluminescence in Monolayer Transition Metal Dichalcogenides**, ***Kathleen McCreary***, *M. Currie, A.T. Hanbicki, B.T. Jonker*, Naval Research Laboratory

The unique electronic band structure in monolayer transition metal dichalcogenides (TMDs) provides the ability to selectively populate a desired conduction band valley by exciting with circularly polarized light. The subsequent valley population can be interrogated by measuring helicity-resolved photoluminescence (PL). A high degree of circular polarization has been theoretically predicted for resonant excitation of TMDs, yet rarely observed experimentally. In fact, a wide range of values for the degree of circularly polarized emission (P_{circ}), has been reported for monolayer TMDs, although the reasons for the disparity are unclear. Here we investigate the room-temperature P_{circ} in several TMD monolayers synthesized via chemical vapor deposition. The samples include as-grown WS_2, as-grown WSe_2, and WS_2 monolayers that have been transferred to a fresh substrate. In each system, a wide range of P_{circ} and PL intensity values are observed. There is a pronounced inverse correlation between P_{circ} and PL intensity: samples that demonstrate weak PL emission and short exciton relaxation time exhibit a high degree of valley polarization. We attribute these effects to sample-dependent variations in the exciton radiative and non-radiative lifetime components. The short exciton lifetime results in a higher measured polarization by limiting opportunity for depolarizing scattering events. These findings clarify the disparities among previously reported values and suggest a means to engineer valley polarization via controlled introduction of defects and non-radiative recombination sites.

This work was supported by core programs at NRL and the NRL Nanoscience Institute, and by the Air Force Office of Scientific Research #AOARD 14IOA018-134141.

9:20am **2D+MI+NS+SS+TF-FrM4 Multi-Junction Lateral 2D Heterostructures of Transition Metal Dichalcogenides**, ***Prasana Sahoo***, University of South Florida, *S. Memaran*, Florida State University, *Y. Xin*, National High Magnetic Field Laboratory, *L. Balicas*, Florida State University, *H.R. Gutierrez*, University of South Florida

Here we demonstrate the successful synthesis of lateral in-plane multi-junction heterostructures based on transition metal dichalcogenides (TMD) 2D monolayers. The heterostructures were synthesized using a modified chemical vapor deposition approach. By only controlling the carrier gas composition, it is possible to selectively growth only one TMD at the time. This introduces an unprecedented flexibility in the CVD process and allows a good control of the lateral size of each TMD segment. Heterostructures only containing MoS_2-WS_2 or $MoSe_2$-WSe_2 multiple segments, were fabricated. We also demonstrate the synthesis of heterostructures based on homogeneous TMD ternary alloys (MoS_xSe_y-WS_xSe_y). Introducing ternary alloys in heterostructures opens the horizon of possible chemical combinations and applications of 2D optoelectronic devices. The band gap modulation as well as spatial chemical distribution were studied by Raman and photoluminescence mapping. The crystalline quality of the heterostructures were characterized within an aberration-corrected scanning transmission electron microscope. Basic devices were also fabricated to study the transport properties across the junctions. Depending of the growing conditions, diffuse and/or sharp seamless interfaces with high-crystalline quality can be produced.

9:40am **2D+MI+NS+SS+TF-FrM5 Novel Electronic, Optoelectronic, and Topological Properties of 2D Materials and Their Heterostructures**, ***Xiaofeng Qian***, Texas A&M University **INVITED**

Low-dimensional materials exhibits dramatically distinct properties compared to their 3D bulk counterpart. 2D materials is such a fascinating platform with many exotic physical properties and unprecedented opportunities. In this talk, I will highlight some examples of interesting 2D materials and their heterostructures, including 2D multiferroics, 2D topological insulators and topological crystalline insulators, 2D nanostructured exciton funnels. First, I will present our discovery of 2D multiferroics in semiconducting Group IV monochalcogenide monolayers with giant spontaneous in-plane ferroelectric polarization and ferroelastic lattice strain that are strongly coupled. The multiferroicity and hence anisotropic 2D excitonic responses as well as low domain wall energy and migration barrier suggest their great potentials for tunable multiferroic functional devices such as 2D ferroelectric and ferroelastic memory, 2D ferroelastoelectric nonvolatile photonic memory, and 2D ferroelectric excitonic photovoltaics. In the second example, I will highlight our discovery on 2D topological insulators in binary and ternary transition metal dichalcogenides, and topological crystalline insulators in monolayer IV–VI semiconductors. We found electric field, elastic strain, and van der Waals stacking are able to induce topological phase transition (TPT), among which the electric-field induced TPT can be utilized for realizing topological field effect transistor distinctly different from conventional MOSFET. In the third example, I will discuss how macroscopic responses of materials can be tuned and configured by nanostructuring such as inhomogeneous strain engineering and van der Waals Moire patterning. Both nanostructures can modify local atomistic configurations and generate spatially varying electronic structures, thereby introducing novel excitonic photon funneling effect. The latter could be exploited for developing more efficient photovoltaics and light-emitting diodes. Finally, I will highlight relevant experimental progresses as well as some critical challenges and opportunities in 2D materials and their nanostructures.

10:20am **2D+MI+NS+SS+TF-FrM7 Imaging Nanoscale Heterogeneity at the Two-dimensional Semiconductor-Metal Heterointerface by Correlated Scanning Probe Microscopy**, ***Deep Jariwala****, California Institute of Technology, *A. Krayev, E. Robinson*, AIST-NT Inc., *M.C. Sherrott*, California Institute of Technology, *M. Terrones*, Pennsylvania State University, *H.A. Atwater*, California Institute of Technology

Transition metal dichalcogenides (TMDCs) of molybdenum and tungsten have recently attracted significant attention due to their band gaps in visible part of the spectrum for optoelectronic device applications. The ability to isolate these materials down to a monolayer with direct band-gap make TMDCs very attractive alternatives to graphene.

*** NSTD Postdoc Finalist**

While a lot of investigation has been devoted to understanding of crystalline and electronic quality of TMDCs in devices, little is known about the spatial distribution of electronic quality and interfaces with metals. Conventional Raman spectroscopy and confocal Raman microscopy have proved to be useful tools in this regard. However, the spatial resolution of these techniques is diffraction limited to a few hundred nanometers only. Tip enhanced Raman scattering (TERS) provides spatial resolution down to few nanometers, along with increased sensitivity due to dramatic enhancement of the Raman signal by the plasmonic tip and is therefore a suitable technique to probe nanoscale heterogeneity in TMDC samples.

Here, we report observation of nanoscale heterogeneity in exfoliated WSe_2 flakes on plasmonic Au and Ag substrates using a combination of spatial mapping with TERS, contact potential difference, topography and conductance measurements. In TERS mapping of exfoliated WSe_2 flakes, we observe the presence of domains with enhanced or depreciated Raman signal compared to adjacent material. We also observe that WSe_2 demonstrates a resonant Raman response with 638nm excitation, the TERS spectra of these domains feature a single peak at around 250 cm^{-1}, typical for non-resonant conditions. Distribution of these domains correlates extremely well with surface potential map, non-resonant areas being negatively charged compared to adjacent areas of WSe_2 that demonstrate a resonant Raman response.

We further correlate the TERS maps with concurrently recorded photocurrent maps, where we observe that domains showing both resonant and non-resonant Raman response, generated significant photocurrent, but of opposite polarities. Based on this observation, we conclude that in exfoliated layers of WSe_2, there exist nanoscale semiconducting domains with opposite doping types when in contact with the underlying metal. This hitherto unobserved heterogeneity is therefore critical to understanding of the metal-two dimensional (2D) semiconductor contact and important for optoelectronic device design and performance. The results presented here show that cross-correlation of TERS with local conductivity, surface potential and photocurrent is a vital characterization technique for nanoscale in-homogenities in 2D semiconductors and devices.

10:40am **2D+MI+NS+SS+TF-FrM8 Two-dimensional Circuitry Achieved by Defect Engineering of Transition Metal Dichalcogenides**, ***Michael G. Stanford****, *P.R. Pudasaini, A.N. Hoffman, P.D. Rack*, The University of Tennessee Knoxville

Two-dimensional materials, such as transition metal dichalcogenides (TMDs), have demonstrated promising semiconducting properties. The electrical and optical properties of TMDs can be fined tuned by altering material thickness as well as chemical composition. Properties can also be tuned by defect engineering. In this work, a focused He^+ beam as well as a remote plasma source were utilized to introduce defects into TMDs such as WSe_2 and WS_2 with fine control. Scanning transmission electron microscopy reveals that defects introduced into the TMDs range from chalcogen vacancies (0D defects) to 1D defects and extended defect networks. Tailoring defect concentration enables tunability of the electronic properties with insulating, semiconducting, and metallic behavior each obtainable. By tuning electronic properties, we demonstrate direct-write logic gates such as resistor loaded inverters with a voltage gain of greater than 5. We also demonstrate the fabrication of edge-contacted field effect transistors by defect engineering homojunctions between metallic and semiconducting WSe_2 with on/off ratios greater than 10^6. Defect engineering of TMDs enables the direct-write of complex devices into single flakes toward the goal of atomically thin circuitry.

11:00am **2D+MI+NS+SS+TF-FrM9 Scanning Tunneling Microscopy and Spectroscopy Studies of Atomically Precise Graphene Nanoribbons on Semiconducting Surfaces**, ***Ximeng Liu***, *A. Radocea, T. Sun*, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, *M. Pour*, Nebraska Center for Materials and Nanoscience, University of Nebraska - Lincoln, *N. Aluru*, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, *A. Sinitskii*, Nebraska Center for Materials and Nanoscience, University of Nebraska - Lincoln, *J.W. Lyding*, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign

Graphene nanoribbons (GNRs) with atomically smooth edges, controllable geometry and therefore tunable electronic band gaps have ignited enormous interest due to their high potential for future electronic devices. Among different techniques for GNR characterization, scanning tunneling microscopy and spectroscopy (STM/STS) provide both topographic details and local electronic structure with atomic resolution. Large-scale production of two different kinds of chevron-type GNRs (the double-wide (w) GNRs and the extended chevron (e) GNRs) was realized by a solution synthesis method [1]. Dry contact transfer technique [2] was implemented for depositing the solution-synthesized GNRs onto clean InAs (110) and hydrogen-passivated Si(100) semiconducting surfaces under ultrahigh vacuum conditions. For both GNRs, their structures were confirmed by high resolution STM imaging. The band gap of the eGNRs was determined to be 2.6eV via STS. For the wGNRs, detailed analysis and mapping of the electronic density of states both spatially and energetically was carried out with STS and current imaging tunneling spectroscopy. We found that the electron orbital shapes at the GNR edges are different from those at the centers, in agreement with computational simulations. The measured band gap of the wGNRs was only 2eV, which may result in a great improvement in conductivity. In addition, these GNRs are found to be transparent to the substrate when scanned at a small tip-sample separation, indicating a strong interaction when GNRs are pushed towards the substrate.

References:

1. Vo, T. H.; Shekhirev, M.; Kunkel, D. A.; Morton, M. D.; Berglund, E.; Kong, L. M.; Wilson, P. M.; Dowben, P. A.; Enders, A.; Sinitskii, A., Large-Scale Solution Synthesis of Narrow Graphene Nanoribbons. *Nat. Commun.* **2014,***5*, 3189.

2. Ritter, K. A.; Lyding, J. W. The influence of edge structure on the electronic properties of graphene quantum dots and nanoribbons. Nat. Mater. 2009, 8 (3), 235−42.

11:20am **2D+MI+NS+SS+TF-FrM10 Perfectly Perforated Monolayer WSe_2**, ***Kirby Smithe***, *C. Bailey*, Stanford University, *A. Krayev*, AIST-NT Inc., *E. Pop*, Stanford University

One of many prospective applications of 2D transition metal dichalcogenides (TMDs) is catalytic splitting of water for hydrogen generation. Strain in TMD layers, chalcogen atom vacancies, and increased length of the edges of TMD flakes all play an important role in increased catalytic activity, with the latter being the most effective way for improving performance. One possible way to achieve increased ratios of edge length to surface area is to use small flakes, preferably a few hundred nm across. Unfortunately, such small flakes are difficult to manipulate, and the structure of such flakes should also differ from the perfect structure of the inner areas of larger flakes[1]. Here we report that WSe_2 monolayers, grown by chemical vapor deposition (CVD) on Si/SiO_2 and transferred from the original substrate by means of dissolving the sacrificial SiO_2 layer, contain a significant concentration of perfect triangular holes. The result is confirmed by correlating the data of topography, the surface potential, friction and tip enhanced Raman spectroscopy (TERS) characterization of transferred flakes. The ratio of edge length to surface area in such perforated flakes could be up to 3 to 4 times higher compared to homogenous continuous flakes. These perforated flakes can be transferred to any surface, including corrugated ones, which should inevitably cause some strain that is also beneficial for hydrogen catalytic activity. The perfect triangular shape of the holes suggests high quality of the atomic structure of the hole edges, which also implies that the perforated flakes can be used as templates for growth of distributed in-plane heterostructures of different TMDs.

1. Nature Commun., Wei Bao*, Nick Borys*, et al. "Visualizing nanoscale excitonic relaxation properties of disordered edges and grain boundaries in monolayer molybdenum disulfide," 6, 7993 (2015)

Plasma Science and Technology Division
Room: 23 - Session PS+NS+SS+TF-FrM

Atomic Layer Etching II
Moderator: Edward Barnat, Sandia National Laboratories

8:20am **PS+NS+SS+TF-FrM1 Quasi-Atomic Layer Etching of Silicon Nitride with Independent Control of Directionality and Selectivity**, ***Sonam Sherpa***, *P.L.G. Ventzek, A. Ranjan*, Tokyo Electron Limited

Atomic layer etching (ALE) has emerged as a viable approach to address the challenges associated with continuous or quasi-continuous plasma processes. To this end, we previously reported the quasi-atomic layer etching of silicon nitride via sequential exposure to hydrogen and fluorinated plasma. The underlying premise was the surface modification via implantation of hydrogen ions into silicon nitride resulting in an anisotropic etch.

In this talk, we will demonstrate that similar enhancement in reactivity of silicon nitride can also be attained via diffusion of hydrogen atoms into silicon nitride with the resultant etch being isotropic. These results confirm the realization of self-limiting etch of silicon nitride with tunable directionality. This tuning capability is critical for sub-7nm technology node.

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* **National Student Award Finalist**

Illustrations of anisotropic (spacer RIE for self-aligned multiple patterning) and isotropic (spacer RIE for nanowire FET) etch by using this process will also be discussed. Selectivity to oxide is > 100 and damage to underlying silicon can be minimized by optimizing the flux of atomic fluorine during the exposure to fluorinated plasma. Thus, hydrogen plasma controls the directionality while fluorinated plasma step determines the selectivity to oxide and underlying silicon.

8:40am **PS+NS+SS+TF-FrM2 WO_3 and W Thermal Atomic Layer Etching Using "Conversion-Fluorination" and "Oxidation-Conversion-Fluorination" Etching Mechanisms**, ***Nicholas Johnson***, *S.M. George*, University of Colorado at Boulder

Atomic layer etching (ALE) of metals is important for the controlled removal of many valuable semiconductor materials such as conductors (e.g. W, Cu), metal gates (e.g. Ta, Ti) and metals in magnetic multilayers (e.g. Co, Fe). However, few reports exist for metal ALE using either plasma or thermal processes. Conventional thermal ALE that has defined recent work on metal oxide [1] and metal nitride [2] materials does not work for metals. New reaction pathways are required to etch metals. This study targets W ALE and examines both WO_3 ALE and W ALE as W oxidation to WO_3 is needed to define self-limiting reactions for W ALE.

WO_3 ALE was demonstrated using an AB exposure sequence with boron trichloride (BCl_3) and hydrogen fluoride (HF). BCl_3 and HF etch WO_3 by a "conversion-fluorination" mechanism. The BCl_3 converts the WO_3 surface to a B_2O_3 layer while forming volatile WO_xCl_y. HF then spontaneously etches the B_2O_3 layer producing volatile BF_3 and H_2O products. WO_3 films were formed by oxidizing W ALD films with an oxygen plasma at 280ºC. *In situ* spectroscopic ellipsometry (SE) studies determined that the BCl_3 and HF reactions were self-limiting versus exposure. WO_3 ALE etch rates increased with temperature from 0.55 Å/cycle at 128°C to 4.19 Å/cycle at 207°C. W served as an etch stop because BCl_3 and HF could not etch the underlying W film.

W ALE was performed using a three-step "oxidation-conversion-fluorination" mechanism. This is an ABC exposure sequence that where the W surface is first oxidized to a WO_3 layer and then the WO_3 layer is etched with BCl_3 and HF. SE could simultaneously monitor the W and WO_3 thicknesses and conversion of W to WO_3. Oxidation of the W surface was performed using O_3. SE measurements showed that the W film thickness decreased linearly with number of ABC reaction cycles. W ALE was shown to be self-limiting with respect to each part of the ABC process. The etch rates for W ALE were 2.4 Å/cycle at 207°C. An oxide thickness of ~20Å remained during W ALE, but could be removed with BCl_3/HF without affecting the W layer.

[1] Younghee Lee, et al., "Trimethylaluminum as the Metal Precursor for the Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions", *Chem. Mater.* **28**, 2994-3003 (2016).

[2] Nicholas R. Johnson, et al., "Thermal Atomic Layer Etching of Crystalline Aluminum Nitride Using Sequential, Self-Limiting HF and $Sn(acac)_2$ Reactions and Enhancement by H_2 and Ar Plasmas", *J. Vac. Sci. Technol. A* **34**, 050603 (2016).

9:00am **PS+NS+SS+TF-FrM3 Solving the Grand Challenges of Plasma Etch with Concurrent Engineering**, ***Mingmei Wang***, TEL Technology Center, America, LLC, *P.L.G. Ventzek, A. Ranjan*, Tokyo Electron Limited **INVITED**

A consequence of multiple patterning approaches enabling Moore's Law scaling to continue through 10nm to 7nm and beyond is that plasma dry etch process faces unprecedented challenges. "Scaling" of plasma etch to seemingly impossible capabilities is the key to meeting Moore's Law scaling. For example, etch process must achieve extremely high (almost infinite) selectivity in applications where self aligned patterning schemes are involved. Etch process is also required to achieve less than half nanometer (atomic scale) CD variations across 300mm wafers including the important "extreme edge" area as small as 2mm exclusion. These are but two examples of etch grand challenges. While the process requirements push the hardware design to the limits, understanding of process mechanisms becomes the most critical bottleneck to explore process regimes that are able to satisfy the most challenging patterning requirements. In fact, without process understanding at the atomic scale, it is difficult to imagine a means to innovate hardware designs.

In this talk, we will discuss concurrent engineering approaches including both modeling and experiment to understand and develop etching processes that meet grand challenge requirements. The core of the approach is an integrated chamber scale HPEM (Hybrid Plasma Equipment Model)-feature scale MCFPM (Monte Carlo Feature Profile Model) model [1]. The concurrent engineering approach comprises stages of development and prediction capability tests using both blanket wafer and patterned stack data and finally process parameter optimization. By using this approach, we are able to provide insights on how to resolve grand challenges in plasma etch with a minimum of engineering resources. The presentation will survey both experimental and computational results representing a few case studies in SAC quasi-ALE [2], Si ALE, organic etch CD uniformity, and LER/LWR improvement in EUV resist patterned sample etch. Furthermore, insights into the relationship between chamber function and critical surface interactions will be discussed.

[1] M.Wang and M.Kushner, J. Appl. Phys 107, 2010.

[2] M.Wang, P. Ventzek, A. Ranjan, J. Vac. Sci. Technol. A 35, 2017.

9:40am **PS+NS+SS+TF-FrM5 Effect of Non-Uniform Polymer Deposition on the Atomic Layer Etching of 3D Features in SiO_2**, ***Chad Huard***, University of Michigan, *Y. Zhang, S. Sriraman, A. Paterson*, Lam Research Corporation, *M.J. Kushner*, University of Michigan

Atomic layer etching (ALE) typically separates the etch process into (at least**)** two self-limited steps, repeated cyclically – a passivation and an etch step. To obtain all of the benefits of ALE, each of the steps should be fully self-limited, and produce no continuous etching during either step. Only by the synergy between the two steps being repeated cyclically is atomic etching achieved. ALE etching mechanisms have been demonstrated for several materials (e.g., Si, Ge) that do not involve thick passivation layers. ALE-like etching has also been demonstrated for SiO_2 and Si_3N_4, however with the etching mechanisms for these materials relying on the non-self-limited deposition of a polymer layer, it is more difficult to obtain the full benefits of ALE in these systems.

To investigate the benefits and limitations of using an ALE-like pulsing scheme for etching SiO_2, a representation of the through-polymer etching mechanism of SiO_2 in $Ar/C_4F_8/O_2$ plasmas was developed and implemented into the 3-dimensional Monte Carlo Feature Profile Model (MCFPM). The model includes diffusion of radical atomic species (F and O) through the polymer capping layer and ion-energy activated reactions at the SiO_2/polymer interface stimulated by ions implanting through the polymer capping layer. These processes allow for the simulation of SiO_2 (and Si) etching through a finite thickness of polymer. The model reproduces systematic trends for selectivity and etch rates as a function of polymer thickness observed for continuous etching.

Results from the model suggest that the non-self-limited nature of the polymer deposition step can limit the benefits of applying ALE techniques to SiO_2, particularly in 3D features. The balance of polymer deposition by radical CF_x species and erosion by F radicals is subject to neutral transport issues and so are more sensitive to geometry and aspect ratio than for fully self-limited passivation, as occurs in ALE of Si using, for example, Cl_2 containing gases. The reactive sticking coefficients of CF_x radicals on the polymer surface depends, in part, on ion generated dangling bonds which can result in a non-uniform polymer thickness in 3D features. The etch depth per cycle (EPC) was found to depend on polymer thickness, introducing non-uniformity and aspect ratio dependent etch rates in 3D features during ALE. Methods for mitigating the dependence of EPC on polymer thickness using carefully controlled ion energies and the introduction of O_2 will be discussed.

Work was supported by Lam Research Corp., DOE Office of Fusion Energy Science and the National Science Foundation.

10:00am **PS+NS+SS+TF-FrM6 Etching with Low Te Plasmas**, ***Scott Walton***, *D.R. Boris, S.C. Hernández*, Naval Research Laboratory, *S.G. Rosenberg*, ASEE Postdoctoral Fellow, NRL, *H. Miyazoe, A.V. Jagtiani, S.U. Engelmann, E.A. Joseph*, IBM T.J. Watson Research Center

Processing with atomic layer precision requires the ability to not only add, remove or modify one monolayer of material but to also leave adjacent layers unchanged. This requires fine control over the flux of species and energy deposition at the surface. The appropriate threshold and process windows are certainly material specific but it is reasonable to assume many applications require low energy ions. Electron beam-generated plasmas are generally characterized by high charged particle densities (10^{10}- 10^{11} cm^{-3}), low electron temperatures (0.3 - 1.0 eV), and in reactive gas backgrounds, a relatively low radical production rate compared to discharges. The flux at the surface will thus be characterized by a comparatively large amount of ions whose energies are < 5 eV, a value commensurate with the bond strength of most materials. Ion energies can be raised with substrate biasing, which makes these sources well-suited to meet the needs of energy requirements for precise, selective etching. In this work, we discuss SiN etching using pulsed, electron beam generated plasmas produced in SF_6 backgrounds. We pay particular attention to the etch rates, selectivity (vs. carbon films, Si and SiO_2), and patterning as function of operating parameters such as relative gas concentration, operating pressure, and substrate bias. These results are compared with plasma diagnostics to gain a better understanding of the process requirements and windows for threshold etching of SiN. This work is partially supported by the Naval Research Laboratory base program.

10:20am **PS+NS+SS+TF-FrM7 Thermal Atomic Layer Etching of Titanium Nitride Using Sequential, Self-Limiting Oxidation and Fluorination Reactions**, ***Younghee Lee***, *S.M. George*, University of Colorado at Boulder

Titanium nitride (TiN) is an important conducting material as a copper diffusion barrier and a gate electrode in semiconductor devices. Previous thermal atomic layer etching (ALE) studies have shown that TiN was not etched using fluorination and ligand-exchange reactions [1]. These results suggest that the ligand-exchange reactions do not produce stable and volatile reaction products.

In this work, a new etching mechanism based on sequential, self-limiting oxidation and fluorination reactions was developed for thermal TiN ALE. The oxidation reactant was either O_3 or H_2O_2. The fluorination reactant was hydrogen fluoride (HF) derived from HF-pyridine. In the proposed reaction mechanism, the O_3 reaction oxidizes the surface of the TiN substrate to a TiO_2 layer and produces gaseous products such as NO. HF exposure to the TiO_2 layer then yields TiF_4 and H_2O as volatile reaction products. The overall reaction can be written as: $TiN + 3O_3 + 4HF \rightarrow TiF_4 + 3O_2 + NO + 2H_2O$.

Quartz crystal microbalance experiments showed that HF can spontaneously etch TiO_2 films. Spectroscopic ellipsometry and x-ray reflectivity analysis showed that TiN films were etched linearly versus the number of ALE cycles using O_3 and HF as the reactants. The etch rate for TiN ALE was determined at temperatures from 150 to 350°C. The etch rates increased with temperature from 0.06 Å/cycle at 150°C to 0.20 Å/cycle at 250°C and stayed nearly constant for temperatures ≥250°C

The thermal ALE of many other metal nitrides should be possible using this new etching mechanism based on oxidation and fluorination reactions. This thermal ALE mechanism should also be applicable to metal carbides, metal sulfides, metal selenides, and elemental metals that have volatile metal fluorides.

[1] Y. Lee, C. Huffman and S.M. George, "Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions", *Chem. Mater.* **28**, 7657 (2016).

10:40am **PS+NS+SS+TF-FrM8 Atomistic Simulations of H_2 Plasma Modification of SiN Thin-Films for Advanced Etch Processes**, ***Vahagn Martirosyan***, *E. Despiau-Pujo*, *O. Joubert*, LTM, Univ. Grenoble Alpes, CEA-LETI, France

Due to high ion bombardment energies and significant fragmentation rates, conventional continuous wave (CW) plasma processes are not able to selectively etch ultra-thin films without damaging the active layers of advanced nanoelectronic devices. In particular, silicon nitride or low-k spacers etching must be performed with nanoscale-precision without creating defects to the underlayer substrate, to preserve device performances and be compatible with epitaxial steps. To solve this problem, one possible alternative is to use a recently developed etch technology, which consists of two steps [1]. In the first step, the material to be etched is exposed to a hydrogen (H2) or helium (He) ICP or CCP plasma; in the second step, the modified material is chemically etched by wet cleaning or exposure to gaseous reactants only.

Due to the complexity of plasma-material interactions, the successful development of such a new etch approach requires a more detailed understanding of the fundamental mechanisms involved in the process. Therefore, we develop Molecular Dynamics (MD) simulations to study the Si-N-He and Si-N-H systems and provide an overview of the reaction processes at the atomic scale. The objective is to understand the role of ion energy in the self-limited ion implantation, and to determine the relationship between the flux/energy of plasma species bombarding the surface and its chemical/structural modifications.

In this work, we investigate the interaction between hydrogen plasma species (Hx+ ions and H radicals) and silicon nitride via MD simulations. We first study the impact of ion energy (5-100eV), ion dose and ion type on a SiN substrate only exposed to ion bombardment. Then, the influence of a mixed exposure to both Hx+ ions and atomic H is investigated to observe how the hydrogen plasma composition will affect the SiN substrate modification. For pure ion bombardment conditions, simulations show an initial Hx+ ion implantation followed by the formation of a stable modified layer at steady state. Few or no SiN etching is observed for ion energies >25eV, which shows that hydrogen ions only induce a volume transformation and can modify the SiN substrate on a precise depth without etching it. By contrast, simulations of mixed ion/radical bombardment show that a high concentration of atomic hydrogen can crucially change the evolution of the substrate, since H radicals are able to slowly etch SiN along with the modification caused by Hx+ ions. Mechanisms of aforementioned phenomena, as well as comparison with experiments, will be discussed during the presentation.

1. N. Posseme, O. Pollet, S. Barnola, Applied Physics Letters 105, 051605 (2014)

11:00am **PS+NS+SS+TF-FrM9 Defectless Nanostructure Patterning of Germanium Using Neutral Beam Etching for Ge FinFET Devices**, ***Shuichi Noda***, Tohoku University, Japan, *W. Mizubayashi*, *K. Endo*, AIST, Japan, *S. Samukawa*, Tohoku Univeversity, AIST, Japan

Germanium FinFET has been becoming a promising candidates for highly scaled CMOS FETs due to large carrier mobility. However, etching mechanisms of Ge and optimization of etching method have not investigated deeply. We have already succeeded to apply a neutral beam etching (NBE) method to Si FinFET fabrication processes and shown excellent device performances owing to low-damage properties of NBE [1]. Since Ge is much more unstable material to apply to FET devices than Si, there must be much more advantages to use NBE method.

The NBE system consists of an inductive coupled plasma (ICP) source and a carbon aperture plate (neutralization plate) on which enormous number of high aspect ratio aperture holes are opened. Positive and negative chlorine ions generated in a pulse time modulated ICP are accelerated toward the aperture plate and effectively converted to the neutral beam by applying rf field on the aperture plate. Etching substrates beneath the aperture plate are etched mainly by directional chlorine neutral beams without any risky matters such as charged particles (electrons and ions) and irradiation of vacuum ultra-violet (VUV) light. We consider that the VUV irradiation has notable effect on the etching characteristics and defect generation that influences device performances.

We compared etching characteristics of Ge between the NBE and a plasma etching using the same ICP source. It was found that the Ge etching rate of NBE was about one order of magnitude smaller than that of the plasma etching. We consider that such a large differences is caused by surface defects induced by the VUV irradiation. Under the VUV irradiation, surface defects, that is high density dangling bonds of Ge, are created and the defect sites react with chlorine radicals actively and the chlorinated layer are etched off by the ion bombardment in the case of the plasma etching. On the other side, the Ge surface exposed to the neutral beam seems to be chlorinated more slowly and probably the chlorinated layer is much thinner than the plasma-like conditions. And the etching reaction occurs by the chlorine neutral atom beam bombardment. This smaller etch rate around 20 nm/min seems a little bit inefficient however it can be said this small etch rate is much more useful characteristics for the nanometer scale low damage etching processes. AFM observation showed that the etched surfaces by NBE were much smoother than that by the plasma etching. Etched side wall (to be Ge channel surface) by NBE were also very smooth and vertical. High magnification TEM images showed substantially atomic revel smooth side wall.

[1] K. Endo *et al.*, IEDM Tech. Dig. (2005) pp. 840-843.

11:20am **PS+NS+SS+TF-FrM10 Thermally-Driven Atomic Layer Etching of Metallic Tungsten Films Using O_2 and WF_6**, ***Wenyi Xie***, *P.C. Lemaire*, *G.N. Parsons*, North Carolina State University

The semiconductor industry is facing the challenge of manufacturing transistor devices with sub-10 nm high aspect ratio features. Understanding and developing self-limiting etching processes that allow precise control over the thickness of materials removed is essential for enabling the manufacturing complex transistor structures. In this work, we investigated chemical vapor etching of tungsten films using oxygen (O_2) as the oxidant source and tungsten hexafluoride (WF_6) as the etchant.

We propose that etching of tungsten proceeds in two steps: 1) oxidation of the tungsten film to form WO_x surface species and 2) formation and removal of volatile metal fluoride species upon reaction with WF_6. Using quartz crystal microbalance (QCM), we found that the oxidation step with O_2 is required for etching to occur during WF_6 exposure. In addition, etching of O_2 treated tungsten films showed saturation towards WF_6 exposure. This indicates that etching of tungsten using oxygen and WF_6 is a self-limiting process, making it promising as an atomic layer etching process. QCM results also showed that the rate of etching depends on the temperature. Minimal amount of etching was measured at temperatures less than 275 °C. Ex-situ characterization techniques were applied to analyze the etching of tungsten films deposited on SiO_2 substrates. Scanning electron microscopy (SEM) results revealed the change in morphology of tungsten films after different number of O_2-WF_6 ALE cycles. The tungsten film on SiO_2 started out as a coalesced film, which transformed into disjointed nuclei, and the nuclei appeared completely removed as the number ALE cycle increased. Lastly, X-ray photoelectron spectroscopy (XPS) analyses further confirmed etching of tungsten film and showed a minimal amount of fluorine remained on the surface after the O_2-WF_6 ALE process.

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