Monday Morning, October 19, 2015

2D Materials Focus Topic
Room: 212C - Session 2D+EM+NS+PS+SP+SS+TF-MoM

2D Materials: Growth and Fabrication
Moderator: Cory Dean, Columbia University, Peide Ye, Purdue University

8:20am 2D+EM+NS+PS+SP+SS+TF-MoM1 Growth and FTIR Characterization of 2D Hexagonal Boron Nitride on Metal Substrates, *Boris Feigelson*, *V.M. Bermudez, J.K. Hite, Z.R. Robinson, V.D. Wheeler, K. Sridhara, S.C. Hernández*, US Naval Research Laboratory
Atomically thin two dimensional hexagonal boron nitride (2D h-BN) is one of the key materials in the development of new van der Waals heterostructures due to its outstanding properties including an atomically smooth surface, high thermal conductivity, high mechanical strength, chemical inertness and high electrical resistance. The development of 2D h-BN growth is still in the early stages and largely depends on rapid and accurate characterization of the grown monolayer or few layers h-BN films.

In this work, the IR-active out-of-plane vibrational mode of 2D h-BN films grown in vertical reactor by atmospheric-pressure CVD on metal substrates (mainly Cu but also Ni) is exploited to identify 2D h-BN directly on substrates and studied both computationally and experimentally.

Fourier transform grazing-incidence infrared reflection absorption spectroscopy (FT-IRRAS) data have been used to characterize monolayer and few-layer h-BN films directly on metal substrates. Two sub-bands of the $A_{2u}(LO)$ vibrational mode were, for the first time, found for thin 2D h-BN films in contact with Cu and Ni [1]. To unveil the nature of the discovered sub-bands, ab-initio calculations were performed and verified using 2D h-BN films grown on various Cu substrates with varying coverage and with individual crystallites of different shapes and size up to 4 mm. It was shown that the lower-energy $A_{2u}(LO)1$ sub-band around 819 cm^{-1} is related to 2D h-BN coupled with Cu substrate, while the higher energy $A_{2u}(LO)2$ sub-band around 824 cm^{-1} is related to decoupled (essentially free standing) 2D h-BN. These findings demonstrate not only a new and facile method for immediate 2D h-BN identification and characterization, but also a method that provides a simple means to characterize the degree of coupling between 2D h-BN and the substrate. This approach also provides an opportunity to determine which growth conditions lead to the absorption of foreign species on the substrate prior to the h-BN deposition and which conditions can prevent the formation of the interfacial layer between h-BN and the substrate. Such interfacial layers, like oxidized Cu, were shown to result in easily-recognizable shifts in the $A_{2u}(LO)$ peak. The degree to which the interaction of the h BN layer with the substrate is uniform and homogenous can also be assessed easily by examining the width and fine structure of the $A_{2u}(LO)$ band. The developed approach can also be used to study growth and formation of h-BN/graphene and other 2D heterostructures.

References

1. B. N. Feigelson, V. M. Bermudez, J. K. Hite, Z. R. Robinson, V. D. Wheeler, K. Sridhara, and S. C. Hernandez, Nanoscale **7**, 3694 (2015)

8:40am 2D+EM+NS+PS+SP+SS+TF-MoM2 Effect of Surface Termination on the Growth of Graphene on Cu Single Crystal Substrates, *Tyler Mowll*, *E.W. Ong,* University at Albany-SUNY, *P. Tyagi,* GLOBALFOUNDRIES, *Z.R. Robinson,* College at Brockport-SUNY, *C.A. Ventrice, Jr.*, SUNY Polytechnic Institute
The most common technique for synthesizing single-layer graphene films with large lateral dimensions is chemical vapor deposition (CVD) on Cu foil substrates. The primary reasons for choosing Cu substrates are the extremely low solubility of carbon in Cu, which allows a self-limited growth of graphene, and the relatively low cost of the Cu foil substrates. However, the transport properties of the CVD grown graphene films are typically a couple of orders of magnitude lower than for graphene flakes mechanically exfoliated from graphite. One of the reasons for the reduction in transport properties is the presence of crystalline defects in the CVD grown films. These structural defects arise in part from the multidomain structure of the Cu films. In order to achieve a better understanding of the influence of the surface termination of the Cu substrate on the crystallization of graphene during the CVD growth process, a systematic study of graphene growth on Cu(100), Cu(110), and Cu(111) crystals has been performed. The growth process is performed in an ultra-high vacuum (UHV) chamber that has been modified to perform CVD growth at pressures as high as 100 mTorr. The precursor gas used is ethylene. This growth procedure allows for the preparation of the clean surfaces in UHV, growth under typical CVD conditions, and characterization of the surface structure in UHV, without exposing the sample to atmospheric contaminants. Our results indicate that the Cu(111) surface has the lowest catalytic activity of the three surfaces for the decomposition of ethylene. In fact, the decomposition rate is so low that graphene growth is suppressed because of the sublimation of Cu at the elevated temperatures used to grow the graphene. By using an Ar overpressure, it was found that graphene could be grown on that surface. The surface symmetry of the Cu substrate has a strong influence on the rotational alignment of the graphene grains as they nucleate on each surface. For Cu(111), single-domain graphene growth can be achieved for ethylene pressures of 5 mTorr or less. For both Cu(100) and Cu(110), a minimum of two graphene domains is always observed.

9:00am 2D+EM+NS+PS+SP+SS+TF-MoM3 Thermally Annealed and Electropolished Cu Substrates for CVD Growth of 2D Materials: Graphene, h-BN and MoS₂, *Karthik Sridhara*, Texas A&M University, *B.N. Feigelson, J.K. Hite,* US Naval Research Laboratory, *A. Nath,* George Mason University, *M. Fuhrer,* Monash University, Australia, *D.K. Gaskill,* US Naval Research Laboratory, *H. Castaneda, L.O. Nyakiti*, Texas A&M University
The growth of two dimensional (2D) materials such as graphene, hexagonal boron nitride (h-BN) and molybdenum disulphide (MoS_2) have been demonstrated by chemical vapor deposition (CVD) on polycrystalline catalytic copper substrates. These Cu foil substrates (25 μm thick) are produced by metallurgical rolling leading to the formation of irregular ridges on the foil surface along with a film of native oxide on the surface. These processing artifacts are a limiting factor for controlled and reproducible large area (several cm^2) growth of 2D materials. Greater control of growth can be achieved by controlling the density of nucleation sites and improving the catalytic activity of Cu by removing the Cu native oxide on the surface. Previous attempts to pre-treat the Cu substrate by using wet chemistry or thermal annealing to control growth has been weakly addressed.

In this work, electropolishing combined with prior thermal annealing at 1030°C for 5 hrs under H_2 is used to control the degree of roughness of cold rolled polycrystalline Cu foils, and subsequently, to explore the influence of electropolishing on the growth of 2D materials: graphene, h-BN and MoS_2. Electropolishing dissolves a thin surface layer of Cu, which contains surface defects and contaminants. This helps in decreasing the density of spontaneous nucleation sites by producing a morphologically uniform and contaminant-free surface. Secondary effects, etch pits which are ascribed to O_2 bubbling at random nucleation sites on Cu surface, are mitigated by using additives, such as acetic acid and ethylene glycol, in the H_3PO_4 electrolyte. Thermal annealing and electropolishing results in this work reveal that a roughness of ~1.2 nm (R_q) can be achieved as measured by Atomic Force Microscope (AFM) along with a greatly planarized Cu foil. AFM will also be used to establish the Cu substrate morphology and its relationship to the growth of 2D materials. Fourier Transform Infrared, and Raman spectroscopy will be used to confirm the existence of the 2D material. Preliminary growth studies of h-BN on these high quality Cu substrates demonstrate improved growth, as assessed by the metrics of size and count of h-BN crystals from Scanning Electron Microscopy (SEM) micrographs [1]. This work will demonstrate that thermal annealing followed by electropolishing leads to optimization of Cu foil surface resulting in the larger crystal size and a reduction in nucleation sites that induce 2D material crystal growth [1].

[1] K. Sridhara. "Growth of hexagonal boron nitride on electrochemically prepared polycrystalline Cu substrates." M.S. Thesis, University of Maryland, College Park, MD, 2014.

9:20am 2D+EM+NS+PS+SP+SS+TF-MoM4 In Situ Optical Diagnostics During Molybdenum Disulfide Chemical Vapor Deposition, *Berc Kalanyan*, *J.E. Maslar, W.A. Kimes, B.A. Sperling,* National Institute of Standards and Technology (NIST), *R. Tieckelmann, T. Orzali,* SEMATECH, *R. Beams, S.J. Stranick, A.V. Davydov,* National Institute of Standards and Technology (NIST)
Two dimensional (2D), layered transition-metal dichalcogenides (TMDs), e.g., MoS_2, are of increasing interest for next-generation nanoelectronic and optoelectronic devices. These materials have thickness dependent optical and electrical properties that make them suitable for a variety of applications including integrated circuits. For many applications, high volume manufacturing (HVM) of devices based on TMDs will require deposition techniques that are capable of reproducibly growing wafer-scale, 2D TMD films with monolayer control. To date, such a capability has not been widely demonstrated with typical TMD deposition processes.

This work aims to identify promising chemistries for HVM TMD chemical vapor deposition (CVD) processes. We focus on MoS_2 CVD using a variety of precursors (including organometallics, elemental sulfur, and organosulfur compounds) in a research grade single-wafer deposition system equipped with *in situ* optical diagnostics. The precursor flux is measured using optical mass flow meters installed on the delivery lines while deposition chemistry is characterized in the reactor volume above the deposition surface using *in situ* Fourier transform infrared (FR-IR) spectroscopy. As-deposited and annealed films are characterized with *ex situ* techniques, including Raman and photoluminescence spectroscopy, scanning and transmission electron microscopy, and X-ray photoelectron spectroscopy.

Stoichiometric MoS_2 films have been prepared from (η^5-ethylcyclopentadienyl)-dicarbonylnitrosyl molybdenum and elemental sulfur. As-grown films are smooth and continuous with major MoS_2 Raman modes present. Film thickness scales approximately with Mo precursor exposure time and few-layer films can be produced using pulsed injection mode. Furthermore, optical *in situ* diagnostics allow us to relate metal precursor flux to film crystallinity and facilitate the study of precursor decomposition in the thermal boundary layer.

9:40am 2D+EM+NS+PS+SP+SS+TF-MoM5 Controlled Interfaces in 2D Materials, *Arend van der Zande*, University of Illinois at Urbana Champaign   **INVITED**
Interfaces are ubiquitous in material science and technologies. For example, grain boundaries often dominate the mechanical and electrical properties in crystalline materials, while interfaces between dissimilar materials form the fundamental building blocks to diverse technologies, such as building electrical contacts in transistors and PN diodes in solar cells. Interfaces become even more important in 2D materials such as graphene and transition metal dichalcogenides, where the lack of dangling bonds enables material stability down to a single monolayer. In this entirely surface-dominated limit, the usual rules governing 3D interface devices, such as depletion regions, break down.

In this talk, we will discuss our work on engineering in- and out-of-plane 2D materials interfaces. We will first examine the structure of atomically-thin membranes and the impact of defects such as grain boundaries on the mechanical, optical, and electronic properties. We fabricate out-of-plane interfaces by stacking 2D materials to form heterostructures, which we utilize to tailor the bandgap in 2D materials and build new optoelectronic devices such as tunable photodiodes. Looking to the future, the rapidly expanding family of 2D materials with a diverse set of electronic properties provide a promising palette for discovering emergent phenomena and a motivation for developing overarching design principles for understanding and controlling interfaces in 2D.

10:40am 2D+EM+NS+PS+SP+SS+TF-MoM8 Obtaining Clean Suspended CVD Graphene: Comparative Examination of Few Transfer and Cleaning Protocols, *Alexander Yulaev*, National Institute of Standards and Technology (NIST), University of Maryland (UMD), *G. Cheng, A. Hight Walker,* National Institute of Standards and Technology (NIST), *M. Leite,* University of Maryland (UMD), *A. Kolmakov*, NIST
Clean suspended graphene is used as supporting media in TEM, filtering membranes, and as electron transparent windows in ambient pressure electron spectroscopy and microscopy. CVD grown graphene is the most popular material for these applications due to its large-scale and high yield production. Multiple approaches such as sacrificial layer based methods [1] and direct transfer method on perforated carbon mesh by IPA droplet [2] have been implemented to transport graphene from copper or nickel foil onto a target substrate. However, the cleanness of the suspended graphene remains to be an issue, and controversial results on lateral size of atomically clean graphene domains have been reported [2-5]. We conduct the comparative analysis of the most widely-used CVD graphene transfer and cleaning protocols. In particular, using extreme surface sensitivity of low energy SEM, we compare the standard PMMA based approach with direct graphene transfer method. We also propose alternative graphene transfer protocol which is based on employment of polycyclic aromatic hydrocarbon (PAH) as a sacrificial layer. The advantage of PAH method over others consists in facile sublimation of sacrificial layer upon heating PAH material within moderate temperature range of 100-150 ºC. All three methods of graphene transfer were compared under the same conditions followed by similar graphene cleaning procedures by platinum catalysis [4] and activated carbon adsorption [5]. Both SEM and TEM study revealed the superiority of PAH method to achieve cleaner suspended CVD graphene. We envision that novel approach of graphene transfer can be employed under conditions when exposure of the sample to moisture is prohibited such as in battery research.

[1] "Transfer of CVD-Grown Monolayer Graphene onto Arbitrary Substrates", Ji Won Suk *et al*., ACS Nano, 2011, 5 (9), pp. 6916.

[2] "A direct transfer of layer-area graphene", William Regan *et al*., Appl. Phys. Lett., 2010, 96, 113102.

[3] "Low-energy electron holographic imaging of gold nanorods supported by ultraclean graphene", Jean-Nicolas Longchamp *et al*., Ultramicroscopy 145 (2014) 80.

[4] "Ultraclean freestanding graphene by platinum-metal catalysis", Jean-Nicolas Longchamp *et al*., J. Vac. Sci. Technol. B 31, 020605 (2013).

[5] "Dry-cleaning of graphene", Gerardo Algara-Siller *et al*., Applied Physics Letters 104, 153115 (2014).

11:00am 2D+EM+NS+PS+SP+SS+TF-MoM9 Low-Energy Electron Microscopy of Transition Metal Dichalcogenides Prepared by Various Methods, *Sergio de la Barrera*, *S. Satpathy, R. Feenstra*, Carnegie Mellon University, *S. Wu, X.D. Xu,* University of Washington, *S. Vishwanath, X. Liu, J. Furdyna, D. Jena, H. Xing,* University of Notre Dame, *Y.-C. Lin, S.M. Eichfeld, J.A. Robinson,* Pennsylvania State University, *P. Mende*, Carnegie Mellon University
Recent work on two-dimensional materials has focused on transition metal dichalcogenides (TMDs), owing to their semiconducting behavior. Characterizing as-grown TMDs is crucial in improving the understanding of the effects of growth conditions, and ultimately improving material quality. Low-energy electron microscopy (LEEM) is a powerful tool for this purpose, providing real-space images with ~10 nm spatial resolution as well as selected-area low-energy electron diffraction (μLEED) of local crystal orientation at length scales down to ~ 1 μm. Additionally, by varying the incident electron beam energy, low-energy electron reflectivity (LEER) spectra are extracted.

In this work, comparative LEEM results are presented from three TMD materials: MoS_2 prepared by exfoliation (onto Si), $MoSe_2$ grown by molecular beam epitaxy (MBE) (on epitaxial graphene), and WSe_2 grown by chemical vapor deposition (CVD) (also on epitaxial graphene). It is found that for TMDs generally, the LEER spectra do not exhibit the oscillatory behavior (in the 0 – 6 eV range) that is seen for both graphene and hexagonal boron nitride (h-BN) for various numbers of monolayers (MLs). This lack of oscillatory behavior is interpreted as being due to the weak coupling of the interlayer states localized in between the MLs, which is itself a result of the relatively large out-of-plane lattice parameter. Nevertheless, additional "band structure" features in the LEER spectra permit clear identification of the TMD materials relative to the substrates. The exfoliated flakes are seen to extend over many 10's of mm, the MBE-grown $MoSe_2$ forms a nearly continuous film, and the CVD-grown WSe_2 forms triangular islands several mm in extent. μLEED studies of the MBE-grown $MoSe_2$ and CVD-grown WSe_2 reveal preferential orientation with the underlying graphene substrates.

The reduced work functions of the TMD materials relative to the underlying substrate are clearly evident in the onset voltages for the LEER spectra (i.e. the onset shifts in accordance with the local work function of the surface). Most significantly, for the WSe_2 islands, a predominant "tail" is observed in this onset, extending about 5V below the usual onset location. This tail is tentatively interpreted as arising from charging of the islands, perhaps due to polar termination at the edges of the TMD islands. Comparison of the data with simulated LEER spectra will be presented, as a test of this model for edge charge of the islands.

11:20am 2D+EM+NS+PS+SP+SS+TF-MoM10 Atomically-Thin 2D Layers of Group IV Semiconductors, *Joshua Goldberger*, The Ohio State University   **INVITED**
Similar to how carbon networks can be sculpted into low-dimensional allotropes such as fullerenes, nanotubes, and graphene with fundamentally different properties, it is possible to create similar "allotropes" of Ge or Sn with unique optoelectronic properties as well. Here, we will describe our recent success in the creation of hydrogen and organic-terminated group 14 graphane analogues, from the topochemical deintercalation of precursor Zintl phases, such as $CaGe_2$. We will discuss how the optical, electronic, and thermal properties of these materials can be systematically controlled by substituting either the surface ligand or via alloying with other Group 14 elements. Additionally, we have also developed an epitopotaxial approach for integrating precise thicknesses of Germanane layers onto Ge wafers that combines the epitaxial deposition of $CaGe_2$ precursor phases with the topotactic interconversion into the 2D material. Finally, we will describe

our recent efforts on the synthesis and crystal structures of Sn-containing graphane alloys in order to access novel topological phenomena predicted to occur in these graphanes.

Atom Probe Tomography Focus Topic
Room: 230A - Session AP+AS+MC+MI+NS-MoM

Atom Probe Tomography of Nanomaterials
Moderator: Daniel Perea, Pacific Northwest National Laboratory

8:20am AP+AS+MC+MI+NS-MoM1 Correlative Multi-scale Analysis of Nd-Fe-B Permanent Magnet, *Taisuke Sasaki*, *T. Ohkubo, K. Hono*, National Institute for Materials Science (NIMS), Japan **INVITED**
(Nd,Dy)–Fe–B based sintered magnets are currently used for traction motors and generators of (hybrid) electric vehicles because of their excellent combination of maximum energy product and coercivity. However, there is a strong demand to achieve high coercivity without using Dy due to its scarce natural resources and high cost. In Nd-Fe-B sintered magnets, thin Nd-rich grain boundary (GB) phase is a key microstructural feature affecting the coercivity. Although Nd-rich phases, e.g. Nd-rich oxides and metallic Nd, located at grain boundary triple junctions affect the formation of the Nd-enriched grain boundary phase during post-sinter annealing, their phase constitution, distribution and orientation relationships are still under debate.

This presentation will introduce examples of advanced characterization works to establish the global microstructural feature that controls the coercivity of Nd-Fe-B sintered magnets, e.g. the clarification of phase constitution and distribution of Nd-rich phases at the grain boundaries by correlative SEM and TEM characterization, and the identification of the structure and chemistry of thin Nd-rich grain boundary phases by high resolution HAADF-STEM and 3D atom probe. We found the coercivity decrease by carbon impurity can be explained by the decrease in the RE (RE: Rare earth) content in the thin Nd-rich grain boundary phase.

9:00am AP+AS+MC+MI+NS-MoM3 Atom-Probe Tomography of Materials with Dimensions in the Nanometer Range, *Dieter Isheim*, Northwestern University **INVITED**
Nanometer-sized materials and particles seem to naturally lend themselves for investigation by atom-probe tomography (APT) which provides analytical imaging with subnanometer-scale spatial resolution in three dimensions. The material's characteristic dimensions may already be close to the one required to produce the electric field necessary for analysis by field-evaporation in an atom-probe tomograph and thus analysis seems straight forward. In practice, however, controlled manipulation and positioning of these nanoparticles or nanowires for APT analysis proves challenging since the support structure of an APT tip must be strong enough to resist the mechanical stresses exerted by the high electric fields involved. Additionally, the nanoparticles should ideally not be altered or damaged in the preparation process. These requirements can be met by modern processing techniques that combine suitable deposition methods for packaging nanoparticles in structures that are either ready for analysis, or suitable for subsequent APT tip preparation by a standard technique. Focused-ion-beam (FIB) microscopes equipped with a micro- or nanomanipulator and gas injection systems for electron- or ion-beam induced deposition provide a versatile platform for packaging, cutting, joining, and manipulating nanostructured materials, and thus to capture and target nanoparticles or specific microstructural features for APT analysis. This presentation explores these techniques to characterize a variety of nanometer sized and nanostructured materials, including nanodiamond particles and catalytically grown silicon nanowires.

9:40am AP+AS+MC+MI+NS-MoM5 Exploring Atom Probe Tomography for Energy Storage and Conversion Materials, *Pritesh Parikh*, University of California, San Diego, *A. Devaraj*, Pacific Northwest National Laboratory, *S. Meng*, University of California, San Diego
The Sun forms the largest and most abundant source of energy on earth, yet it is not exploited to its full potential. Solar energy is a burgeoning field with a real chance to replace fossil fuels. The intermittent presence of sunlight can be mitigated by combining energy conversion devices such as solar panels with energy storage devices, namely Li ion batteries. A true solution is possible with the integration of both solar panels and batteries. With the general impetus towards adopting renewable sources for large scale energy storage and supply, fundamental studies on solar panels and batteries will provide new clues to design the next generation of energy devices. A Perovskite solar cell is one such technology that has the potential

of high efficiency and low processing costs but a clear understanding of the role of different materials and their individual interactions is still lacking. The ability to identify and understand interfaces and multiple layers in a complex device such as solar cells and batteries is the need of the hour. Here we report on laser assisted atom probe tomography of energy storage and conversion devices to identify the spatial distribution of the elements comprising the various layers and materials. Recent progress and significant challenges for preparation and study of perovskite solar cells and battery materials using laser assisted atom probe tomography will be discussed. This opens up new avenues to understand complex mutli-layer systems at the atomic scale and provide a nanoscopic view into the intricate workings of energy materials.

10:00am AP+AS+MC+MI+NS-MoM6 Atom Probe Tomography of Pt-based Nanoparticles, *Katja Eder*, *P.J. Felfer, J.M. Cairney*, The University of Sydney, Australia
Pt nanoparticles are commonly used as catalysts in fuel cells. There are a lot of factors which influence the activity of a catalyst, including the surface structure and geometry [1], d-band vacancy of the metal catalyst [2], the type of metal oxide support [3] and the oxidation state of the surface [4]. It is not yet fully understood in which way these factors influence the activity of the catalyst, since it is experimentally very difficult to get atomic scale information about the distribution of the atoms within such particle with conventional methods like transmission electron microscopy (TEM), scanning electron microscopy (SEM), scanning tunnelling microscopy (STM) and others. Models available which try to explain the structure-activity relationships therefore vary widely and there is much debate in the scientific literature about the underlying mechanisms of catalysis. For this reason it is crucial to conduct more research with methods that are able to obtain chemical information with a resolution on the atomic scale. In the past few years atom probe tomography (APT) has successfully been used in several studies to analyse nanoparticles [4-6]. APT provides a 3D reconstruction of the original specimen, which gives information about the chemical composition and the microstructure at a very high resolution. This method will enable us to have a closer look at the surface and interfaces as well as the composition of individual nanoparticles and solute atoms. In this talk we will present APT results of Pt nanoparticles, describing our efforts to prepare specimens with a reasonable yield and improved throughput compared to earlier studies, as well as some of the approaches used to overcome the difficulties that this challenge presents.

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[3] T. Akita, M. Kohyama, M. Haruta, Accounts of chemical research, (2013).

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[5] Y. Xiang, V. Chitry, P. Liddicoat, P. Felfer, J. Cairney, S. Ringer, N. Kruse, Journal of the American Chemical Society, 135 (2013) 7114-7117.

[6] D.J. Larson, A.D. Giddings, Y. Wu, M.A. Verheijen, T.J. Prosa, F. Roozeboom, K.P. Rice, W.M.M. Kessels, B.P. Geiser, T.F. Kelly, Ultramicroscopy, (2015).

10:40am AP+AS+MC+MI+NS-MoM8 APT & TEM Observations on Local Crystallization of NbO$_2$ used in Switching Devices, *J.-H. Lee*, Pohang University of Science and Technology (POSTECH), Samsung Electronics, Republic of Korea, *J.-B. Seol*, *C.-G Park*, Pohang University of Science and Technology (POSTECH), National Institute for Nanomaterials Technology (NINT), Republic of Korea **INVITED**
Threshold switching is the basis of electrical or thermal-driven phase change mechanism of oxide layer. That is, some oxide can change their conductivity from the level of insulators to that of metals with above certain current density. Although the mechanism responsible for threshold switching is not fully understood at present, it can be used as a switching device for the solution of sneak leakage problem. In order to apply the bipolar switching materials as the active layer of Resistive-switching Random Access Memory (RRAM), selection device which can minimize the sneak leakage current is needed. Among various candidates, we chose Nb-oxide for the selection device due to its superior compatibility with semiconductor structure. We have elucidated the mechanism of threshold switching of the amorphous NbO$_2$ layer by using in-situ transmission electron microscopy (TEM) technique combined with atom probe tomography (APT).

In this study, we proved that through an ex-situ experiment using TEM the threshold switching of amorphous NbO$_2$ accompanies local crystallization. The change in I-V characteristics after electroforming was examined by evaluating the concentration profile. APT combined with in-situ TEM probing technique was performed to understand the threshold switching in

amorphous NbO_2. The local crystallization in amorphous NbO_2 was validated by the observed difference in time-of-flight (ToF) between amorphous and crystalline NbO_2. We concluded that the slower ToF of amorphous NbO_2 (a-NbO_2) compared to that of crystalline $NbO2$ (c-NbO_2) is due to the resistivity difference and trap-assisted recombination.

11:20am AP+AS+MC+MI+NS-MoM10 Correlating Atom Probe Tomography with High-Resolution Scanning Transmission Electron Microscopy and Micro-Photoluminescence Spectroscopy: The Case of III-Nitride Heterostructures, *Lorenzo Rigutti*, University of Rouen **INVITED**

Correlating two or more microscopy techniques on the same nanoscale object may yield a relevant amount of information, which could not be achieved by other means. In this contribution, we present several results of correlated studies of micro-photoluminescence (μ-PL), high-resolution scanning transmission electron microscopy (HR-STEM) and laser-assisted atom probe tomography (APT) on single nano-objects containing AlGaInN quantum well and quantum dot systems. We will show how this approach can be applied to the study of heterostructure interface definition, presence of defects, carrier localization and optical emission in III-N quantum confined systems [1]. Furthermore, we will show how the use of complementary techniques may be extremely helpful for a correct interpretation of atom probe results [2]. The possible implementation of micro-photoluminescence as an in-situ technique within the atom probe itself will finally be discussed [3].

[1] L. Rigutti et al., Nano letters (2014), 14, 107–114.

[2] L. Mancini et al. J. Phys. Chem. C (2014) 118, 24136-24151.

[3] L. Rigutti et al., Ultramicroscopy (2013), 132, 75-80.

Electronic Materials and Processing
Room: 210E - Session EM+NS+PS-MoM

More Moore! Materials and Processes to Extend CMOS Another Decade
Moderator: Christopher Hinkle, University of Texas at Dallas

8:20am EM+NS+PS-MoM1 Effects of Deposition Temperature and Pre-rapid Thermal Process on Electrical and Interfacial Characteristics of Alumina on GaSb, *Seongkyung Kim, H.J. kim*, Seoul National University, Korea, Republic of Korea

Recently Ⅲ-Ⅴ compound materials have attracted significant attention as promising channel materials for sub-10 nm logic MOSFET due to their high mobility. GaSb is a strong candidate for pMOSFETs because of its high hole mobility in addition to the insolubility of its native oxides. Even with the outstanding electrical properties of GaSb, there are some drawbacks related to the instability of its native oxides and metallic layer of elemental Sb. The native oxides and metallic layer of elemental Sb are considered to be sources of Fermi level pinning and flat C-V curves. Therefore, it is necessary to improve surface treatment methods. Since it is possible to eliminate its native oxides and elemental Sb by heating them, it is essential to research temperature related surface treatments.

In this study, various ALD temperatures from 190 ^{o}C to 310 ^{o}C and pre-RTP(Rapid Thermal Process), which is first introduced here as a pre-deposition treatment, have been adopted for eliminating the remaining native oxides after cleaning. N_2 gas atmosphere is used to suppress the oxygen to interact with GaSb surface for the pre-RTP. GaSb metal-oxide-semiconductor capacitors were fabricated on p-type GaSb, which has a carrier concentration of $1.0 \sim 2.0 \times 10^{17}$ cm^{-3}. GaSb was degreased with acetone, ethanol, and isopropane for 5 minutes each and then etched by HCl. 10 nm of Al_2O_3 has been deposited as a gate dielectric with TMA and DI water by thermal ALD. For the metal gate, a Pt electrode has been deposited with an electron-beam evaporator.

When the deposition temperature increases, the Ga_2O_3 peak increases and the substrate peak decreases under XPS analysis. It is observed that the amount of Sb increases at the GaSb/Al_2O_3 interface as the deposition temperature increases in AES depth profiles. Both Ga_2O_3 and elemental Sb have increased generation as the deposition temperature increases, since the surface chemical reactions are accelerated by increased temperature. The CV curve becomes flat as the deposition temperature increases. It indicates that Ga_2O_3 has a flattening effect of the CV curve and the more amount of Ga_2O_3 that is generated, the flatter the CV curve will become.

Desorption of the native oxides and elemental Sb should occur by annealing the substrate. After the pre-RTP, the amount of elemental Sb increases, since the remaining native oxide, after cleaning, is reduced by increased

temperatures. The remaining native oxide Sb_2O_3, after cleaning, supplies oxygen to the substrate and becomes elemental Sb. The leakage current increases with pre-RTP. It shows that the elemental Sb increases the leakage current. Further study on optimizing pre-RTP conditions is needed.

8:40am EM+NS+PS-MoM2 Selective Wet Etching of III-V Semiconductors with HCl and H_2O_2, *Pablo Mancheno-Posso, . Jain, A.J. Muscat*, University of Arizona

The etching of III-V semiconductors is needed to insert these materials into current device flows to extend CMOS transistor technology. III-V oxides are detrimental to electrical performance and must be removed, because they adopt different oxidation states and can be soluble in water. Plasma etching to create profiles can damage and change the stoichiometry of the surface. Wet etching of these oxides can control the roughness and chemical termination of the surface by choice of oxidant and etchant, concentration, and pH. Wet etching of III-V semiconductors is accomplished by oxidizing acid and base chemistries that can preferentially remove group III or V atoms. In new 3 D transistor architectures, the formation of the channel fin requires a low etching rate to ensure a smooth surface and a highly selective etching bath with respect to other materials or crystal faces that are exposed. In this work, we varied the group III and V atoms across five binaries (GaAs, InAs, InP, GaSb, and InSb) and measured etching rates. These materials were etched using mixtures of HCl (0.01 M) and H_2O_2 (0.0001-5 M). The etching rate was measured using profilometry on wafers patterned with conventional photolithography. The chemical composition was monitored using X-ray photoelectron spectroscopy (XPS). The etching rate of GaAs and InAs (same group V atom) exhibited a volcano-shaped dependence on H_2O_2 concentration. At H_2O_2 concentrations of 5 to 100 mM, the etching rate increased linearly from 0.08 ± 0.03 to 1.1 ± 0.1 nm/s for GaAs and from 0.06 ± 0.04 to 0.9 ± 0.3 nm/s for InAs. The rate decreased to 0.04 ± 0.01 nm/s for GaAs and 0.26 ± 0.13 nm/s for InAs at 1 M H_2O_2. InP, which is often exposed during etching of another III-V, showed a linear dependence on H_2O_2 concentration (0.01 to 5 M), increasing from 0.003 ± 0.001 to 0.012 ± 0.009 nm/s. The selectivity of etching GaAs to InP at three points along the volcano was about 55, 140, and 4 at H_2O_2 concentrations of 0.01, 0.1, and 1 M. Like the arsenides, the antimonides etched at about the same rate, but the volcano dependence moved to lower peroxide concentrations. The etching rate of GaSb increased from 0.07 ± 0.04 to 0.21 ± 0.04 nm/s and InSb from 0.09 ± 0.03 to 0.38 ± 0.09 nm/s for H_2O_2 concentrations from 0.1 to 1 mM. The group V atom determined the etching rate and is involved in the rate determining step in the reaction. The presence of As-Cl bonds on the surface after etching GaAs in HCl was confirmed by temperature programmed desorption (TPD) experiments after immersion in 1.7 M HCl. The mechanism for etching III-V semiconductors will be discussed based on the etching rate data and chemical composition of the surface.

9:00am EM+NS+PS-MoM3 Border Trap Analysis and Reduction for ALD High-k InGaAs Gate Stacks, *Kechao Tang*, Stanford Univ., *R. Winter*, Technion – Israel Inst. of Tech., *T. Kent*, UC, San Diego, *M. Negara*, Stanford Unive., *R. Droopad*, Texas State Univ., *A.C. Kummel*, UC, San Diego, *M. Eizenberg*, Technion – Israel Inst. of Tech., *P. McIntyre*, Stanford Univ.

For future high performance III-V n-channel MOS devices, $In_{0.53}Ga_{0.47}As$ is a promising material for the channel due to its high electron mobility. Atomic layer deposited (ALD) Al_2O_3 has a large conduction band offset to InGaAs and can form a low defect-density interface with InGaAs [1]. ALD-HfO_2 can achieve a very low EOT (effective oxide thickness) with low gate leakage [2]. Therefore, both of these oxides have received extensive attention as candidate dielectric layers for InGaAs nMOSFETs. Apart from the well-known oxide/InGaAs interface charge traps that may pin the Fermi level of the channel, traps in the oxide layer, called border traps, may also reduce the charge in the channel and thus degrade the on-state performance of InGaAs MOSFET devices. We report a study of the effects of various approaches to reduce the density of border traps (N_{bt}), such as variation of the ALD temperature, and of post-gate metal forming gas (5% H_2/95% N_2) anneal (FGA) conditions.

Experimental methods employed include quantitative interface trap and oxide trap modeling [3, 4] of MOS capacitor data obtained over a range of frequencies and temperatures. We find that MOS capacitors fabricated using trimethylaluminum (TMA)/H_2O at an ALD temperature of 120°C have a considerably lower border trap density while maintaining a low interface trap density (D_{it}) compared to samples prepared with a more standard 270°C Al_2O_3 ALD temperature. It is also found that large-dose (~6,000 L) exposure of the $In_{0.53}Ga_{0.47}As$ (100) surface to TMA immediately after thermal desorption of a protective As_2 capping layer in the ALD chamber is an important step to guarantee the repeatability of high quality Al_2O_3/InGaAs samples made at Al_2O_3 ALD temperatures much lower than 270°C. The reduction of N_{bt} is consistent with time-of-flight secondary ion mass spectrometry depth profiles that show more effective hydrogen

incorporation in the low-temperature ALD-grown Al_2O_3 films during post-gate FGA.

The N_{bt} of Al_2O_3 under various conditions will be compared with that of low-temperature ALD-grown HfO_2 films on InGaAs substrates. For the HfO_2 case, we also confirm the independence of border trap response on the electrical measurement temperature and check the influence of the crystal orientation of the InGaAs surface on MOS interface characteristics.

This work was supported by the US-Israel Binational Science Foundation.

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9:20am EM+NS+PS-MoM4 Self-LIMITING CVD of an Air Stable Silicon Oxide Bilayer for Preparation of Subsequent Silicon or Gate Oxide ALD on InGaAs(001)-(2x4), *Mary Edmonds*, *T. Kent, S. Wolf*, University of California at San Diego, *J. Kachian, N. Yoshida, M. Chang*, Applied Materials, *D. Alverez*, Rasirc, Inc, *R. Droopad*, Texas State University, *A.C. Kummel*, University of California at San Diego

A broader range of channel materials allowing better carrier confinement and mobility could be employed if a universal control monolayer (UCM) could be ALD or self-limiting CVD deposited on multiple materials and crystallographic faces. Si-OH is a leading candidate for use as the UCM, as silicon uniquely bonds strongly to all crystallographic faces of $InGa_{1-x}As$, $In_xGa_{1-x}Sb$, $In_xGa_{1-x}N$, SiGe, and Ge enabling transfer of substrate dangling bonds to silicon, which may then subsequently be functionalized with an oxidant such as HOOH(g) in order to create the UCM terminating Si-OH layer. This study focuses on depositing a saturated Si-OH seed layer on InGaAs(001)-(2x4) at a substrate temperature of 350°C. XPS in combination with STS/STM were employed to characterize the electrical and surface properties of the saturated Si-OH seed layer on InGaAs(001)-(2x4).

The 350°C self-limiting CVD procedure includes a decapped $In_{0.53}Ga_{0.47}As(001)$-(2x4) surface dosed with total 87.6 MegaLangmuir Si_2Cl_6 followed by 210.55 MegaLangmuir total anhydrous HOOH(g). Complete saturation of silicon coverage is determined to occur once further dosing with Si_2Cl_6 leads to no further increase in the silicon 2p or further decrease in the substrate gallium 3p peak areas. Complete surface saturation of $Si-O_x$ on InGaAs(001)-(2x4) was determined to occur once no further increase in the O 1s peak was seen with additional anhydrous HOOH(g) doses. Following Si-OH surface saturation, 300,000 L TMA was dosed at 250°C, and XPS shows the emergence of Al 2p and C 1s peaks indicative of TMA surface nucleation. The surface was then dosed with 500 L atomic H at 250°C to remove the methyl groups on the surface aluminum and replace with -H termination as well as remove any residual chlorine left on the surface. The surface was then exposed to air for 30 minutes, dosed with an additional 500 L atomic H at 250°C, and then STS measurements were performed. STM measurements of the $Si-O_x$ surface show uniform surface coverage. STS measurements show the surface Fermi level position moves towards midgap due to a surface dipole formation from –OH groups and oxygen bonding to the surface. TMA dosed on the $Si-O_x$ surface shifts the Fermi level back towards the conduction band, consistent with unpinning and the -OH induced surface dipole being lessened through surface bonding with dimethylaluminum groups. Following hydrogen dosing and air exposure, the surface Fermi level remains near the conduction band edge consistent with the surface being stable and unreactive in air. Preliminary MOSFET studies on InGaAs(001) show equivalent performance with Si_2Cl_6 predosing compared to in-situ cleaning with atomic H.

9:40am EM+NS+PS-MoM5 Going Big in Two-Dimensions, *Joshua Robinson*, The Pennsylvania State University INVITED
The last decade has seen nearly exponential growth in the science and technology of two-dimensional materials. Beyond graphene, there are a variety of layered materials that provide a broad range of electronic characteristics useful for transistors, flexible electronics, sensors, and photodetectors, to name a few. However, bridging the gap between science and teechnology often lies in one's ability to synthesize materials on the wafer scale (or bigger). In this talk, I will discuss recent breakthroughs for direct growth of two-dimensional atomic layers and heterostructures with scalable techniues such as metal-organic chemical vapor deposition. We have demonstrated the direct growth of MoS_2, WSe_2, MoS_2/WSe_2, and hBN on epitaxial graphene to form large area van der Waals heterostructures. We reveal that the properties of the underlying substrate dictate properties of the layers and heterostructures, and that the direct synthesis of TMDs on epitaxial graphene exhibits atomically sharp interfaces. Our work has lead to a better understanding of vertical transport in 2D heterostructures, and we have identified new phenomenon in multi-junction heterostructures that has

lead to resonance tunneling between layers and ultimately negative differential resistance.

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10:40am EM+NS+PS-MoM8 2D Bipolar Devices for Novel Logic Applications: Fabrication, Characterization and Applications, *Ji Ung Lee*, SUNY Polytechnic Institute INVITED
The three pillars in semiconductor device technologies are (1) the p-n diode, (2) the MOSFET and (3) the Bipolar Junction Transistor (BJT). They have enabled the unprecedented growth in information technology that we see today. For any new material, therefore, the development of these three devices is critical for providing benchmark performance against highly scaled Si-based technologies. Here, we will describe our efforts to fabricate and characterize these three benchmark devices in 2D materials, including graphene and transition metal dichalcogenide semiconductors (TMDs).

Although graphene is gapless, we will describe device concepts based on graphene p-n junctions that can lead to steep subthreshold slope devices. Critical to realizing such devices is the demonstration of relativistic Klein tunneling, a property of chiral carriers that arise from the unique electronic structure of graphene. Here, we will describe the fabrication and characterization of graphene p-n junctions, and discuss the unique tunneling properties that arise in these junctions and our efforts to realize high efficiency switching devices.

Using TMD materials, we have fabricated a single device that can reconfigure into p-n, MOSFET, and BJT devices. The reconfigurable device allows us to provide fundamental linkages between material properties and device performance not possible by fabricating the three devices individually. We will provide our method of fabrication and describe electrical and optical properties of the reconfigurable device.

11:20am EM+NS+PS-MoM10 Electron Transport and Tunneling in Graphene-based Heterostructures, *Emanuel Tutuc*, The University of Texas at Austin INVITED
Vertical heterostructures consisting of atomic layers separated by insulators can open a window to explore the role of electron interaction in these materials, otherwise not accessible in single layer samples, as well as to explore device applications.

We describe here the realization of vertical heterostructures consisting of graphene, hexagonal boron nitride (hBN), and transition metal dichalcogenides realized using a layer-by-layer transfer. In double bilayer graphene heterostructures separated by hBN dielectric [1] where the two layers are rotationally aligned the interlayer tunneling current measured as a function of interlayer bias reveals a gate-tunable resonance thanks to momentum conserving tunneling. [2, 3] We discuss potential device application based on these experimental observations, as well as metrics that allow a benchmarking of their performance.

We also discuss the realization and characterization of graphene-MoS_2 heterostructures, which reveal a strong negative compressibility in the MoS_2 layer as a result of electron-electron interaction. [4]

Work done in collaboration with Kayoung Lee, Babak Fallahazad, Sangwoo Kang, Stefano Larentis, Hema C. P. Movva, Sanjay K. Banerjee, Leonard F. Register, Takashi Taniguchi, and Kenji Watanabe, and with support from the NRI-SWAN Center, Office of Naval Research, and Intel Corp.

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Energy Frontiers Focus Topic
Room: 211B - Session EN+AS+EM+NS+SE+SS+TF-MoM

Solar Cells I
Moderator: Jason Baxter, Drexel University, Chintalapalle Ramana, University of Texas at El Paso

8:20am EN+AS+EM+NS+SE+SS+TF-MoM1 Elevated Temperature Phase Stability of CZTS-Se Thin Films for Solar Cells, *E. Chagarov, K. Sardashti,* University of California at San Diego, *D.B. Mitzi,* Duke University, *R.A. Haight,* IBM T.J. Watson Research Center, **Andrew C. Kummel**, University of California at San Diego
Density-functional theory simulations of CZTS, CZTSe and $CZTS_{0.25}Se_{0.75}$ photovoltaic compounds have been performed to investigate stability of $CZTS_{0.25}Se_{0.75}$ alloy vs. decomposition to CZTS, CZTSe and other secondary compounds. The Gibbs energy for vibration contribution was estimated by calculating phonon spectra and thermodynamic properties at finite temperatures. It was demonstrated that $CZTS_{0.25}Se_{0.75}$ alloy is stabilized not by enthalpy of formation but by vibration and mixing contributions to the Gibbs energy. A set of phase diagrams was built in multidimensional space of chemical potentials at 300K and 900K temperatures to demonstrate alloy stability and boundary compounds at various chemical conditions. The Gibbs energy gain/loss for several decomposition reactions was calculated as a function of temperature with/without Cu/Zn intermixing and vibration contributions to the Gibbs energy demonstrating $CZTS_{0.25}Se_{0.75}$ that even defect-free (no Cu/Zn intermixing) $CZTS_{0.25}Se_{0.75}$ can be stable at typical processing temperatures.

8:40am EN+AS+EM+NS+SE+SS+TF-MoM2 Chemical and Electrical Characterization of Polycrystalline CZTS,Se and CIGS,Se Grain Boundaries by NanoAuger and Kelvin Probe Force Microscopy (KPFM), **Kasra Sardashti**, UC San Diego, *P.D. Antunez, R.A. Haight,* IBM T.J. Watson Research Center, *A.C. Kummel,* UC San Diego
Polycrystalline Copper-zinc-tin-sulfide/selenide (CZTS,Se) compounds have received wide research interest due to their potential as inexpensive absorber materials composed of earth-abundant elements. Photovoltaic devices fabricated on CZTS,Se have reached conversion efficiencies of 12.6 %. One of the key parameters to further boost the conversion efficiency is to control the concentration of recombination sites at the surface, secondary phase interfaces and in the grain boundaries. To determine the presence of secondary phases on the surface and composition of grain boundaries, this work has employed Auger nanoprobe electron spectroscopy (NanoAuger) with 8nm lateral resolution combined with high resolution ambient Kelvin Probe Force Microscopy (KPFM) with dual-lock-in setup. NanoAuger was performed in planar and cross-sectional modes on CZTS,Se surfaces before and after top surface oxide removal by NH_4OH clean. Elemental maps before and after NH_4OH clean show Sn-/O-rich and Cu-poor grain boundaries suggesting that grain boundaries are terminated by tin-oxide (SnOx). Secondary phases such as SnSe and ZnSe were observed in the cross-sectional maps. Kelvin probe force microscopy (KPFM) on the cleaned surfaces showed that SnOx-terminated grain boundaries have 80-200 mV larger work function than grains, resulting in upward band bending between grains and grain boundaries. The upward band bending accompanied by the large valence band offset between the SnOx and CZTS,Se lead to relatively large energy barriers for both electrons and holes to travel into the grain boundaries and recombine. Comparison with the elemental maps for CIGSe (with device efficiencies as high as 18%) revealed the absence of the grain boundary oxide passivation.

9:40am EN+AS+EM+NS+SE+SS+TF-MoM5 Spin Coating Thin Film CZTS for Efficient, Low-Cost Solar Cells on Flexible Glass Substrates, *D. Kava, J. Galindo, C.O. Sana, S. Shahriar,* **Deidra Hodges**, University of Texas at El Paso
Photovoltaic's contribution to energy production continues to grow as costs continue to decrease. As silicon cells approach their limits, other materials are emerging. The development of Cu_2ZnSnS_4 (CZTS) thin film solar cells using non-vacuum liquid-based spin coating techniques have been previously investigated. The focus of this paper is the optimization of p-type CZTS thin film solar cells onto flexible substrates. Flexible solar panel costs are higher than their traditional counterparts. CZTS currently reports only a 3.2% efficiency on flexible glass, while the record for CZTS on non-flexible substrates is 12.6%. The cells are created using a single solution ink sol–gel method. All metals are dissolved in a single step prior to deposition onto substrates (nickel foil and corning willow glass) as a thin film. Corning Willow glass is a new material introduced recently to the market, while nickel is a inexpensive flexible reflective foil. The Corning Willow glass is coated with a molybdenum layer as a reflective back contact layer. By using a single step and a solution deposition method, lower production cost are achievable. For thin film deposition, we used a non-vacuum spin coater (WS650 spin processor, Laurell Technologies) with an optimized spin coat programming. Annealing took place under vacuum in a RTP furnace while time, temperature and ramp functions were varied. The other layers of the device consists of cadmium sulfide n-type window layer and a zinc oxide doped with aluminum transparent top contact layer. Characterization and analysis of the thin films were performed using Raman spectroscopy, scanning election microscope (Zeiss NEON 40), X-ray diffraction (Philipps X'Pert), proflimeter (Veeco Dektak 150), UV-Vis-NIR Spectrophotometer (Carry 5000), Hall Effect measurement system (HMS3000) and 4 point probe (Lucas Labs) measurements. Results show CZTS thin film solar cells on flexible glass is obtainable.

10:00am EN+AS+EM+NS+SE+SS+TF-MoM6 Band Gap Profile of Cu(In,Ga)(Se,S) 2 Thin Films via High-Resolution Reflection Electron Energy Loss Spectroscopy, *Sung Heo, H.I. Lee, J.B. Park, G.S. Park,* Samsung Advanced Institute of Technology, Republic of Korea, *D.H. Lee, J.G. Nam,* Samsung, Republic of Korea, *H.J. Kang,* Chungbuk National University, Republic of Korea, *B.D. Choi*, Sungkyunkwan University, Republic of Korea
$Cu(In,Ga)Se_2$ (CIGS)-based solar cells was investigated with an aim of enhancing cell performance because these cells provided high conversion efficiency at relatively low cost. The efficiency of CIGS cells has recently approached 19.7% at small sizes. In general, $Cu(In_{1-x},Ga_x)(Se_{1-y}S_y)_2$(CIGSS) composition profiles are double-graded, and they can improve the open-circuit voltage (V_{OC}) and the efficiency of solar cells because band gaps increase toward both the surface (i.e., with the increase of sulfur) and the bottom (i.e., with the increase of gallium). It is important to accurately measure the band gap at the top and the bottom of the CIGSS cell. Nevertheless, the band gap profile measurement of the CIGSS as a function of depth is challenging.

In this study, we obtained the depth profile of the CIGSS cell using the quantitative Auger Electron Spectroscopy method, for which the relative sensitivity factor was corrected using the inductively coupled plasma-atomic emission spectrometry (ICP-AES) method. We also measured the band gap directly using high-resolution reflection electron energy loss spectroscopy (HR-REELS) with a monochromatic electron gun, which has low electron energy at 300 eV.

For the direct measurement of a band gap profile, HR-REELS spectra were obtained as a function of depth during Ar ion sputtering at 3.0 kV. The band gap profile shows a double-graded band gap as a function of depth. The band gap values are 1.32 eV at the surface (E_{g1}), 1.08 eV at the depth between 0.3 and 0.7μm ($E_{g\,min.position}$), and 1.50 eV at the depth of about 2.2 μm (E_{g2}), respectively. Our findings suggest a new analytical method which directly determines the band gap profile as function of depth.

10:40am EN+AS+EM+NS+SE+SS+TF-MoM8 Spatial Atmospheric ALD of Zinc Oxysulfide Buffer Layers for CIGS Solar Cells, *C. Frijters, P.J. Bolt, P. Poodt,* **Andrea Illiberi**, Solliance/TNO, Netherlands
Copper Indium Gallium di-Selenide (CIGS) solar cells are a promising approach in photovoltaic technology, having low production costs, high conversion efficiencies (> 20 %), as well as the possibility to manufacture them on flexible substrates. State-of-the-art in CIGS solar cells manufacturing is to use a stack of CdS, intrinsic ZnO (*i*-ZnO) and an Al-doped ZnO TCO on top of the CIGS film. Replacement of CdS by a non-toxic Cd-free layer with wider band gap (> 2.4 eV) would *a)* decrease the production cost by avoiding the expensive treatment of toxic wastes and *b)* increase the overall cell efficiency by enhancing the quantum efficiency in the blue range. Moreover, the use of a "soft" and highly conformal

deposition technique is preferred to improve the electrical properties of the buffer layer/CIGS interface.

In this paper we present spatial atmospheric atomic layer deposition of a Zn(O,S) buffer layer as CdS replacement for CIGS solar cells. Spatial ALD is emerging as an industrially scalable deposition technique at atmospheric pressure which combines the advantages of temporal ALD, i.e. excellent control of film composition and uniformity on large area substrates, with high growth rates (up to nm/s). Films are grown by sequentially exposing the substrate to oxygen and sulfur precursors (H_2O, H_2S) and the zinc metal precursor (i.e., DEZn). By controlling the kinetics of surface reactions between evaporated precursors and reactive sites at the film surface, the composition of Zn(O,S) can be precisely tuned. The incorporation of S into ZnO results in a bowing of the band gap in the range from 3.3 eV (ZnO) to 2.7 (S/O+S ~ 0.5) and 3.4 eV (ZnS), as measured by spectrophotometry. The morphology of the $Zn(O_{x-1},S_x)$ films varies from polycrystalline (for $0<x<30$ and $70<x<100$) to amorphous ($30<x<70$), as measured by X-ray diffraction. CIGS solar cells with a Spatial ALD Zn(O,S) buffer layer show an increased spectral response around 400 nm compared to solar cells with a CdS buffer layer. The solar cells with the Zn(O,S) buffer layer had an efficiency of 15.9 %, compared to 15.5 % for the reference solar cells with a CdS buffer layer.

11:00am **EN+AS+EM+NS+SE+SS+TF-MoM9 Deep Level Electron Traps in Epitaxial CuInSe$_2$ Probed using Photo-Modulated X-ray Photoelectron Spectroscopy**, *Nicole Johnson*, University of Illinois at Urbana-Champaign, *P. Aydogan*, Bilkent University, Turkey, *A. Rockett*, University of Illinois at Urbana-Champaign, *S. Suzer*, Bilkent University, Turkey

Performance in a variety of electronic devices is largely controalled by minority carrier charge capture on point defects. To date there is no experimental method to directly identify these point defects in a chemically specific fashion. Photo-modulated X-ray Photoelectron Spectroscopy (XPS) utilizes the chemical and charge sensitivity of XPS to identify changes in peak shape due to changing atomic charge state from capture of light-generated minority carriers. Epitaxial thin films of CuInSe$_2$ (CIS) were chosen as a case study for this technique because their defect chemistry is still relatively unknown as compared to traditional solar cell materials. The 500-1000nm thick films were grown by a hybrid sputtering and evaporation technique on GaAs(001) substrates at600-700°C. Aligned surface morphology features matching the substrate geometry in scanning electron microscopy (SEM) images indicate epitaxial growth, which was confirmed by x-ray diffraction (XRD).A layer of CdS was deposited on the CIS via chemical bath deposition to protect the CIS surface from oxidation in storage and to duplicate the heterojunction used in solar cells. Prior to loading in the XPS, the CdS was etched off to expose a Cd doped CIS surface for analysis. The photo-modulated XPS used monochromatic AlKα x-rays with a 532 nm laser as the illumination source. Under illumination, each film constituent was observed to exhibit unique binding energy shifts. Based on their peak shifts relative to the surface photovoltage profile, Cd and In were found to be right at the surface while Cu and Se were deeper into the film, consistent with a Cd-doped, In-rich surface. The technique is therefore shown to provide a chemically-sensitive depth profile non-destructively that can be obtained even on a relatively rough sample. Additionally, shape changes in the Se 3d doublet spectra indicate electron capture in a deep trap state that is likely due to cation vacancies. Measurements at varying temperatures indicate air-induced surface recombination states are passivated by annealing at 80C, allowing the surface photovoltage to persist. At 230C, an irreversible change happens in the surface properties such that the surface photovoltage gets much smaller and reverses sign. This work was supported by a joint NSF-TUBITAK collaborative research project (NSF Grant No: 1312539 TUBITAK Grant No: 212M051).

11:20am **EN+AS+EM+NS+SE+SS+TF-MoM10 The Role of ZnTe Buffer Layers on the Performance and Stability of CdTe Solar Cells**, *Jiaojiao Li*, Colorado School of Mines, *A. Abbas*, Loughborough University, UK, *D.M. Meysing, J.D. Beach, D.R. Diercks*, Colorado School of Mines, *M.O. Reese, T.M. Barnes*, National Renewable Energy Laboratory, *C.A. Wolden*, Colorado School of Mines, *J.M. Walls*, Loughborough University, UK

The use of ZnTe buffer layers at the back contact of CdTe solar cells has been credited with contributing to recent improvements in both record cell efficiency and module stability. To better understand the underlying reasons high resolution transmission microscopy (HR-TEM) and atom probe tomography (APT) were used to study the evolution of the back contact region before and after rapid thermal activation of this layer. During activation the 150 nm ZnTe layer, initially nanocrystalline and homogenous, transforms into a bilayer structure consisting of an amorphous region in contact with CdTe characterized by significant Cd-Zn interdiffusion, and a crystalline layer that shows evidence of grain growth

and twin formation. This graded layer may passivate interface defects and account fo the improved open circuit voltage and fill factor that accompanies the RTP activation step. Copper, co-evaporated uniformly within ZnTe, is found to segregate dramatically after rapid thermal activation, either collecting near the ZnTe|Au interface or forming Cu_xTe clusters in CdTe at defects or grain boundaries near the interface. Further examination of the Cu_xTe clusters revealed that they are encased in a thin layer of Zn, and it is postulated that this structure may limit the extent of diffusion into CdTe and play an important role in device stability.

11:40am **EN+AS+EM+NS+SE+SS+TF-MoM11 The Performance and Durability of Broadband Anti-Reflection Coatings for Thin Film CdTe Solar Cells**, *G. Womack, P.M. Kaminski, John Walls*, Loughborough University, UK

Light reflection from the glass surface of a photovoltaic (PV) module is a significant source of energy loss for crystalline silicon and all types of thin film PV devices. The reflection at the glass and air interface accounts for ~4% of the total energy. Single layer anti-reflection coatings using magnesium fluoride or porous silica with sufficiently low refractive index have been reported but these are only effective over a narrow range of wavelengths. In this paper we report on the design, deposition and testing of multilayer broadband anti-reflection coatings that reduce the weighted average reflection over the wavelength range used by thin film CdTe devices to ~1.22% resulting in a useful 3.6% increase in photocurrent. In this study we have used multilayer stacks consisting of silica and zirconia layers deposited using a reactive magnetron sputtering process. Details of the stack design, sputtering process parameters and the optical and micro-structural properties of the layers are provided.

Thin film CdTe devices pose a special problem because the anti-reflection coating is applied to one side of the glass while device layers are deposited directly on to the opposite glass surface in the superstrate configuration In thin film CdTe production, the glass is exposed to high temperature processes during the absorber deposition and during the cadmium chloride activation treatment. If glass pre-coated with a broadband anti-reflection coating is to be used then the coating must withstand temperatures of up to ~550°C. Surprisingly, our studies have shown that multilayer silica/zirconia anti-reflection coatings on soda lime glass remain unaffected by temperatures up to 600 °C at which point mild crazing is observed. This is an important observation since it means that low cost glass which is pre-processed with a broadband anti-reflection coating by glass manufacturers is potentially useable in thin film CdTe module production

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

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

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

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

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

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

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

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10:40am **MG+BI+MS+NS+TF-MoM8 Controlled Spontaneous Nanoscale Patterning of Nonstoichiometric Reconstructions for Catalysis and Light Harvesting**, *J.M. Martirez, D. Saldana-Greco,* University of Pennsylvania, *W.A. Saidi,* University of Pittsburgh, *J.S. Lim, Andrew Rappe*, University of Pennsylvania **INVITED**
The ability to manipulate the atomic and electronic structure and stoichiometry of surfaces is of utmost importance in optimizing heterogeneous catalysts. A critical requirement in this endeavor is a deep thermodynamic and kinetic understanding of surface reconstruction behavior, under various thermal and chemical constraints. We explore the reconstruction behaviors of Ti- and Mn-based perovskite type oxides: $BaTiO_3$, $PbTiO_3$, and $CaMnO_3$: the former two exhibit ferroelectricity, while the latter undergoes surface-induced magnetic ordering. Due to the characteristic properties of these oxides, we investigate the effect of their switchable polarization (for ferroelectric oxides) and near surface magnetic ordering ($CaMnO_3$) in their surface phase evolution, in addition to the effects of temperature and the chemical potentials of their constituent elements. We find that these oxides undergo surface reconstruction transformations that generally result in enrichment of their catalytically active components (Ti and Mn). These reconstructions show rich bonding and structural motifs that affect the active sites' reactivity and accessibility. Furthermore, these surface transformations, as in $BaTiO_3$ and $PbTiO_3$, can be tuned with the help of an electric field. An applied electric field changes the material's polarization, which then alters the surface electronic properties, and thereby also affects their sensitivity towards stoichiometric changes. In addition to the thermodynamic understanding of the surface reconstructions, we introduce the kinetic tunability of the surface reconstruction. We demonstrate this from a particular surface phase coexistence observed in $BaTiO_3$, namely the c(2x2) and c(4x4), where the diffusion behavior of the TiO units that compose both surfaces strongly dictate their degree of agglomeration. Finally, based on our interest in $CaMnO_3$ (001) surfaces, we have started to explore the more complex $CaMn_7O_{12}$. The electronic properties of this oxide yield interesting physical phenomena including charge ordering, non-collinear magnetism and improper ferroelectricity. We are currently investigating the ground state non-collinear magnetic configuration in this compound and its role on the stability of the charge-ordered state.

11:20am **MG+BI+MS+NS+TF-MoM10 Developing Evolutionary Algorithms for *a priori* Crystal Structure Prediction and Applications towards Novel Pressure-Stabilized Materials**, *Eva Zurek*, University at Buffalo-SUNY **INVITED**
One way to accelerate the development of new materials is via *a priori* crystal structure prediction (CSP) of hitherto unknown systems, followed by the computation of their properties and determination of promising synthesis conditions. A number of algorithms designed to solve global optimization problems have recently been applied to CSP with much success, and evolutionary algorithms (EAs) have emerged as one of the most promising methods for systems where little or no experimental data is available. Therefore, we have developed the open-source XtalOpt EA for CSP as an extension to the widely used chemical builder and visualizer, Avogadro. In this talk we present new developments within XtalOpt that allow it to successfully predict the structures of crystals with larger and more complex unit cells. Furthermore, we summarize the application of XtalOpt towards the prediction of hydrogen-rich solids with unique stoichiometries that are computed to be stable at pressures that are attainable within diamond anvil cells. The influence of the structure of the

hydrogenic lattice on the electronic structure and the propensity for high temperature superconductivity is discussed.

Nanometer-scale Science and Technology
Room: 212B - Session NS-MoM

Nanotools and Nanodevices
Moderator: Jun Nogami, University of Toronto, Canada

9:00am **NS-MoM3 Peter Mark Memorial Award Lecture: Taking Control of the Nanoscale with Scanning Programming Microscopy**, *Peter Maksymovych**, Oak Ridge National Lab **INVITED**
Manipulation of single atoms and molecules is undoubtedly one of the most striking achievements of nanoscience. It has been repeatedly utilized to create clean model systems for surface physics, and it foretold the dream of atom-by-atom synthesis and atomic-scale control. However, it is also apparent that establishing atomic manipulation as a synthetic methodology for realistic materials faces major challenges. The first of these is scaling the complexity of atomic control – extending onto crystalline lattices, 3D objects, larger scales and increasingly complex chemical interactions. A related and equally potent challenge is increasing the energy scale of manipulation (and, conversely, the stability of manipulated matter), which necessitates control over chemical bond breaking. Essentially, we need to advance atomic manipulation toward the accuracy of macroscopic chemistry while retaining control over 1-100 nm length-scales. Over the last several years, we have explored the effects of large electric field, electronic current density and mechanical stress in progressively complex chemical reactions on surfaces and solid state materials with rich defect chemistry. Our goal is to peer into "pre-breakdown" window of material properties, that would normally be associated with destruction, desorption or amorphization. Quite on the contrary, using the unique capabilities of scanning probe microscopy, we have found this regime to be rich in chemical and electrochemical transformations, including reversible motion of oxygen vacancies in deep sub-surface volume of perovskite oxides (1-4) and delocalized chemical reactions involving rearrangements of chemical bond-order and strongly chemisorbed molecules (5-8. We established that local electrochemical control is key to understand and subsequently control specific phenomena, such as metal-insulator transitions in perovskite oxides in non-uniform stress and electric fields. Furthermore, hot-electron currents and electric fields can drive chemistry that is not thermally accessible, pointing toward novel catalytic and surface reactions. At the same time, many of these transformations exhibit memory, hysteresis and training. We therefore speculate that they provide a stepping stone to programmable materials, a distinct paradigm where the shape and function of the materials will be defined by a programmed protocol of excitation, relaxation and stresses. Programmable materials can be made adaptive and eventually even computing. Ultimately, we envision programmable metamaterials, wherein a "quilt" of nanoscale chemical compositions with distinct chemical boundaries produces a unique collective function.

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9:40am **NS-MoM5 Directing Nanoscale Mass and Energy Transport using Cantilever-Free Scanning Probes**, *Keith A. Brown, D.J. Eichelsdoerfer, C.A. Mirkin*, Northwestern University **INVITED**
Advances in lithography have driven the information revolution by allowing semiconductor manufacturers to shrink integrated circuits at an exponential rate for nearly 50 years. Given the explosion of interest in biomedical

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* Peter Mark Memorial Award Winner

research and engineering, a major challenge that must be addressed in the coming decades will be the difficulty in developing high quality techniques for patterning soft and bioactive materials at the nanoscale. Scanning probe techniques are poised to be a major player in this advance because they allow one to direct mass transport at the nanoscale, thus attaining high resolution without processing steps that might damage biological materials. Despite their promise, the chief limitation inherent to scanning probe techniques is throughput, as patterning with a single probe is in many cases prohibitively slow. Recently, it has been shown that this problem can be circumvented by replacing the cantilever that conventionally supports a single probe with an elastomeric film on a rigid surface that supports a massive array of probes. While this new cantilever-free architecture intrinsically addresses the scalability challenge, many questions remain about how these probe arrays differ from their cantilever-based counterparts, specifically relating to how the transfer of energy and materials is governed by the hard/soft composite probe array. Here, we explore such transfer processes including the transport of liquids and light from cantilever-free tips to a surface. Specifically, we overview the transfer of polymeric solutions from a tip to a surface and find that, in many cases, the details of materials transfer are dictated by how the capillary bridge between the tip and surface ruptures. This observation allows for the patterning of sub-20 nm polymer features. Ultimately, however, our work is motivated by the desire to answer previously inaccessible questions through the development of new synthetic techniques. Thus, we explore these probe arrays as candidate techniques for performing massive-scale combinatorial experiments in nanoscience, and develop new methods for pushing the state-of-the-art in terms of ink complexity, feature size, and feature density. Based upon these advances, we describe preliminary screening experiments for the identification of novel nanoparticle-based heterogeneous catalysis. This work sets the stage for scanning probe-based tools to fill many emerging needs in nanoscience, biology, and materials science.

11:20am **NS-MoM10 NSTD Nanotechnology Recognition Award Talk: Nanomaterials in Sensor and Electronics Development**, *Meyya Meyyappan**, NASA Ames Research Center **INVITED**
Nanomaterials such as carbon nanotubes (CNTs), graphene and silicon nanowires (SiNWs) have received much attention for sensors and nanoelectronics due to their interesting properties. This talk will provide an overview of recent development in these fields at NASA Ames Center for Nanotechnology. We have developed CNT based chemical sensors for space exploration needs such as crew cabin air quality monitoring and fuel leak detection; the chemiresistor based sensor array is operated as an electronic nose and demonstrated for the detection of various gases and vapors at ppm-ppb levels. Routine astronaut health monitoring and water quality monitoring in the International Space Station and future crew vehicles require compact, low power lab-on-a-chip that can provide rapid analysis. Our nanoelectrodes array based biosensor uses PECVD-grown vertically aligned carbon nanofibers and provides electrochemical response from CV and/or impedance spectroscopy upon probe-target interaction. Sample results for the sensitive detection of three biomarkers for heart disease and the potential for multiplexing will be presented. We have also taken a "More-than-Moore" philosophy in the construction of radiation sensors where a conventional silicon FINFET-like structure uses a radiation-responsive gel dielectric in the nanogap created from the removal of SiO_2 dielectric. Both n- and p- type devices show excellent response to gamma radiation, demonstrating the potential to construct a radiation nose. Finally, we have been developing nanoscale vacuum tubes using entirely silicon technology for future radiation-immune electronics. Devices with a 50 nm source-drain gap provide an excellent drive current, on/off ratio of 10^6 and drive voltage of < 5 V. The author acknowledges contributions from Jessica Koehne, Ramprasad Gandhiraman, Adaikappan Periyakaruppan, Jin-woo Han, Ami Hannon, Beomsok Kim, Yijiang Lu, Taiuk Rim, Chang-Ki Baek and Jeong-Soo Lee.

Advanced Surface Engineering
Room: 212A - Session SE+AS+NS+TR-MoM

Nanostructured Thin Films and Coatings
Moderator: Robert Franz, Montanuniversität Leoben, Austria, Andrey Voevodin, Air Force Research Laboratory

8:20am **SE+AS+NS+TR-MoM1 Reactively Sputter Deposited Ternary AlN-based Coatings**, *Joerg Patscheider*, Empa, Switzerland, *E. Lewin*, Uppsala University, Sweden
The protection of surfaces against preventing premature failure by abrasion-resistant nitride coatings has been investigated and put into daily operation ever since. Despite these efforts, the wide range of available protective coatings cannot be used, when glass and other optically transparent materials have to be protected due to the opacity of transition metal nitrides for visible light. For such applications thin films based on Al-A-N with additions of elements from group 14 with A = Si , Ge or Sn are attractive candidate materials, as their transparency in the visible range opens new opportunities of applications. Furthermore, the addition of these elements causes the formation of solid solutions and of nanocomposites, leading to enhanced hardness in the case of A = Si and Ge. Once nanocomposites are formed, enhanced hardness of more than 30 GPa is observed in the case of Al-Si-N and more than 20 GPa for Al-Ge-N and Al-Sn-N. The choice of the additional A element allows for the preparation of highly transparent coatings for the case of Si and the control of color in the range from yellow to red by tuning of the UV absorption edge in the case of Ge and Sn. The role of deposition conditions and their implications on the structure these ternary nitride coatings will be discussed.

8:40am **SE+AS+NS+TR-MoM2 Mo₂BC Coatings for Metal Forming: Interactions Between Tool Surface and Aluminium by Theory and Experiment**, *Jochen Schneider*, RWTH Aachen University, Germany, *H. Bolvardi*, Oerlikon Balzers, Liechtenstein, *D. Music*, RWTH Aachen University, Germany
Low temperature growth strategies for Mo_2BC coatings are reviewed and initial theoretical and experimental data pertaining to the applicability of these coatings during forming of Al based alloys are discussed. A $Mo_2BC(040)$ surface was exposed to O_2. The gas interaction was investigated using *ab initio* molecular dynamics and x-ray photoelectron spectroscopy (XPS) of air exposed surfaces. The calculations suggest that the most dominating physical mechanism is dissociative O_2 adsorption whereby Mo – O, O – Mo – O and Mo_2 – C – O bond formation is observed. To validate these results, Mo_2BC thin films were synthesised utilizing high power pulsed magnetron sputtering and air exposed surfaces were probed by XPS. MoO_2 and MoO_3 bond formation is observed and is consistent with here obtained *ab initio* data. Additionally, the interfacial interactions of O_2 exposed $Mo_2BC(040)$ surface with an Al nonamer is studied with *ab initio* molecular dynamics to describe on the atomic scale the interaction between this surface and Al to mimic the interface present during cold forming processes of Al based alloys. The Al nonamer was disrupted and Al forms chemical bonds with oxygen contained in the O_2 exposed $Mo_2BC(040)$ surface. Based on the comparison of here calculated adsorption energy with literature data, Al – Al bonds are shown to be significantly weaker than the Al – O bonds formed across the interface. Hence, Al-Al bond rupture is expected for a mechanically loaded interface. Therefore the adhesion of a residual Al on the native oxide layer is predicted. This is consistent with experimental observations. The data presented here may also be relevant for other oxygen containing surfaces in a contact with Al or Al based alloys for example during forming operations.

9:00am **SE+AS+NS+TR-MoM3 Molecular Dynamics Simulations of TiN/TiN(001) Growth**, *Daniel Edström*, *D.G. Sangiovanni, V. Chirita, L. Hultman,* Linköping University, Sweden, *J.E. Greene, I. Petrov,* University of Illinois at Urbana Champaign
The Modified Embedded Atom Method (MEAM) interatomic potential within the classical Molecular Dynamics (MD) framework enables realistic, large-scale simulations of important model materials such as TiN. As a step toward s understanding atomistic processes controlling the growth of TiN on a fundamental level, we perform large-scale simulations of TiN/TiN(001) deposition using a TiN MEAM parameterization which reproduces experimentally-observed surface diffusion trends, correctly accounts for Ehrlich barriers at island step edges [1], [2], and has been shown to give results in excellent qualitative and good quantitative agreement with Ab Initio MD based on Density Functional Theory (DFT) [3], [4]. 85% of a monolayer of TiN is deposited on 100x100 atom TiN(001) substrates at a rate of 1 Ti atom per 50 ps, resulting in simulation times of 212.5 ns. The TiN substrate is maintained at a typical epitaxial growth temperature, 1200 K during deposition using N:Ti flux ratios of 1:1,

2:1, and 4:1 and incident energies of 2 and 10 Ev to probe the effects of N_2 partial pressure and substrate bias on TiN(001) growth modes. We observe nucleation of Ti_xN_y molecules; N_2 desorption; the formation, growth and coalescence of mixed <100>, <110>, and <111> faceted islands; as well as intra- and interlayer mass transport mechanisms. For equal flux ratios at 2 Ev incidence energy, islands begin to form atop existing islands at coverages $\gtrsim$ 0.25 ML, leading to 3D multilayer growth. Increasing the N:Ti flux ratio shifts the growth mode to layer-by-layer growth and changes the stoichiometry from under- to over-stoichiometric. We discuss the implications of these results on thin film growth and process tailoring. Our classical MD predictions are supported and complemented by DFT-MD simulations.

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9:20am SE+AS+NS+TR-MoM4 Stress Design of Multi-layered Coatings, *Wolfgang Seidl*, Christian Doppler Laboratory for Application Oriented Coating Development at the Institute of Materials Science and Technology, Vienna University of Technology, 1040 Vienna, Austria, *M. Arndt*, Oerliko Balzers, Oerlikon Surface Solutions AG, 9496 Balzers, Liechtenstein, *P. Polcik*, Plansee Composite Materials GmbH, 86983 Lechbruck am See, Germany, *P.H. Mayrhofer*, Vienna University of Technology, Austria

Residual stresses within physical vapour deposited coatings are a major concern, as they are often the origin of failure and delamination. Furthermore, stresses, which typically scale with the thickness, limit the thickness of the coating. With increasing stresses, the interface region is increasingly stressed and weakened, promoting delamination and buckling effects. CrN coatings are known to allow for moderate compressive or even tensile stresses, enabling the preparation of coating thicknesses above 20 µm. Although CrN coatings exhibit excellent tribological and wear resistance properties, their thermal stability with respect to Cr-N dissociation is limited to 900 °C, which limits their application field. However, several applications require higher thermal stability in combination with relatively thick ceramic coatings. Therefore, we study in detail the requirements to develop nitride-based coatings with thicknesses exceeding 20 µm.

The residual stresses of arc evaporated TiN, CrN, TiAlN, CrAlN, and TiAlTaN coatings, prepared with an industrial sized coating plant (Balzers Oerlikon INNOVA), are investigated as a function of their thicknesses by measuring the curvature of one-side coated Si(100) cantilevers. Based on these studies we developed multilayer arrangements of TiN/CrN, TiAlN/CrN, TiAlN/CrAlN, and TiAlTaN/CrAlN thick coatings. Their stresses are designed through variations in bilayer period and arrangements of the cathodes at the sidewalls of the industrial chamber.

The individual coatings and multilayers are additionally investigated with respect to growth morphology (by cross sectional scanning electron microscopy), hardness and indentation moduli (by nanoindentation), structure and crystallographic phases (by X-ray diffraction).

9:40am SE+AS+NS+TR-MoM5 Atomistic Guided Development of Hard Coatings and Thin Films for Severe Applications, *Paul Mayrhofer*, Vienna University of Technology, Austria **INVITED**
This work summarizes recent developments on applying thin film structure and architecture concepts to hard coatings for optimized performance in various application fields.

The hardness of materials rapidly decreases at elevated temperatures as generally the density of structural defects, such as point defects, dislocations, and grain boundaries, decreases. Additional strengthening can be provided by age-hardening mechanisms, which originate from decomposition-processes of supersaturated phases to form new obstacles retarding plastic deformation. Furthermore important is the resistance against oxidation and corrosive attack.

By using ab initio calculations and sophisticated experimental methods we will have a detailed insight into various mechanisms responsible for excellent mechanical strength, thermal stability and oxidation resistance properties of Ti–Al–N based hard coatings. For these materials we will also compare the effect of various architecture and alloying concepts with e.g., Y, Zr, Hf, Nb, and Ta.

Another important class of hard coatings is based on the material systems CrN and Cr–Al–N. After a short overview on ab inito and experimental studies in comparison to their sister system Ti–Al–N, we will have a small excursion on the influence of architecture – using the model system CrN/AlN multilayers or their superlattices – on the mechanical properties and especially fracture toughness. Furthermore, based on recent ab initio investigations suggesting that the inherent fracture toughness of CrN can be increased by alloying with Mo or W, we will explore in detail the challenges in studying Cr–Mo–N or Cr–W–N materials by ab inito and experiments.

The various thin film structure and architecture concepts allow the utilization of multifunctional properties facilitating the development of next generation's hard coatings.

10:40am SE+AS+NS+TR-MoM8 Crystallographic Stabilization of δ-WC Thin Films by Alloying with B, using Reactive Magnetron Sputtering of W in Trimethylboron $(CH_3)_3B$, *Hans Högberg*, *L. Tengdelius, M. Samuelsson, G. Greczynski, F. Eriksson, L. Hultman*, Linköping University, Sweden
The hardness, oxidation resistance, and high temperature stability of hexagonal δ-WC (B_h) in cemented carbide is a key component in metal cutting. Such a property envelop suggest many potential thin film applications. However, the literature shows that thin film growth of δ-WC by for instance magnetron sputtering is complicated typically resulting in the deposition of films containing the phase γ-WC (B1) with a carbon content lower than nominal, i.e. WC_{1-x}. As the properties of this phase is less favorable compare to those of δ-WC, growth of WC_{1-x} must be avoided in an optimized thin film material. In this study, we attempt to promote the formation of δ-WC films by alloying with B. Our hypothesis is that the preferred growth of WC_{1-x} films depends on the preference of C to occupy octrahedral sites found in the B1 structure and where the larger B atom may act to stabilize the B_h structure by better filling out the larger trigonal prism interstitials in this structure. We use reactive magnetron sputtering of W, using trimethylboron $(CH_3)_3B$ (TMB) as C and B precursor. The 5 min depositions were carried on Si(100) substrates in a Kr plasma held at a constant pressure of 0.53 Pa. The gaseous TMB was introduced close to the substrates. The influence of TMB flow, ranging from 1-10 mln, was studied for a growth temperature of 500 °C. Also, the influence of growth temperature, from room temperature to 900 °C, was investigated for a constant TMB flow of 10 mln. X-ray photoelectron spectroscopy shows that the content of B and C scales with the flow into the plasma with no B and ~3 at.% C at 1 mln and 6.5 at.% B and 17.8 at.% C at 10mln. In contrast, temperatures up to 600 °C show no impact on the B and C content in the films, while higher temperatures give a solid state reaction with the substrate. X-ray diffraction shows broad peaks indicative of small grain sizes and with peaks at 2θ angles matching those of the phases WC_{1-x} or W. In the in the temperature range 300 to 600 °C, 100-textured WC_{1-x} films are deposited and with a shift to a weak 111 orientation at lower temperatures. At 500 °C, TMB flows of 5 to 10 mln results in the growth of 100-textured WC_{1-x} films, while lower flows yield W films. Films are deposited with thicknesses up to ~1000 nm, corresponding to a deposition rate of 3.3 nm/s. The microstructure is generally fine-grained, but with broken columns at 500 and 600 °C and a TMB flow of 1 mln. The mechanical properties of the films will be reported.

11:00am SE+AS+NS+TR-MoM9 Epitaxial and Polycrystalline WNx and MoNx Films Deposited by Reactive DC Magnetron Sputtering, *Brian Ozsdolay*, *K. Balasubramanian*, Rensselaer Polytechnic Institute, *C.P. Mulligan*, U.S. Army Armament Research Development & Engineering Center, Benét Laboratories, *M.J. Guerette, L. Huang, D. Gall*, Rensselaer Polytechnic Institute
WN_x layers, 1.45-µm-thick, were deposited by reactive magnetron sputtering on MgO(001), MgO(111), and Al_2O_3(0001) in 20 mTorr N_2 at T_s = 500-800 °C. X-ray diffraction ω-2θ scans, ω-rocking curves, φ scans, and reciprocal space maps show that all layers deposited from 500-700 °C exhibit the cubic rock-salt structure, with a relaxed lattice constant that decreases from 4.299 to 4.171 Å as the N-to-W ratio decreases from x = 1.20 for T_s = 500 °C to x = 0.83 for T_s = 700 °C, as measured by energy dispersive and photoelectron spectroscopies. T_s = 500-600 °C yields a polycrystalline 111-textured microstructure on all substrates. In contrast, deposition at 700 °C results in epitaxial growth of WN(111) and WN(001) on MgO(111) and MgO(001), respectively, while deposition on Al_2O_3(0001) yields a 111-preferred orientation, misoriented cubic WN grains as well as N-deficient BCC W. T_s = 800 °C causes nitrogen loss and WN_x layers with primarily BCC W grains and x = 0.04-0.06. The measured elastic modulus ranges from 110-260 GPa for T_s = 500-700 °C and decreases with increasing N-content, and increases to 350 GPa for T_s = 800 °C. For samples deposited at T_s = 700 °C, nanoindentation on WN on

MgO(001), MgO(111), and Al_2O_3(0001) provides hardness values of 9.8 ± 2.0, 12.5 ± 1.0, and 10.3 ± 0.4 GPa, and elastic moduli of 240±40, 257±13, and 242±10 GPa, respectively. The corresponding shear moduli measured by Brillouin light scattering are 127±2 GPa, 121±2 GPa and 115±2 GPa. MoN_x layers, 1- μm-thick, deposited on MgO(001) also exhibit a cubic rock salt structure with x decreasing from 1.18 for T_s = 500 and 600 °C to x = 0.76 for T_s = 800 °C but remaining approximately constant for T_s = 800-1000 °C. Layers with T_s > 700 °C contain both epitaxial MoN_x(001) and 111-oriented grains. The out-of-plane lattice constant decreases from 4.22 to 4.18 Å for 111 oriented grains and from 4.17 to 4.06 Å for epitaxial 001-oriented grains, as T_s is increased from 700 °C to 1000 °C.

11:20am SE+AS+NS+TR-MoM10 Phase Stability and In Situ Growth Stresses in Thin Cu/Nb Multilayered Films, *Qianying Guo*, L. Wan, R.L. Martens, G.B. Thompson, University of Alabama

As the length scale of individual layers are reduced in a Cu/Nb multilayer, fcc to bcc and bcc to fcc transformations were noted for Cu and Nb respectively. These transitions have been modeled using a thermodynamic phase diagram where interfacial and volumetric energy considerations determine stability and the bilayer thickness of the multilayer is a state variable for predicting those transformations. Using HRTEM, the evolution of the interface from incoherent-to-semicoherent-to-coherent is determined and related to the structural component of the interfacial energy reduction that drives the crystalline transformations. When equal thicknesses of each layer were < 1 nm, the layers underwent an additional transformation from a crystalline to amorphous structure. This has been rationalized by the positive enthalpy of mixing between these two species as they intermixed during the sputter deposition process. The chemical intermixing and local clustering at and near the interface has been quantified by atom probe tomography. These phase transformations have been related to real-time, intrinsic growth stress measurements. All of the multilayers were in a compressive stress state, but a notable reduction in the compressive stress value occurred with each transformation. The collective characterization of the film, via TEM, atom probe, and stress evolution, have provided insights into the structural stability of crystalline phases at the nanoscale.

11:40am SE+AS+NS+TR-MoM11 Droplets in Cathodic Arc Evaporated (Al,Cr)₂O₃-based Coatings and the Nucleation of Dedicated Crystalline Structures, *Christian M. Koller*, CDL AOS, TU Wien, Austria, *R. Hahn,* TU Wien, Austria, *J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein, *S. Kolozsvári,* Plansee Composite Materials GmbH, Germany, *P.H. Mayrhofer*, CDL AOS, TU Wien, Austria

Corundum-type Al_2O_3 coatings demonstrate excellent thermo-mechanical properties, giving rise to widespread applications as protective films on, e.g., cutting inserts or components. These coatings are typically synthesised by chemical vapour deposition (CVD) at temperatures of 900 °C or higher, which excludes temperature sensitive substrates. Physical vapour deposition (PVD) proved to be a suitable method for low temperature synthesis of nitrides with excellent properties. However, the growth of single-phased corundum-type α-Al_2O_3 by PVD is still a difficult task under standard production conditions. In general, a mixed phase composition of metastable cubic phases is observed, which influence the thermo-mechanical performance of the coating. The utilisation of targets produced by powder metallurgical methods allows for the combination of aluminium with other elements, suitable to promote dedicated crystal structures as demonstrated by AlCr and more recently AlCrFe, where dense crystalline coatings with an increased amount of hexagonal phase fractions were realised. Although the alloying with Cr and Fe is a promising concept with good prospects, the mechanism to form the hexagonal structure in these materials is yet not understood. Therefore, the aspect of layer-nucleation is investigated in more detail. A significant part of hexagonal crystallites in $(Al,Cr,Fe)_2O_3$ coatings is triggered by nucleation onto small particles incorporated in the coating. They originate from the cathode surface and are generated during the cathodic arc process. Cathode surface modifications, macroparticle incorporation and the associated coating microstructures are elucidated by detailed X-ray diffraction and electron microscopy studies. Implications on the coatings' properties and possible technological concepts are discussed.

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

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

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

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

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

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

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

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

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

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

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

Electronic Materials and Processing
Room: 210E - Session EM+NS+PS-MoA

More Moore! II
Moderator: Christopher Hinkle, University of Texas at Dallas, Andrew C. Kummel, University of California at San Diego

2:20pm EM+NS+PS-MoA1 Effect of *Ex Situ* and *In Situ* Surface Cleaning on the Quality of Al_2O_3-SiGe(001) Interfaces, *K. Sardashti, Kai-Ting Hu,* UC San Diego, *S. Madisetti,* College of Nanoscale Science and Engineering, Albany-SUNY, *K. Tang,* Stanford University, *S. Oktyabrsky,* College of Nanoscale Science and Engineering, Albany-SUNY, *P.C. McIntyre,* Stanford University, *S. Siddiqui, B. Sahu,* Globalfoundries, *N. Yoshida, J. Kachian,* Applied Materials Inc., *A.C. Kummel,* UC San Diego

Silicon-Germanium has shown a great promise for future CMOS technology by combining the high hole and electron mobility of Ge with the ability to have both tensile and compressive strain by fabrication of alloys of higher and lower Ge content. In contrast to Si, SiGe native oxide is a combination of SiO_2 and GeO_2, $SiGeO_x$, which has low interface quality and stability in comparison with SiO_2 due to the presence of the GeOx. Therefore, instead of thermal oxide growth, it is necessary to employ atomic layer deposition (ALD) for gate oxide deposition in SiGe MOS devices. The effects of the ex-situ wet chemical clean (such as HF and $(NH_4)_2S$ dip) and in-situ NH_3 plasma clean prior to ALD, were determined on Al_2O_3/SiGe; interface quality quantified by oxide leakage, interfacial trap density, and near-interface trap density. MOS capacitors fabricated by Al_2O_3 ALD at 120°C. Compared to HF clean, both ex-situ $(NH_4)_2S$ clean and in-situ NH_3 plasma resulted in smaller density of interface and smaller leakage current in accumulation. Furthermore, both methods resulted in high surface stability in air; queue times up to an hour could be tolerated. Angle-resolved X-ray photoelectron spectroscopy (AR-XPS) measurements on SiGe(001) with 0.8nm thick Al_2O_3 showed that $(NH_4)_2S$ clean significantly reduces the amount of GeOx at the in Al_2O_3/SiGe(001) interface, compared to HF clean.

2:40pm EM+NS+PS-MoA2 Surface Passivation for ALD-Al_2O_3/SiGe MOS Devices, *Liangliang Zhang,* Stanford University, *V. Hassan, C. Lo, C. Olsen, M.A. Foad,* Applied Materials Inc., *P.C. McIntyre,* Stanford University

We report a study of passivation of the SiGe surface, a critical challenge for future SiGe MOSFET technology. Epitaxially grown p-type SiGe films on lightly doped Si substrates are investigated. The layered surface structures of native oxide coated, as-received SiGe samples are characterized using soft x-ray synchrotron photoemission electron spectroscopy (PES). It is observed that the surface of as- received SiGe wafers have a mixed SiO_x/GeO_x oxide layer. Angle-resolved PES shows that this layer is SiO_x-rich at the top surface and GeO_x-rich below. Lab source x-ray photoelectron spectroscopy (XPS), hard x-ray PES and x-ray reflectivity (XRR) are used to characterize the interface region between atomic layer deposited (ALD) Al_2O_3 gate dielectrics and SiGe. Prior to ALD, 2% HF(aq) solution is used to remove the surface oxides, and a high quality Al_2O_3 layer on the SiGe substrate is deposited with the help of efficient sites for $Al(CH_3)_3$ (TMA) precursor adsorption produced by H_2O oxidant pre-dosing of the SiGe surface immediately prior to the TMA/H_2O ALD process. It is observed from XPS and PES that there is an increase of the SiO_x peak intensity after Al_2O_3 deposition, while there is little or no detectable Ge core level feature associated with GeO_x. The thermodynamic preference of Si (compared to Ge) atoms bonding to oxygen agrees well with the identity of the layered oxide structures extracted by fitting measured XRR data from the processed samples.

Both Pt, a metal that is a known catalyst for H_2 dissociation, and Al are investigated as gate metals for ALD-Al_2O_3/SiGe MOS capacitors (MOSCAPs) subjected to post metal forming gas (5% H_2/95% N_2) anneal (FGA). The effects of the gate metal on post-FGA interfacial oxide composition and interface trap response is studied. Capacitance-voltage analysis of Al/Al_2O_3/p-SiGe MOSCAPs detects minimal frequency dispersion in depletion and accumulation. The extracted density of interface

traps is peaked near the valence band, with a maximum value of $\sim 3x10^{11}$ $(eV^{-1}cm^{-2})$.

3:00pm EM+NS+PS-MoA3 Harnessing Chemistry to deliver Materials and Process for theNext 10 Years of CMOS Evolution, *Robert Clark*, TEL Technology Center, America, LLC   **INVITED**
Harnessing Chemistry to Deliver Materials and Processes for the Next 10 Years of CMOS Evolution

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The continued scaling of the Integrated Circuits (ICs) according to Moore's law has led to a doubling of the number of devices per unit area in semiconductor microchips approximately every 2 years since 1962. Over the past decade traditional scaling by simple linear shrinking has effectively ceased as IC makers have adopted new 3-dimensional device structures, complex integration schemes and new processes and materials for an expanding number of applications in order to overcome fundamental physical limits. In order to continue Moore's law in the coming decade this trend will not only continue, but intensify as devices are scaled to a level approaching atomic dimensions. Broadly speaking, two major trends are influencing the development of future IC manufacturing processes: the need to harness the third dimension to extend Moore's law; and the need for "self-something" processes. "Self-something" processes refers to processes or schemes that are directed chemically to attain a desired result and includes processes that are self-limited (e.g. ALD or ALE), self-directed (e.g. directed self-assembly or selective deposition), or self-aligned (e.g. self-aligned contacts) in some way that enables device density scaling. "Self-something" processes are required in order to harness the third dimension and make use of new non-planar device architectures (e.g. FinFETs and DRAM capacitors), device arrays/stacking (e.g. 3D NAND and cross-point memory), and 3D integration (e.g. monolithic 3D, and chip stacking). Highly tailored ALD processes are being investigated to fabricate functional material layers. Interspersed treatments and doping may be used to modify the physical and electrical properties of ALD films further in order to optimize the resulting physical or electrical properties. To improve device contacts, ultra-thin dielectric and metal layers may be deposited inside of high aspect ratio contact structures in order to provide lower contact resistivity. Selective deposition processes can be used to deposit functional materials only where they are needed, thus reducing the patterning burden during IC manufacturing. Depositing dopant layers by ALD for thermal solid source doping can be used to conformally dope 3-D device structures without the damage caused by implantation. Examples of these and similar processes will be described and discussed along with the chemical processes and transformations governing film deposition, composition, structure, and interface control.

3:40pm EM+NS+PS-MoA5 Materials Selection for Oxide-based Resistive Random Access Memory (RRAM), *John Robertson*, *Y. Guo*, Cambridge University, United Kingdom of Great Britain and Northern Ireland   **INVITED**
Resistive random access memory (RRAM) is a main challenger non-volatile memory technology to Flash memory. The favored materials are based on the formation of a conductive filament of oxygen vacancies across a film of a wide gap oxide. However, a wide range of material systems are presently being studied, which use various different switching mechanisms. Materials selection requires us to understand which material properties control each aspect of device performance, such as switching speed, resistance window, retention time and endurance. Here, the energies of various atomic processes in resistive random access memories (RRAM) are calculated for four typical oxides, HfO_2, TiO_2, Ta_2O_5 and Al_2O_3, to define a materials selection process. Oxygen vacancies have the lowest defect formation energy in the O-poor limit, and to dominate the processes. A band diagram defines the operating ranges of Fermi energy and O chemical potential. It is shown how scavenger metals can be used to vary the O chemical potential and thus vary the O vacancy formation energy. The high stability of amorphous phase of Ta_2O_5 is relevant to the high endurance of its RRAM.

4:20pm EM+NS+PS-MoA7 Lower Temperature Silicon Nitride ALD on Si$_{0.5}$Ge$_{0.5}$(110) with No Solid By-product Formation, *Steven Wolf, M. Edmonds, T. Kent,* University of California at San Diego, *D. Alvarez,* RASIRC, *R. Droopad,* Texas State University, *A.C. Kummel,* University of California at San Diego

A silicon nitride passivation layer on semiconductor surfaces can serve several practical uses, such as acting as a diffusion barrier or channel passivation layer prior to dielectric deposition in FinFets or MOSFETs. When employed as a channel passivation layer, further reaction with an oxidant, such as anhydrous peroxide, can leave Si-N-OH termination, which is reactive with all metal ALD precursors thereby providing high nucleation density. Previous studies show stoichiometric ALD Si$_3$N$_4$ growth on Si(100) by hydrazine and Si$_2$Cl$_6$ at temperatures in excess of 350°C with solid ammonium chloride by-product formation[1]. The first half reaction of N$_2$H$_4$ leaves N-H$_x$ surface termination, and the second reaction with Si$_2$Cl$_6$ adds silicon to the surface and creates a gaseous HCl by-product. An ammonium chloride by-product is usually caused by wall reactions of unreacted precursors. This study focuses on developing a low temperature silicon nitride ALD process with no unwanted solid by-product formation. STM/STS and XPS are employed to characterize SiN$_x$ film growth on Si$_{0.5}$Ge$_{0.5}$(110).

A test chamber consisting of a reactor chamber, dosing lines, and a dry pump was created and heated to 125°C for 12 hours to allow for sufficient heating of all stainless steel components. In excess of 100 ALD cycles were ran in the test chamber with no visible evidence of powder formation on any walls, and it was concluded that this lengthy heating process prior to SiN$_x$ ALD is necessary to eliminate the unwanted powder by-product formation. Next, at a substrate temperature of 275°C and wall temperature of 20°C, the silicon nitride ALD procedure was performed on a p-type Si$_{0.5}$Ge$_{0.5}$(110) surface that underwent an ex-situ wet organic clean followed by a dip into a 2% HF/water solution with a toluene layer on top. The sample was pulled through toluene and loaded into UHV as quickly as possible to minimize native oxide formation. After a 315 MegaLangmuir anhydrous hydrazine dose, XPS shows N-H$_x$ surface termination, and removal of half of the initial carbon contamination. A subsequent 21 MegaLangmuir Si$_2$Cl$_6$ dose followed by 17 cycles of 3 MegaLangmuir hydrazine and 3 MegaLangmuir Si$_2$Cl$_6$ leads to increased silicon nitride growth as shown by a large increase in XPS Si 2p and N 1s peaks, as well as a decrease in the Ge 3d substrate peak. After the ALD cycling with room temperature walls, a white powder, presumed to be ammonium chloride, was seen in the reactor, but will now be avoided using the 125°C wall temperature.

1. S. Morishita *et. al.*, Appl. Surf. Sci., **112**, p:198-204 (1997).

4:40pm EM+NS+PS-MoA8 Novel Delivery of Unstable Precursors for Atomic Layer Deposition, *Daniel Alvarez, J. Spiegelman, E. Heinlein, R. Holmes, C. Ramos, S. Webb, K. Johnson,* RASIRC

A considerable amount of effort has gone into the development of novel metal precursors for Atomic Layer Deposition (ALD). This is primarily driven by the need for new high *K* materials and metals films. Largely ignored has been the need for novel oxidants and sources of nitrogen. This paper focuses on the delivery of anhydrous hydrogen peroxide and anhydrous hydrazine for ALD applications.

Hydrogen Peroxide (H$_2$O$_2$) in aqueous form is commonly used in semiconductor manufacturing for cleaning and surface preparation operations. Thirty percent and fifty percent two-component mixtures have been investigated in a few ALD studies with moderate success. Especially noteworthy are Kummel's findings that the use of hydrogen peroxide leads to a 3x increase in nucleation density on Ge versus water. However, H$_2$O$_2$ has limited general utility in aqueous form due to the volatility of water. At 30C, Raoult's law predicts a headspace concentration of 294ppm H$_2$O$_2$ and 32373ppm for water, where the H$_2$O/H$_2$O$_2$ ratio is over 100. Clearly these are not optimal conditions for hydrogen peroxide ALD. However, in its pure state, hydrogen peroxide is highly unstable and has a propensity to decompose, forming water and oxygen. Our approach entails the use of a membrane delivery system where 99.6% hydrogen peroxide is dissolved in an organic solvent. Hydrogen peroxide permeates the membrane and is delivered to the ALD chamber, while the solvent does not permeate and remains in the liquid state. In this way, concentrations much higher than predicted by Raoult's law for aqueous mixtures are delivered to the process chamber in the absence of water.

Next generation devices have low thermal budgets and high aspect ratio structures that create new challenges for ALD grown nitride films. The use of ammonia is limited due to temperature constraints. Known Plasma methods cannot uniformly coat the side walls of the device structures and create surface damage. Hydrazine (H$_2$NNH$_2$) has been proposed as a thermal ALD low temperature nitride source.Hydrazine is highly flammable and its flash point decreases with reduced water content. In an analogous approach, we have developed a new method and formulation for the delivery of anhydrous Hydrazine by the use of an inert organic solvent and

membrane delivery system. Precursor vapor pressure is maintained at levels viable for ALD. Moreover, the addition of a high boiling solvent lowers the risk of explosion by raising the solution flash point.

Preliminary ALD data will be presented showing unique properties of these new precursors along with theoretical data on precursor delivery under variable ALD conditions.

5:00pm EM+NS+PS-MoA9 Passivation and Functionalization of SiGe(001) and (110) for ALD Nucleation in FinFET Structure, *SangWook Park, H. Kim,* University of California at San Diego, *B. Sahu, S. Siddiqui,* GLOBALFOUNDRIES U.S. Inc., *N. Yoshida, A. Brandt,* Applied Materials, Inc., *E. Chagarov, A.C. Kummel,* University of California at San Diego

Silicon Germanium (SiGe) is a promising candidate for FinFET channels, sources, and drains due to its high mobility and utility in strain engineering. Since FinFETs are composed of three-dimensional structures utilizing multiple crystalline planes, the cleaning and passivation must provide uniform and clean surfaces in each plane to combine high mobility with low interface trap density (Dit). In this study, passivation and functionalization of SiGe(001) and (110) surfaces are discussed, using scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and x-ray photoelectron spectroscopy (XPS).

The SiGe(001) is dimer terminated while the SiGe(110) is dimer-free leading to differences in surface stoichiometry and order. STM and XPS measurements indicate that clean (001) is mostly terminated with Ge atoms with a uniform and well-ordered structure while (110) is terminated with adatoms of both Si and Ge atoms and lower surface order. STS measurements indicate the clean (001) surface is unpinned while the clean (110) surface is pinned mid gap between the valence and conduction band edge due to adatom dangling bonds. The sputter cleaned SiGe(110) surface was dosed at 300°C with 3,600L dose of atomic H to passivate the dangling bonds of the adatoms. STS measurements demonstrate the atomic H dosed (110) surface is unpinned with a Fermi level near the valence band due to Si-H and Ge-H bonds on adatoms. The unpinned SiGe (001) and (110) surfaces were dosed at room temperature with a saturation dose of H$_2$O$_2$(g) leaving the SiGe surface terminated with an ordered monolayer of only Ge-OH sites on (001) and both of Ge-OH and Si-OH sites on (110). STS shows that on the HOOH dosed SiGe(001) and (110), the Fermi level is shifted to near the valence band edge due to the large surface dipole from the hydroxyl bonds. TMA was subsequently dosed on the HOOH/SiGe(001) and HOOH/atomic H/SiGe(110) surfaces forming an ordered monolayer of Al-O-Si bonds. In order to understand the thermal stability of the TMA dosed SiGe surfaces, the surface was annealed to 300°C and XPS measurements verify that Al-O bonds are totally transferred from Ge atoms to Si atoms forming Al-O-Si bonds on both (001) and (110) indicating that the strong affinity between Si and oxygen is pulling Si atoms toward the surface to bond with oxygen or hydroxyls while pushing Ge atoms into the subsurface during the annealing. STS indicates this unpins the Fermi level on both surfaces, leaving an electrically passive ordered layer which serves as an ideal template for further high-k ALD.

5:20pm EM+NS+PS-MoA10 Band Structure and Critical Points of Pseudomorphic Ge$_{1-y}$Sn$_y$ Alloys on Ge, *Nalin Fernando, T.N. Nunley, S. Zollner,* New Mexico State University, *D. Zhang, R. Hickey, J. Kolodzey,* University of Delaware

We calculate the dependence on composition and strain of the band structure of Ge$_{1-y}$Sn$_y$ alloys grown pseudomorphically on Ge and compare with spectroscopic ellipsometry measurements. Germanium is an indirect band gap material with limited optoelectronic applications. Because the band structure of Ge is a strong function of strain, a transition from an indirect to a direct band gap has been found for Ge under a tensile strain, which constrains the layer thickness and the composition of the substrate for heterostructure growth. Indirect to direct band gap crossover of unstrained Ge$_{1-y}$Sn$_y$ has been reported for y~6-10% indicating the possibility of widespread applications of Ge-based photonic devices and paving the way for the design of Ge$_{1-y}$Sn$_y$ lasers. Hence it is important to study the compositional dependence of the Ge$_{1-y}$Sn$_y$ band structure through measurements of the optical properties of Ge$_{1-y}$Sn$_y$ alloys. The complex pseudodielectric functions of pseudomorphic Ge$_{1-y}$Sn$_y$ alloys grown on Ge by MBE were measured using spectroscopic ellipsometry at 300 K in the 0.76-6.6 eV energy range for Sn contents up to 11%. Dielectric functions of Ge$_{1-y}$Sn$_y$ alloys were obtained to investigate the compositional dependence of the E$_1$ and E$_1$+ Δ_1 critical point (CP) energies. CP energies and related parameters were obtained by analyzing the second-derivative of the dielectric function. Our experimental results are in good agreement with the theoretically predicted E$_1$ and E$_1$+ Δ_1 CP energies of compressively strained Ge$_{1-y}$Sn$_y$ on Ge based on deformation potential theory. We will discuss the compositional and strain dependence of the direct and indirect band gaps as well as E$_1$ and E$_1$+ Δ_1 CP energies and related parameters of Ge$_{1-y}$Sn$_y$ alloys. We will present the nature of the band gap of pseudomorphic Ge$_{1-y}$Sn$_y$ on

Ge and will discuss the effects of strain which critically depend on the bowing parameter of the lattice constant.

Energy Frontiers Focus Topic
Room: 211B - Session EN+AS+EM+NS+SE+SS+TF-MoA

Solar Cells II
Moderator: Adrie Mackus, Stanford University

2:20pm EN+AS+EM+NS+SE+SS+TF-MoA1 Influence of Annealing Temperature in the Bulk Defect Formation in Perovskite Thin Films, *Weina Peng*, B.X. Anand, L.-H. Liu, S.C. Sampat, B.E. Bearden, A.V. Malko, Y.J. Chabal, University of Texas at Dallas
Perovskites are emerging as front-runners for solar cell applications because of their superior optoelectronic properties. Over the past few years the grain size of perovskites has been continuously improved from several hundred of nanometers to a few millimeters which resulted in better solar conversion efficiencies. In addition to surface and grain boundary related defects, perovskites are prone to the formation of bulk defects as well. However the role of bulk defects in the determination of photovoltaic performance of perovskites is rarely explored. To this end we investigate the impact of annealing temperature on the defect density in polycrystalline $CH_3NH_3PbI_3$ thin films of ~1 micron average grain size prepared using vapor assisted solution process (VASP). The photoluminescence (PL) intensity and lifetime show systematic reduction when the annealing temperature is increased from 150°C to 200°C. A rough estimate of the defect state density obtained using fluence dependent PL measurements reveal a 5 fold increase in defect density for a 25°C increase in annealing temperature although the average grains size stays unchanged. Furthermore, surface passivation of perovskite films using Al_2O_3 via atomic layer deposition leads to an improvement in PL intensity and lifetime. But the PL quantum efficiency, as well as the lifetime, of the surface passivated 200°C annealed sample remains significantly lower than that of the un-passivated 150°C annealed sample indicating that the majority of the defects states we observe in the high temperature annealed samples originate from bulk defects. Thus the present study shows that minimizing the number of bulk defects, in addition to surface defects, is very important in the realization of highly efficient perovskite solar cells.

3:00pm EN+AS+EM+NS+SE+SS+TF-MoA3 Tandem Solar Cells Using Perovskites, Silicon and CIGS, M.D. McGehee, *Tomas Leijtens*, Stanford University **INVITED**
The efficiency of perovskite solar cells has soared from a few percent to over 20% in the last 3 years. They are very attractive for multijunction solar cell applications because the bandgap of perovskite semiconductors can be easily tuned in the range of 1.55 to 2.2 eV and the open circuit voltage of the cells is large. We have made highly efficient semitransparent perovskite solar cells using silver nanowire meshes as the top electrode. These cells can be used in combination with either silicon or copper indium gallium diselenide solar cells to make four-terminal and two-terminal tandems. We will also present detailed characterization of perovskite semiconductors made with different processing conditions to show what needs to be done to minimize recombination and make the solar cells stable.

3:40pm EN+AS+EM+NS+SE+SS+TF-MoA5 Lifetime, Mobility, and Diffusion of Photoexcited Carriers in Ligand-Exchanged Lead Selenide Nanocrystal Films Measured by Time-Resolved Terahertz Spectroscopy, G.W. Guglietta, Drexel University, B.T. Diroll, E.A. Gaulding, J.L. Fordham, University of Pennsylvania, S. Li, Drexel University, C.B. Murray, University of Pennsylvania, *Jason Baxter*, Drexel University
Colloidal semiconductor nanocrystals have been used as building blocks for electronic and optoelectronic devices ranging from field effect transistors to solar cells. Properties of the nanocrystal films depend sensitively on the choice of capping ligand to replace the insulating synthesis ligands. Thus far, ligands leading to the best performance in transistors result in poor solar cell performance, and vice versa. To gain insight into the nature of this dichotomy, we used time-resolved terahertz spectroscopy measurements to study the mobility and lifetime of PbSe nanocrystal films prepared with five common ligand-exchange reagents. Non-contact terahertz spectroscopy measurements of conductivity were corroborated by contacted van der Pauw measurements of the same samples. The films treated with different displacing ligands show more than an order of magnitude difference in the peak conductivities and a bifurcation of time-dynamics. Inorganic chalcogenide ligand-exchanges with sodium sulfide (Na_2S) or ammonium thiocyanate (NH_4SCN) show high THz mobilities above 25 $cm^2V^{-1}s^{-1}$,

which is desirable for transistors, but nearly complete decay of transient photocurrent within 1.4 ns. The high mobility with NH_4SCN and Na_2S exchanges is more than offset by their short lifetimes and results in diffusion lengths of only ~200 nm. In contrast, ligand exchanges with 1,2-ethylenediamine (EDA), 1,2-ethanedithiol (EDT), and tetrabutylammonium iodide (TBAI) show ~5x lower mobilities but much longer carrier lifetimes, with ~30% of photoexcited carriers remaining for >10 ns. The long lifetimes with EDA, EDT, and TBAI yield diffusion lengths of at least 500 nm, which is approaching the film thickness desired for strong light absorption in solar cells. This bifurcated behavior may explain the divergent performance of field-effect transistors and photovoltaics constructed from nanocrystal building blocks with different ligand exchanges.

4:00pm EN+AS+EM+NS+SE+SS+TF-MoA6 iCVD Synthesis and Integration of Poly(vinylpyrrolidone) and Poly(4-vinylpyridine) as Polymer Electrolytes in Dye Sensitized Solar Cells, *Yuriy Y. Smolin*, S. Janakiraman, A.J. Sauter, M. Soroush, K.K.S. Lau, Drexel University
Initiated chemical vapor deposition (iCVD) is used to synthesize and integrate poly(4-vinylpyridine) (P4VP) and polyvinylpyrrolidone (PVP) as polymer electrolytes within the mesoporous TiO_2 photoanode of dye sensitized solar cells (DSSCs). DSSCs with conventional liquid electrolytes are prone to leakage and evaporation, which hinders DSSC durability and field implementation. In addition, liquid electrolytes lead to significant electron recombination within the cells that limit DSSC performance. In contrast, polymer electrolytes do not suffer from the practical disadvantages and could potentially enhance the cell's I-V behavior.

However, in order to enable good contact between the TiO_2 electrode and the polymer electrolyte, a major obstacle is the difficulty in achieving good pore filling of the polymer into the mesoporous TiO_2 layer. Mesoscale pore diameter, high aspect ratio, and tortuous pore structure of the photoanode along with liquid surface tension, poor wettability, and solute steric hindrance make pore filling extremely limited when using liquid techniques. This leads to poor electrical contact and lower efficiency. To overcome the challenges of pore filling, we directly synthesized polymer electrolytes inside the pore volume of the photoanode using the solvent-free technique of iCVD. iCVD relies on the vapor delivery of monomer and initiator, which facilitates infiltration into the porous TiO_2 substrate, and by controlling the relative rates of diffusion and surface polymerization through iCVD process parameters, uniform and conformal growth of polymer is achieved. The pore filling of the polymer electrolyte into 5–10 μm photoanodes using iCVD is typically 90–100% which is significantly better than that achievable with liquid techniques like spin coating.[1]

In this work, we will show that iCVD P4VP and PVP polymer electrolytes can be effectively integrated within TiO_2 mesoporous photoanodes to produce enhanced DSSCs. By varying the polymer electrolyte chemistry including the use of a crosslinking agent during iCVD to stabilize the resulting polymer structure, DSSC I-V characteristics, such as open-circuit voltage, short-circuit current density and fill factor, are tuned.[2] To gain a better understanding on the effect of the polymer electrolyte, experimental techniques such as linear sweep voltammetry, intensity modulated spectroscopy, and impedance spectroscopy are used. Mathematical modeling of DSSC behavior is also performed to relate these experimental observations with the dynamics of the operation of the cell.

1. S. Nejati and K. K. S. Lau, *Nano Lett.*, 2010, 11, 419-423.

2. Y. Y. Smolin et al., *J. Power Sources*, 2015, 274, 156-164.

4:20pm EN+AS+EM+NS+SE+SS+TF-MoA7 Interfacial Effects on Device Performance in Organic Solar Cells, *Huanxin Ju*, J.F. Zhu, University of Science and Technology of China, D.S. Ginger, University of Washington
The better understanding of the underlying mechanisms is essential for the further development of highly efficient organic photovoltaics (OPVs) devices. In this paper, the transient photovoltage (TPV) and charge extraction (CE) measurements in combination with the synchrotron radiation photoemission spectroscopy (SRPES) were used to gain insights intothe correlation between the microscopic interfacial properties and macroscopic device performance. The OPV devices based on PCDTBT: $PC_{70}BM$ with Ca interlayer were studied as a reference system to investigate the interfacial effects on device performance. The charge carrier decay dynamics demonstrated that the device with the Ca interlayer exhibited a lower recombination constant (k_{rec}) than that only with the Al cathode at a given charge carrier density (n). In addition, the interfacial energy band structures indicated that the strong dipole moment produced by the Ca interlayer can facilitate electron extraction as well as drive hole away at the cathode/polymer interface, resulting in retarding interfacial recombination losses. Finally, we examined the device performance with the Ca interlayer to find that the efficiency is improved by 28% as compared to that without the Ca interlayer, which shows good correlation with the observed interfacial properties.

4:40pm EN+AS+EM+NS+SE+SS+TF-MoA8 Tungsten-Titanium Mixed Oxide Thin Films for Improved Structural and Optical Properties for Solar Driven Applications, *Mirella Vargas*, The University of Texas at El Paso, *N.R. Murphy*, Air Force Research Laboratory, *R.V. Chintalapalle*, The University of Texas at El Paso

Tungsten oxide (WO_3) is a well-established n-type semiconductor possessing unique optical and electronic properties. WO_3 has become the most interesting inorganic material for electrochromic applications due to the reversible spectral absorption properties associated with WO_3. WO_3 thin films and nanostructures exhibit an optical band gap that permits efficient use of the solar spectrum including absorption in the blue part of the visible region and the ultraviolet region, as well as a high transmission region that extends from the near-infrared (IR) to the visible spectrum. Coupled with good electronic transport properties, photosensitivity, and chemical integrity, WO_3-based materials are attractive for applications related to sustainable energy production including energy efficient windows and architecture, photoelectrochemical (PEC) water-splitting, photocatalysis and solar cells. Anion or cation doping into WO_3 has been extensively studied as this offers the opportunity to tailor the transport properties that may influence the efficiency of solar driven devices. Titanium doping into WO_3 has proven to enhance the electrochromic response and the cyclic lifetime by a factor of five in PEC devices. In the present case a systematic investigation of progressively increasing the Ti content in the W-Ti target for reactive sputtering has been employed to tune the structure, chemistry, and properties of the films. Tungsten-titanium (W-Ti) mixed oxide thin films were fabricated using reactive sputtering of W-Ti alloy targets with Ti content ranging from 0 to 30 wt.%. X-ray photoelectron spectroscopy confirms the existence of W and Ti in their highest oxidation states of +6 and +4, respectively. Quantification of binding energy shifts for W and Ti core-level transitions confirms the formation of WO_3-TiO_2 composite oxide films. Optical analyses made from spectrophotometry measurements indicate a decrease in band gap with a discrete amount of Ti incorporation. The band gap decreases with increasing Ti from 3.0 eV to 2.5 eV. Such films are expected to have the possibility for tuning the electrical conductivity while retaining the optical transparency to make them efficient for photoelectrochemical cells and photovoltaics.

5:00pm EN+AS+EM+NS+SE+SS+TF-MoA9 Potential Resolution to the "Doping Puzzle" in Pyrite FeS_2, *X. Zhang, M. Li, L. O'Brien, J. Walter, M. Manno, F. Mork, J. Kakalios*, **Eray Aydil**, *C. Leighton*, University of Minnesota

In principle, pyrite FeS_2 is one of the most suitable photovoltaic materials for sustainable low-cost, large-scale solar cell manufacturing because it has high absorbance in the visible and comprises earth-abundant inexpensive elements. However, current efficiencies of solar cells based on pyrite FeS_2 have not exceeded 2.8%. Early research on this material concluded that unintentionally doped FeS_2 thin films are *p*-type and subsequent solar cell work evolved based on this presumption. In fact, it is now widely accepted that FeS_2 thin films almost always exhibit *p*-type conduction even though single crystals are typically found to be *n*-type. This discrepancy between single crystals and thin films is perplexing and to date this puzzle remains unexplained. In this talk we reexamine the conclusion that undoped FeS_2 films are predominantly *p*-type and provide an explanation for this "doping puzzle" in pyrite. Using a combination of Hall effect, thermopower, and temperature-dependent resistivity measurements on a large set of well characterized single crystals and thin films, we show that the widely accepted predominant *p*-type behavior in pyrite films may, in fact, be an artifact of hopping conduction and should be revisited. Specifically, both Hall effect and thermopower measurements establish that all of our high-mobility (>1 $cm^2V^{-1}s^{-1}$) films and single crystals are *n*-type. Temperature-dependent resistivity measurements on these high mobility films and crystals establish diffusive electronic transport. We find that films with lower mobility (4×10^{-3}-1 $cm^2V^{-1}s^{-1}$) also show *n*-type Hall effect but exhibit a *p*-type Seebeck coefficient, leading to a discrepancy in the measured carrier type. Temperature-dependent resistivity measurements on these intermediate mobility films show a transition from diffusive to hopping transport. Finally, both Hall and Seebeck coefficients are strongly suppressed and invert in the lowest mobility thin films ($<4 \times 10^{-3}$ $cm^2V^{-1}s^{-1}$) indicating apparent *p*-type conduction. Temperature-dependent resistivity measurements establish unambiguous hopping behavior in these lowest mobility films. Based on this evolution of Hall and Seebeck coefficients with carrier mobility, and the well-known suppression of the Hall and Seebeck effects in conductors with hopping electronic transport, we conclude that the apparent crossover from *n*-type to *p*-type with decreasing mobility is, in fact, an artifact of hopping conduction.

5:20pm EN+AS+EM+NS+SE+SS+TF-MoA10 Interparticle Contact Radius and Electron Transport in Thin Films Comprised of Nanocrystals, *Elijah Thimsen, D. Lanigan*, Washington University, St. Louis

Thin films comprised of nanocrystals are being explored for a variety of applications that involve electron transport. For traditional applications such as photovoltaic solar cells, the goal is often to utilize solution processing to make an inexpensive thin film that essentially behaves as a bulk material with diffusive transport. For other applications, such as neuromorphic computing, variable range hopping (VRH) transport is more desirable because it enables a given nanocrystal to have orders of magnitude more nearest neighbors than it physically touches. It is of paramount importance that the structure-property relationships that control electron transport mechanism be elucidated. Previous work has demonstrated that interparticle separation distance affects charge carrier mobility. However, for films comprised of nanocrystals that are physically touching, what is the effect of contact radius? In this work, we present a systematic experimental study of the effect of interparticle contact radius on the electron transport mechanism in thin films comprised of heavily-doped ZnO nanocrystals embedded in Al_2O_3. As the contact radius increased, the electron transport mechanism crossed over from VRH to diffusive conduction. For large contact radius between nanocrystals, the room-temperature electron mobility in the film approached the local mobility within a nanocrystal, approximately 10 cm^2 V^{-1} s^{-1}. The conclusion is that for nanocrystals that are physically touching, the interparticle contact radius determines the transport mechanism. With the ability to control the electron transport mechanism in films comprised of ZnO nanocrystals, we performed an exploratory study of the Hall effect in these materials. Hall effect measurements are of great utility and are routine for determining charge carrier mobility and type, but the interpretation of data for materials that exhibit VRH has been difficult in the past. For well-connected ZnO nanocrystals that exhibit diffusive conduction, the Hall coefficient was independent of temperature, as expected for the high doping level. Alternatively, for films with small contact radius between nanocrystals, which exhibited a VRH transport mechanism, we observed an anomalous behavior of the Hall coefficient at low temperature (100 to 200 K). Surprisingly, for films that exhibited VRH, the magnitude of the Hall coefficient increased exponentially with decreasing temperature, in stark contrast to the conventional wisdom that the Hall effect is suppressed for VRH.

Accelerating Materials Discovery for Global Competitiveness Focus Topic
Room: 114 - Session MG+2D+MI+NS+TF-MoA

Design and Discovery (Bio and Other Interfaces)
Moderator: Sean Jones, National Science Foundation (NSF), Lynnette Madsen, National Science Foundation (NSF)

3:00pm MG+2D+MI+NS+TF-MoA3 Rational Accelerated Design of Polymer Dielectrics, *Rampi Ramprasad*, University of Connecticut
INVITED

To date, trial and error strategies guided by intuition have dominated the identification of materials suitable for a specific application. We are entering a data-rich, modeling-driven era where such Edisonian approaches are gradually being replaced by rational strategies which couple predictions from advanced computational screening with targeted experimental synthesis and validation. Consistent with this emerging paradigm, we propose a strategy of hierarchical modeling with successive down-selection stages to accelerate the identification of polymer dielectrics that have the potential to surpass `standard' materials for a given application. Specifically, quantum mechanics based combinatorial searches of chemical space are used to identify polymer repeat units that could lead to desirable dielectric properties, followed by configurational space searches to determine the 3-dimensional arrangement of polymers (and their properties) built from the desirable repeat units. Successful synthesis and testing of some of the most promising identified polymers and the measured attractive dielectric properties (which are in quantitative agreement with predictions) strongly supports the proposed approach to material selection.

3:40pm MG+2D+MI+NS+TF-MoA5 Method to Make a Stable Copper-Carbon Alloy, *Ivan Shchelkanov, D.N. Ruzic, I. Jasiuk*, University of Illinois at Urbana Champaign

Modern industry demands advanced materials with enhanced properties. To expand a range of available materials the covetic alloy is studied. Covetic is a novel alloy invented and patented by Third Millennium Metals, LLC

(TMM). This is a new hybrid material made of a carbon and a metal, where the carbon forms a super lattice structure inside a metal. The base metal can be copper, aluminium, lead, tin or other low-melting point metals. In normal conditions the metal does not wet and does not form chemical bond with the carbon. However, the amount of carbon in the covetic alloy exceeds carbon solubility in the metal by several orders of magnitude. Such a composition is achieved by supplying a current to a volume of molten metal while it is being blended with micron size carbon particles. The alloy is prepared in vacuum.

The process of covetic formation is influenced by chemical composition of the base metal, a cast volume temperature change rate, external electric and magnetic fields, compound viscosity, surface and interphase tension coefficient, density, and thermal and electric conductivities of the metal and carbon particles. A part of the process of covetic alloy formation, which involves carbon particles dissolving, can be compared to phenomena occur in dust plasma. This assumption provides a possibility to visualise processes of microparticles spatial distribution and decomposition into single atoms with subsequent formation of a carbon supper lattice inside the metal lattice.

The current work focuses on: the electric current influence on the alloy structure formation and carbon atoms distribution inside the metal; copper covetic hardness, conductivity, and tensile strength change as a function of carbon composition; and a phenomenological model for covetic alloy formation.

4:00pm MG+2D+MI+NS+TF-MoA6 Development of Nanoporous Solid Phase Microextraction (SPME) Fibers by Sputtering, *Matthew Linford, C.V. Cushman, B. Singh, A. Diwan*, Brigham Young University
Solid phase microextraction (SPME) is a solventless, fast, easy and relatively inexpensive sample preparation technique that integrates sampling, extraction and preconcentration of samples such as food, waste water, air, and biological fluids in one step. However, commercial SPME coatings may be expensive, show relatively short lives, extract limited numbers of compounds, and have relatively low thermal and mechanical stability. The aim of this study is to develop an SPME device that is thinner, robust, long lasting, has higher mechanical strength, greater thermal and solvent stability, and is devoid of the other drawbacks of commercial coatings. We describe a new method for the preparation of nanoporous SPME coatings via the oblique-angle sputtering of silicon and subsequent functionalization with silanes. The thickness of the sputtered coatings was controlled by varying the sputtering time. To increase the density of –OH groups on the surfaces, the coatings were treated in piranha solution and then reacted with n-octadecyldimethylmonomethoxysilane to render the surfaces hydrophobic. The coatings were robust and were characterized at each step in the process using XPS, water contact angle goniometry, spectroscopic ellipsometry, and scanning electron microscopy. Our sputtered, silanized fiber yielded comparable and/or better extraction efficiencies than a commercial 7 µm PDMS fiber, especially for higher molecular weight species. In the case of a series of primary alcohols, and aldehydes, our fiber outperformed the commercial PDMS fiber by a factor of 2 – 3. In the evaluation of two real world samples: a sea water extract and beer, our fiber showed unique selectivity. Our 1.1 µm fiber yielded comparable signals to 65 µm PDMS-DVB and 85 µm CAR-PDMS commercial fibers for higher molecular weight analytes. For a ~2.2 µm fiber, the performance of our fiber increased substantially.

Nanometer-scale Science and Technology
Room: 212B - Session NS+AS+SP-MoA

Optical Spectroscopy at the Nanoscale
Moderator: Craig Prater, Anasys Instruments

2:20pm NS+AS+SP-MoA1 Nanoscale Infrared Spectroscopy Characterization of Amyloid Aggregates Structure, *Francesco Simone Ruggeri,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland*, T. Muller,* University of Cambridge, UK*, D. Galante,* CNR, Italy*, T.P.J. Knowles,* University of Cambridge, UK*, H. Lashuel,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland*, C. D'Arrigo,* CNR, Italy*, G. Dietler,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**
Aging of world population has increased the onset of several neurodegenerative disorders (ND). These diseases are connected with insoluble fibrillar proteins aggregates, termed Amyloid. During their aggregation, starting monomeric proteins undergo internal structural rearrangement bringing to fibrils with a final universal cross β-sheet quaternary structure. This structure is independent by the monomeric initial one and it is the fingerprint of amyloid and related diseases. Previously, the final fibrillar cross-β sheet structures were considered the cause of the

illnesses. Nowadays, there is strong evidence that the intermediate oligomeric stages of fibrillation could be the cytotoxic one and most of the research groups are investigating the early stages of fibrillation and the inter-conversion of monomers into fibrils. Infrared spectroscopy is a key method for studying conformational properties of proteins and their structural conversion during amyloid fibrillation. Unfortunately, this and others bulk techniques are just able to give average information of the heterogeneous aggregating amyloid solution. To study the chemical structure of amyloid species at the nanoscale, we utilized a thermomechanical detection technique based on atomic force microscopy (nanoIR). If an IR pulse is absorbed by a sample, the local temperature rises and leads to a local thermal expansion. This deformation excites mechanical resonances of the AFM cantilever, in contact with the sample, allowing simultaneously acquiring topography, nanoscale chemical IR maps and/or spectra. We focused on the study of different amyloidogenic proteins, as α-synuclein, lysozyme and αβ42. We measured chemical spectra and IR maps of monomeric and fibrillar aggregates. For the first time, we distinguished chemically different amyloid structures at the single aggregate nanometer scale. Nanoscale chemical characterization of amyloidogenic structures as oligomers, protofibrils and fibrils is central to understand how proteins misfold and aggregate, to unravel the structural rearrangement of monomers inside amyloid fibrils and to target pharmacological approach to ND.

3:00pm NS+AS+SP-MoA3 Recent Progress in Tip-Enhanced Mid-Infrared Photoexpansion Nanospectroscopy, *M. Jin, F. Lu, Mikhail Belkin*, The University of Texas at Austin **INVITED**
Mid-infrared absorption spectroscopy in the molecular fingerprint region ($1/\lambda \sim 600$-4000 cm^{-1}) is widely used for chemical identification and quantitative analysis. The ability to perform mid-infrared spectroscopy with nanometer spatial resolution is highly desired for applications in chemical, materials, and life sciences. Nanoscale mid-infrared spectra can be obtained by detecting mechanical forces exerted by sample on an atomic force microscope (AFM) tip upon sample light absorption and photoexpansion. The first demonstration that photoexpansion of bulk polymers can be detected by AFM and used for mid-infrared nanospectroscopy was by Alexander Dazzi and co-workers [1]. However, only relatively thick polymer samples (approximately 50-nm-thick or thicker) produced detectable cantilever deflections in these experiments, even when mid-infrared optical intensity was close to sample damage. We demonstrated that the sensitivity of mid-infrared photoexpansion nanospectroscopy, also known as AFM-IR, may be improved by several orders of magnitude if we send low-power laser pulses at a repetition frequency that is tuned in resonance with the mechanical vibrational frequency of an AFM cantilever and if we further employ tip-enhancement of the optical field below a sharp gold-coated AFM tip. As a result, monolayer sensitivity and 25 nanometer spatial resolution was achieved for molecular imaging in air [2]. We will discuss details of these experiments and recent progress of this technique, including development of background suppression methods that may lead to further enhancement in sensitivity and progress towards achieving photoexpansion nanospectroscopy of samples in aqueous environment that requires mitigation of liquid damping of cantilever vibration and strong infrared absorption.

[1] A. Dazzi, R. Prazeres, F. Glotin and J.M. Ortega, Opt. Lett. 30, 2388 (2005).

[2] F. Lu, M. Jin and M.A. Belkin, Nature Photonics **8**, 307 (2014).

3:40pm NS+AS+SP-MoA5 Nano-photonic Phenomena in van der Waals Heterostructures, *Dmitri Basov*, University of California San Diego **INVITED**
Layered van der Waals (vdW) crystals consist of individual atomic planes weakly coupled by vdW interaction, similar to graphene monolayers in bulk graphite. These materials can harbor superconductivity and ferromagnetism with high transition temperatures, emit light and exhibit topologically protected surface states. An ambitious practical goal is to exploit atomic planes of vdW crystals as building blocks of more complex artificially stacked heterostructures where each such block will deliver layer-specific attributes for the purpose of their combined functionality. We investigated van der Waals heterostructures assembled from atomically thin layers of graphene and hexagonal boron nitride (Hbn). We observed a rich variety of optical effects due to surface plasmons in graphene and hyperbolic phonon polaritons in Hbn. We launched, detected and imaged plasmonic, phonon polaritonic and hybrid plasmon-phonon polariton waves in a setting of an antenna based nano-infrared apparatus. Peculiar properties of hyperbolic phonon polaritons in Hbn enabled sub-diffractional focusing in infrared frequencies. Because electronic, plasmonic and phonon polaritonic properties in van der Waals heterstructures are intertwined, gate voltage and/or details of layer assembly enable efficient control of nano-photonic effects. I will also discuss an ability to manipulate plasmonic response of in these structures at femto second time scales that we have demonstrated using a novel technique of pump-probe nano-infrared spectroscopy.

4:20pm NS+AS+SP-MoA7 Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy and Fluorescence of a Self-Assembled Porphyrin Monolayer, *Naihao Chiang**, *N. Jiang*, Northwestern University, *D. Chulhai*, Pennsylvania State University, *E. Pozzi, M.C. Hersam*, Northwestern University, *L. Jensen*, Pennsylvania State University, *T. Seideman, R.P. Van Duyne*, Northwestern University

The study of ultrahigh vacuum tip-enhanced Raman and fluorescence spectroscopy (UHV-TERS/TEF) has been raised to an unprecedented level. UHV-TER and TEF spectra for a self-assembled meso-tetrakis-(3,5-di-tertiarybutylphenyl)-porphyrin (H_2TBPP) on Ag(111) have been observed with five different laser excitations in the Q-band region. The observed TERS spectra are complemented by the time-dependent density functional theory (TDDFT) simulations. Chemical information of different vibronic excited states is revealed. The observed TEF spectra suggest a weak coupling of H_2TBPP to the surface due to the t-butyl groups. Therefore, the strong tip-enhancement is sufficient to overcome the quenching effect of the metal substrate. This study demonstrates the potential of combining TERS and TEF for studying surface-mounted porphyrins, thus setting the stage for future investigation into porphyrin-based photovoltaics and photocatalysis.

4:40pm NS+AS+SP-MoA8 Nano-Optical Spectroscopic Imaging of Monolayer MoS₂, *Wei Bao‡*, UC Berkeley, *N. Borys*, Lawrence Berkeley National Lab, *C. Ko, J. Suh, W. Fan*, UC Berkeley, *A. Thron*, Lawrence Berkeley National Lab, *Y. Zhang, A. Buyanin*, UC Berkeley, *J. Zhang, S. Cabrini, P. Ashby, A. Weber-Bargioni*, Lawrence Berkeley National Lab, *S. Tongay*, Arizona State University, *S. Aloni, D. Ogletree*, Lawrence Berkeley National Lab, *J. Wu*, UC Berkeley, *M.B. Salmeron*, Lawrence Berkeley Lab, UC Berkeley, *P. Schuck*, Lawrence Berkeley National Lab

With their remarkable electrical and optical properties, two dimensional (2D) monolayer transition metal dichalcogenide (ML-TMDC) semiconductors are ideal building blocks for atomically thin, flexible optoelectronic devices. Yet their performance falls far below theoretical expectations, particularly for critical factors such as carrier mobility and quantum yield. Overcoming these problems requires a fundamental understanding of the optoelectronic properties of these materials at the nanoscale, which is best obtained with optical microscopy and spectroscopy tools with spatial resolution below the diffraction limit. Here, we use the recently-developed "Campanile" nano-optical probe[1] to spectroscopically image for the first time key optoelectronic properties in ML-MoS₂ with deeply sub-wavelength resolution – i.e., at a resolution commensurate with characteristic distances such as the exciton diffusion length. We find that synthetic ML-MoS₂ is composed of two distinct optoelectronic regions: a locally-ordered but mesoscopically heterogeneous interior, where photoluminescence (PL) intensity correlates with the local ratio of the exciton and trion populations, and an unexpected edge region ~300 nm wide of energetically disordered states. In addition, we directly visualize the spatially-varying optical properties of inter- and intra- flake grain boundaries and quantify the characteristic length over which they quench excitons. Complimentary Nano-Auger elemental analysis reveals that the optically "defective" grain boundary and edge regions are sulfur-deficient. The nanoscale structure-property relationships established here have broad implications for the development of atomically thin transistors, quantum optical components, photodetectors and light-emitting devices based on high-quality ML-TMDCs.

1 Bao, W. Mapping local charge recombination heterogeneity by multidimensional nanospectroscopic imaging. , 1317-1321 (2012).

5:00pm NS+AS+SP-MoA9 Hybrid Peak-force Tapping/near-field s-SNOM Microscope for Nano-chemical and Nano-mechanical Imaging of Proteins and Other Nanoscale Systems, *Martin Wagner*, Bruker Nano Surfaces, *K. Carneiro, S. Habelitz*, University of California, *T. Mueller*, Bruker Nano Surfaces

Infrared spectroscopy can give valuable information on chemical composition, but far-field techniques such as FTIR spectroscopy are limited in spatial resolution. S-SNOM is a well-established near-field technique [1] that can overcome this diffraction limit, allowing an improvement in spatial resolution down to 10 nm.

Our s-SNOM instrument is based on an atomic force microscope whose tip is illuminated with a quantum cascade laser. Field-resolved detection of the scattered light measures absorption [2]. We have combined the instrument with peak-force tapping, a technique that allows Pn-level force control between tip and sample. Besides being able to image fragile material systems, one can extract valuable nano-mechanical information such as adhesion or modulus with molecular resolution [3].

Here, amongst other brief examples, we study an amelogenin sample. Amelogenin is a protein that is critical to dental enamel formation [4,5]. In the presence of calcium and phosphate ions it self-assembles into ordered, self-aligned nanoribbon bundles. Since the ordering is similar to the one observed in phosphate-based apatite crystals that comprise dental enamel, it is likely that the bundles form a template for these crystals. To help clarify that open question, we map the distributions of phosphate and hydroxyapatite nanocrystals within the bundles consisting of <30 nm narrow nanoribbons that have only a height of a few nm down to 1nm.

We present correlated topography, near-field and nano-mechanical data. While the presence of phosphate could be identified using s-SNOM absorption maps, no apatite nanocrystals with higher modulus than the ribbons were observed in peak-force tapping. This indicates that for these in vitro preparation conditions apatite crystals have not formed yet, but also highlights the high chemical sensitivity of the instrument.

In summary, using a novel combination of near-field imaging and peak-force tapping we study the phosphate distribution and crystallization in protein samples. Our findings help to understand the formation processes of dental enamel and the role of amelogenin protein.

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[2] X. Xu, A. Tanur, G. Walker, J. Phys. Chem. A 117, 3348 (2013)

[3] F. Rico, C. Su, S. Scheuring, Nano Lett. 11, 3983 (2011)

[4] O. Martinez-Avila et al., Biomacromolecules 13, 3494 (2012)

[5] B. Sanii et al., J Dent Res 93 (9), 918 (2014)

Thin Film
Room: 111 - Session TF+2D+MG+NS-MoA

ALD, CVD, MLD, and PLD on Special Materials
Moderator: Giovanna Scarel, James Madison University, Mark Davidson, University of Florida

2:20pm TF+2D+MG+NS-MoA1 Optical Enhancement of Polyethylene Teraphthalate Films Modified by Organometallic Vapor Infiltration, *Halil Akyildiz*, North Carolina State University, *J.G. Simmons*, Redstone Arsenal, *H.O. Everitt*, Duke University, *J.S. Jur*, North Carolina State University

Polyethylene terephthalate is recyclable thermoplastic polymer that has wide application area including packaging, textiles and insulation applications. Due to the ring structures on the backbone of the polymer it shows weak luminescence in the blue spectrum upon UV light absorption by pi electrons. It has previously been shown that vapors of organometallic ALD precursors are able to infiltrate and react with the polymer to form organic inorganic hybrid materials. Infiltration of trimethylaluminum into PET to form polymer-alumina coordination complexes enhanced the photoluminescence and internal quantum efficiency of the material. In this study we present how the polymer morphology (i.e. crystallinity) and the infiltration temperature are able to affect the optical properties of the resulting PET films. Four unique emission bands are observed in pristine PET films; (2) stronger emissions in high crystallinity films attributed to the crystalline regions of the polymer and (2) peaks that show stronger emission in low crystallinity films attributed to the amorphous regions. After the low temperature infiltration (60 °C) emissions attributed to the amorphous regions demonstrate increases intensity, indicating that the infiltration reaction is predominant in the amorphous regions of the polymer. After infiltration at 150 °C, a very high red shift is observed alongside a complete emission spectra changes, suggesting the reactions taking place at high temperatures are different than low temperature processing. This detailed understanding of the photoluminescence behavior of the hybrid films can provide insight for use of these hybrid materials with a bandgap ideal for unique optical applications.

2:40pm TF+2D+MG+NS-MoA2 Organic and Hybrid Organic-Inorganic Thin Film Deposition by Resonant Infrared, Matrix-Assisted Pulsed Laser Evaporation, *Adrienne Stiff-Roberts*, Duke University
INVITED

Over the past fifteen years, matrix-assisted pulsed laser evaporation (MAPLE) has been developed to deposit organic thin films[1-6], inorganic nanoparticles, and hybrid organic-inorganic nanocomposites[4, 7-9]. One variation of the MAPLE technique, resonant infrared matrix-assisted pulsed laser evaporation (RIR-MAPLE), reduces the laser energy (e.g., Er:YAG laser ~2.94μm peak wavelength) in order to minimize polymer degradation. In addition, because the frequency of the IR laser energy is resonant with OH bond vibrational modes in water, a frozen emulsion (comprising a mixture of the guest material dissolved in an organic solvent and water) is used as the target. Therefore, the unique advantage of emulsion-based RIR-

MAPLE is that most of the energy from the IR laser is absorbed by water in the frozen emulsion, which evaporates and gently transfers the guest material to the substrate with minimal solvent exposure and degradation.

In the case of hybrid organic-inorganic nanocomposites, inorganic nanoparticles are embedded in a polymer matrix to achieve specific materials properties or functionality; however, nanoparticles that are mixed with a polymer in solution tend to aggregate due to a polarity difference with polymers[10]. In contrast, RIR-MAPLE is fundamentally different from solution processing and reduces nanoparticle phase segregation by eliminating the need to co-dissolve nanoparticles and polymers into a single common solvent; and by depositing the nanoparticles and polymers in a relatively dry state.

We will demonstrate the capability of RIR-MAPLE to deposit continuous nanoparticle films with the same optical properties as nanoparticles in solution and to minimize nanoparticle phase segregation in hybrid films. We will also demonstrate hybrid organic-inorganic thin films deposited by RIR-MAPLE for application to solar cells. This work is supported in part by ONR.

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3:40pm TF+2D+MG+NS-MoA5 Integrating Ultrathin ALD/ALE Films with 1D and 2D Materials to Enable New Device Structures, *Virginia Wheeler*, *N. Nepal*, U.S. Naval Research Laboratory, *A. Nath*, George Mason University, *A.D. Koehler, Z.R. Robinson, J.K. Hite, K.M. Daniels, M.A. Mastro*, U.S. Naval Research Laboratory, *E. Self, P. Pintauro*, Vanderbilt University, *J.D. Caldwell, R.L. Myers-Ward, D.K. Gaskill, C.R. Eddy Jr.*, U.S. Naval Research Laboratory   **INVITED**
As device features continue to approach nanoscale dimensions, requisite structures continually grow in complexity often resulting in 3D architectures, nanowires, and/or 2D van der Waals materials. This reduction in size leads to new phenomena, such as quantum confinement effects in electronics or strong localization of light in nanophotonics, which can potentially enable new devices. Realization of novel device structures that exploit these effects requires integration of scalable thin films of various electronic materials onto nanostructures. Atomic layer deposition (ALD) is the preferred method to conformally coat nominally planar as well as complex, high surface area nanostructures with abrupt interfaces, wafer-scale uniformity, and angstrom-scale control of thickness. Additionally, ALD is a low temperature process which allows incorporation with many temperature sensitive nanostructure materials that are not compatible with other deposition techniques. Alternatively, a slightly higher deposition temperature can facilitate atomic layer epitaxy (ALE) of crystalline thin films with all the same beneficial characteristics of ALD. However, the inert nature of 1D and 2D materials often inhibit direct application of ALD/ALE films with desired coverage and uniformity. In this work, we will discuss crucial aspects of ALD/ALE growth, such as surface functionalization and *in situ* nucleation sequences, required to obtain uniform, conformal films on nanostructured substrates.

The essential requirements for integration of ALD/ALE layers with 1D and 2D materials will be evaluated through several case studies including: 1) integration of III-N films on graphene for a hot-electron transistor; 2) coating of carbon fibers for battery and electrode applications; and 3) functional oxide layers on SiC nanopillars to modify their optical response for several potential devices. The substrates in these cases have varying degrees of surface reactivity, so we will address the need for and our current *ex situ* and *in situ* approaches to obtaining sufficient reactivity between the substrate and ALD precursors. Moreover, it was found that ALD parameters (temperature, pulse and purge durations, etc.) impact the effectiveness of uniform, conformal coating of these structures. Other factors, such as sample suspension, are sometime critical to overcoming these limitations while still operating in ALD/ALE windows. Initial devices results will be presented, when appropriate, to demonstrate the feasibility of the integration of ALD thin films in new device structures.

4:20pm TF+2D+MG+NS-MoA7 Development of the Optical Properties of Silicon Rich Oxide Films Growth by CVD Techniques for Possible Photovoltaic Applications, *Karim Monfil-Leyva*, Benemérita Universidad Autónoma de Puebla, Mexico, *A.L. Muñoz-Zurita*, Universidad Politécnica Metropolitana de Puebla, Mexico, *E. Ojeda-Durán, A. Benítez, J. Carrillo-López, J.A. Luna-López, R.C. Ambrosio-Lázaro*, Benemérita Universidad Autónoma de Puebla, Mexico
Currently, electronics and semiconductor studies have focused a great effort to overcome the intrinsic disadvantages of bulk-Si to develop optoelectronic devices. In particular, the Silicon Rich Oxide (SRO) has been proposed as a cheap and effective alternative to develop ultraviolet absorbers or silicon-based light emitters. SRO can be deposited by several chemical vapor deposition techniques like Low Pressure Chemical Vapor Deposition (LPCVD) or Hot Filament Chemical Vapor Deposition (HFCVD). Silicon excess in SRO films obtained by LPCVD can be controlled by pressure ratio Ro = N_2O/SiH_4. Meanwhile, silicon excess in SRO films obtained by HFCVD can be controlled by changing the hydrogen flow (H_F).

In this work, we report a study of the optical and structural properties of thin SRO films obtained by LPCVD and HFCVD. Silicon excess was changed by the pressure ratio Ro in the range of 15 and 45 (SRO15 to SRO45) and H_F was changed between 25 and 75 sccm. SRO LPCVD films were annealed at 1100 ºC. Ellipsometry and step measurements were applied to calculate thickness and the refractive index. Fourier transform infrared (FTIR) measurements were obtained from SRO films to confirm a change on stoichiometry. Absorbance spectra of SRO films showed rocking and bending vibration modes similar to stoichiometric silicon dioxide but an asymmetric stretching mode revealed the non-stoichiometric nature of our semiconductor films. SRO films by LPCVD showed a strong photoluminescence (PL) at room temperature (RT) on two bands, a blue band from 400 to 550 nm or a red band from 575 nm to 875 nm depending on Ro. Blue and red emission bands were related to donor acceptor decays between traps promoted by defects. SRO films by HFCVD also showed a red band from 500 to 1100 nm (depending on the H_F) and this emission was attributed to defects produced by the transport of the precursors. SRO films showed suitable optical properties for possible photovoltaic applications.

5:00pm TF+2D+MG+NS-MoA9 Radical-Enhanced Atomic Layer Deposition Enabled Multiferroic Composite Synthesis, *C. Pham, Jeffrey Chang, J.P. Chang*, University of California at Los Angeles
Multiferroic materials, which exhibit controllable magnetic (ferroelectric) behavior via electric (magnetic) field, are of great interest due to their wide spectrum of new device applications such as non-volatile memory devices. Unfortunately, such behavior is extremely rare in natural single-phase systems. Furthermore, the properties of the few single phase multiferroic materials are too insignificant to be integrated into current device designs. Therefore, alternative strategies involving composite materials are proposed to combine the ferroelectricity and magnetism of different materials, achieving multiferroic behavior. By utilizing piezoelectric and magnetostrictive effects in different material phases, a strain-mediated approach shows great promise for applications. In such a strategy, the interface area per volume, as well as the material crystallinity of each constituent, will greatly influence composite properties. The conformal and high quality film growth with atomic layer deposition (ALD) shows great potential for enabling the multiferroic composites described above.

In this work, lead-free ferroelectric/antiferromagnetic $BiFeO_3$ (BFO) and ferrimagnetic $CoFe_2O_4$ (CFO) thin films were grown on $SrTiO_3$ (001) (STO) substrate by radical enhanced ALD (REALD) using metalorganic precursors, $Bi(tmhd)_3$ (tmhd = 2,2,6,6-tetramethylheptane-3,5 dione), $Co(tmhd)_2$, and $Fe(tmhd)_3$. The use of oxygen radicals as an ALD oxidant provides extra process flexibility. Film crystallinities and properties were studied under different conditions. The BFO films showed epitaxial single crystalline growth in a (001) pseudocubic orientation after annealed at 650 °C while the CFO films are polycrystalline due to the lattice mismatch between the film and substrate (~ 1% for BFO and ~7% for CFO). The piezoelectric properties of BFO films were confirmed using PFM while weak ferromagnetic behavior was also observed. Tunable CFO magnetic properties were shown using thickness-related strain relaxation over the range of 5~90 nm.

Synthesis of multiferroic composites was enabled by REALD. When fixing the total thickness at 40nm, 2-2 BFO/CFO nanolaminate composites with an increasing number of sub-layers showed a controllable competition between magnetic and shape anisotropy. 0-3 CFO/PZT composites were enabled by growing conformal CFO ALD films onto mesoporous PZT medium. SEM confirmed the gradual and conformal coating with increasing ALD cycles. It was found that the pore necks limit the incorporation of CFO inside the mesoporous media as it blocks precursor penetration. The volumetric magnetic properties were found to exceed the values found in literature with 0-3 configurations.

5:20pm TF+2D+MG+NS-MoA10 Plasma Enhanced Deposition of Nanocrystalline Silicon Thin Films from SiF4 by RF-PECVD and MDECR: Key Aspects of Growth Dynamics, *JK. Wang, P. Bulkin, I. Florea, J.L. Maurice,* **Erik Johnson**, LPICM-CNRS, Ecole Polytechnique, France

For the growth of thin-film hydrogenated silicon by low temperature plasma-enhanced chemical vapor deposition (PECVD), SiF_4 has recently attracted interest as a precursor for numerous reasons, most importantly due the resilient optoelectronic performance of the resulting layers and devices, even when grown in a slightly oxygen-contaminated growth environment. Nevertheless, many questions remain concerning the critical factors determining the quality of hydrogenated microcrystalline silicon (μc-Si:H) thin films grown from this precursor.

To advance knowledge on this subject, we present studies performed on two very different types of PECVD reactor: a standard capacitively coupled RF-PECVD reactor, using a process gas mixture consisting of Ar/SiF4/H2 and at deposition rates up to 4A/s, and a matrix-distributed electron cyclotron resonance (MDECR) PECVD reactor operating at much lower pressures but achieving a higher deposition rate (8 A/s) and using simply an SiF_4/H_2 mixture. In doing so, we reveal key details concerning the growth process. We underline recently obtained results concerning three critical experimental findings about the use of SiF4 as a growth precursor: (1) the importance of temperature for high-deposition rate, low-pressure conditions, (2) the vital role of ion bombardment energy on the quality of growth, and (3) the vastly increased challenge of the nucleation process when using high-density plasma processes. The films generated in these studies have furthermore been studied by cross sectional HR-TEM, revealing more specific details about the changing nature of the films during growth, and the dependence of these dynamics on the maximum ion energy impinging on the surface. These studies - along with residual gas analysis studies and optical emission spectroscopy results – allow us to examine the precise growth mechanism of such films when using an SiF_4/H_2 mixture.

Tuesday Morning, October 20, 2015

2D Materials Focus Topic
Room: 212C - Session 2D+EM+NS+SS+TF-TuM

Optical and Optoelectronic Properties of 2D Materials
Moderator: Andrea Young, University of California at Santa Barbara

8:00am 2D+EM+NS+SS+TF-TuM1 The Tri-Angular Lattice Exciton (3ALE) Model: Exciton Physics at the Atomic Scale, *F. Tseng,* NRC Research Associate, *E. Simsek,* George Washington University, *Daniel Gunlycke*, Naval Research Laboratory

Descriptions of excitons in pristine semiconducting crystals usually rely on the hydrogen model adopted for excitons. Owing to the weak screening in monolayer transition-metal dichalcogenides, however, the electron and hole separation in the strongest bound excitons is on the atomic scale, necessitating atomistic treatment. In this presentation, we present a minimalistic exciton model that accounts for the lattice and the spin-orbit and exchange interactions, thus making this model appropriate across the spectrum from Wannier to Frenkel excitons. Using this model, we show that the exciton lifetimes could be extended by transitioning the excitons into excitonic dark states. Longer exciton lifetimes could make these materials candidates for applications in energy management and quantum information processing.

This work has been funded by the Office of Naval Research (ONR), directly and through the Naval Research Laboratory (NRL). E.S. and F.T. acknowledge support from NRL through the ONR Summer Faculty Program and the NRC Research Associateship Program, respectively.

8:20am 2D+EM+NS+SS+TF-TuM2 Opposite Dependence of Microwave-Induced vs. Field-Induced Imaging Contrast in NV⁻ based Fluorescence Microscopy as Function of Optical Excitation, *Etienne Goovaerts, S.K.R. Singam,* University of Antwerp, Belgium, *M. Nesladek,* Hasselt University, Belgium, *M. Giugliano*, University of Antwerp, Belgium

The charged nitrogen-vacancy (NV⁻) center is a remarkable defect in diamond which allows interrogation of spin state through its fluorescence. Among the proposed applications, background-free imaging based on fluorescent nanodiamond (FND) was demonstrated [1-3]. The FNDs emission can be discriminated from spurious fluorescence by switching on resonant microwaves (MW) and/or a static magnetic field [1-3], as demonstrated in cells [1] and potentially in small animals [2]. It is now important to understand the origin of the contrast in either of these approaches, and the optimal experimental parameters.

NV⁻ defects in single-crystal diamond as well as in FNDs were excited by a 532nm laser through the microscope objective. A compact spectrometer combined with appropriate filters allowed to measure the NV⁻ and NV⁰ emission. MW-induced contrast is achieved using a broadband circular antenna (i.d. 1mm) on a printed plate, and for field-induced contrast we use a small-sized permanent magnet (~300mT). They are placed closely behind the sample with in each case the magnetic field component along the optical axis of the objective.

For shallow implanted NV in (100) diamond as well as for FNDs the fluorescence is quenched by application of either resonant MWs or static field, with contrast levels systematically higher in the single crystal case than for deposited nanoparticles. The contrast values were measured for laser powers covering 6 orders of magnitude. After an initial rise at very low excitation (max. 13% in crystal, 7% in FND), the MW-induced contrast significantly decreases at higher laser powers. In parallel, field-induced contrast increases from about 12% to values of 38% and 20% for the single crystal and FNDs. This is described under steady state conditions using a 5-level model that includes radiative and nonradiative decay and ground state spin relaxation. The MW-contrast results from induced spin transitions in the triplet ground state while the field effect relies on state mixing within the ground and the excited triplets which change the decay rates. The analysis also shows that the applied excitation rates runs through 3 regimes from below the spontaneous relaxation rate, via an intermediate regime, to above the decay rate of the intermediate singlet.

This work demonstrates the advantages of field-induced contrast microscopy over the MW-induced approach. These become particularly important at high excitation rates which are more often applied in confocal microscopy.

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8:40am 2D+EM+NS+SS+TF-TuM3 2D Materials and Heterostructures for Applications in Optoelectronics, *Thomas Mueller*, Vienna University of Technology, Austria **INVITED**

Two-dimensional (2D) atomic crystals are currently receiving a lot of attention for applications in (opto-)electronics. In this talk I will review our research activities on photovoltaic energy conversion and photodetection in 2D semiconductors. In particular, I will present monolayer p-n junctions, formed by electrostatic doping using a pair of split gate electrodes, and MoS2/WSe2 van der Waals type-II heterojunctions. Upon optical illumination, conversion of light into electrical energy occurs in both types of devices. I will present measurements of the electrical characteristics, the photovoltaic properties, and the gate voltage dependence of the photoresponse. In the second part of my talk, I will discuss photoconductivity studies of MoS2 field-effect transistors. We identify photovoltaic and photoconductive effects, which both show strong photoconductive gain. We envision that the efficient photon conversion, combined with the advantages of 2D semiconductors, such as flexibility, high mechanical stability and low costs of production, could lead to new optoelectronic technologies.

9:20am 2D+EM+NS+SS+TF-TuM5 Excitations and Ultrafast Charge Response in Bilayer Transition-Metal Dichalcogenides, *Volodymyr Turkowski, T.S. Rahman*, University of Central Florida

We analyze the absorption spectrum and ultrafast charge dynamics in bilayer 2L-MoS2 , 2L- MoSe2 and MoS2-WS2 systems by using time-dependent density functional theory in the density-matrix representation. In particular, we calculate the values of the binding energies of excitons in these structures for both intra- and inter-layer electron-hole excitations and demonstrate that, similar to the case of a single layer, these energies can be as large as hundred(s) of meVs. We also analyze the ultrafast dynamics of the electrons, holes and excitons in the photoexcited bilayers. We pay special attention to the ultrafast hole transfer in these systems and find transfer times of the order 100fs, in agreement with the experimental finding for the MoS2-WS2 system. We perform a detailed *ab initio* study of the spatially- and time-resolved charge density in the systems during the hole transfer and conclude that sulfur and selenium orbitals play an important role in the process. Finally, we discuss possible applications of the results in light harvesting technologies.

Work supported in part by DOE Grant No. DOE-DE-FG02-07ER46354

9:40am 2D+EM+NS+SS+TF-TuM6 Automatic Localization and Identification of 2D-Material Flakes by Spectroscopic Imaging Ellipsometry, *Sebastian Funke, P.H. Thiesen,* Accurion GmbH, Germany, *G. Greg Hearn*, Accurion Inc.

With the rising of 2D materials in surface sciences, the localization of mono- to few-layers of 2D materials, such as graphene, Molybdenum disulfide, hexagonal boron nitride is a time consumptive task. With the help of imaging spectroscopy ellipsometry flakes of 2D materials can be found and its layer numbers can be differentiated.

Therefore a spectroscopical mapping of the sample is done. At selected wavelengths nulling ellipsometry for each pixel in the field of view is done to measure Δ/Ψ. The measurement of all pixels is done simultaneously. To cover larger areas than the field of view a XY-patterning is done automatically. For each XY-position spectroscopic Δ/Ψ maps are obtained. Every pixel of a Δ/Ψ map represents the spectroscopic angle Δ/Ψ respectively. By comparing the spectral Δ/Ψ values for each pixel with the ellipsometric model of e.g. graphene monolayer, flakes of graphene monolayers on the sample can be found. To ensure, that only flakes are found, a grid with a threshold is used. The threshold indicates the number of pixels in the grid that need to fit to the model.

In the talk we present the capability of imaging ellipsometry to localize and identify monolayer to few-layers of 2D Materials. Flakes of MoS₂ with a size smaller than 10 μm can be localized. Monolayer of graphene can be distinguished from bilayers of graphene. To improve the time factor, the use of a Scheimpflug corrected objective is presented. Further investigations on different 2D materials, e.g. h-BN and the implementation of a Raman System is in progress.

11:00am 2D+EM+NS+SS+TF-TuM10 Systematic Hydrogen Intercalation of Epitaxial Graphene for THz Plasmonics, *Kevin Daniels*, National Research Council postdoc working at NRL, *A. Boyd*, American Society for Engineering Education postdoc working at NRL, *R.L. Myers-Ward, D.K. Gaskill*, Naval Research Laboratory

Epitaxial growth of graphene via sublimation of silicon and graphitization of carbon atoms from silicon carbide (SiC) is ideal for large scale manufacturing of plasmonic devices but due to partially covalent bonding between the SiC (0001) substrate and the first carbon layer ($6\sqrt{3}$ buffer layer), the high room temperature mobility necessary for THz plasmonics is reduced significantly compared to exfoliated graphene. The objective of this work is to improve THz response of EG by increasing the mobility and carrier concentration of graphene through hydrogen intercalation where the Si atoms covalently bound to the buffer layer are satisfied by hydrogen atoms and create quasi free standing graphene.

Epitaxial graphene was grown from 6H-SiC (0001) in an Aixtron/Epigress VP508 horizontal hot-wall reactor, etching in H_2 during temperature ramp to 1570°C and growing graphene in Ar ambient at 1580°C. H-intercalation of EG was carried out in the same reactor at 1050°C with a flow of 80slm of H_2 and chamber pressure of 900mbar for 15-75 minutes. Morphology of the quasi-free standing graphene was observed by AFM and SEM. Raman spectroscopy using a 532nm laser (9.6mW) and spot size of 0.3μm were used to take 80x10μm maps of each sample where release of the buffer layer is observed, with broadening of the 2D peak full-width-half-max (FWHM) before and after H-intercalation is observed on the graphene terraces and step edges. Number of monolayers before and after H-intercalation was determined by XPS.

From SEM, AFM, Raman and Hall we observe changes in degree of hydrogen intercalation with respect to time. Large areas of partially intercalated EG is observed at 15 minutes which confirmed by a mix of charge carriers and reduced carrier mobility at ~250cm^2/Vs. At 30 minutes some graphene terraces remain coupled to the SiC substrate with carrier mobility ~2250cm^2/Vs. From 45, 60 and 75 minutes the buffer layer becomes mostly quasi free standing with small spots possibly coupled to the substrate as observed in the SEM with mobilities of ~3900, ~4000 and ~3700cm^2/Vs respectively. Measurements of the resulting THz transmission spectra are currently underway to determine if the increase in mobility and carrier concentration results in narrower THz response.

11:20am 2D+EM+NS+SS+TF-TuM11 Determining the Optical Properties of Exfoliated 2D Molybdenum Disulfide on Various Substrates with Imaging Spectroscopic Ellipsometry, *Peter H. Thiesen*, Accurion GmbH, Germany, *S. Funke*, HAWK, Germany, *B. Miller, E. Parzinger*, TU München, Germany, *G. Hearn*, Accurion Inc., *A.W. Holleitner, U. Wurstbauer*, TU München, Germany

Ellipsometry is a non-destructive optical method for determining film thickness and optical properties. It measures the change in the state of polarization of the light reflected from the film interfaces. Imaging ellipsometry, which combines the power of ellipsometry with microscopy, has overcome the limitation of poor sample lateral resolution found in conventional non-imaging ellipsometers. The enhanced spatial resolution of imaging ellipsometers potentially expands ellipsometry into new areas of microanalysis, microelectronics, and bio analytics.

Molybdenum disulfide is a layered transition metal dichalcogenide. From the point of current research, 2D-nano materials based on MoS_2 are very promising because of the special semiconducting properties. The bulk material has an indirect 1.2 eV electronic bandgap, but single layer MoS_2 has a direct 1.8 eV bandgap. The monolayer can be used in prospective electronic devices like transistors (MOSFETs) or photo detectors.

Wavelength spectra of ellipsometric parameters Delta and Psi of the MoS_2 monolayers and multilayers were recorded as well as microscopic maps. In case of Sapphire, The psi maps at wavelength of higher energies than the bandgap show a clear contrast between the monolayer and the substrate and at lower energies there is no contrast between the monolayer and the substrate, but the multilayer areas still show a clear contrast-making the unique properties of MoS_2 monolayers directly visible. The advantage of imaging ellipsometry is the visualisation of the shape of the monolayer and the opportunity to classify the homogenity of the optical properties of the microcrystallite. To quantify the optical properties, different approaches of optical modelling will be discussed.

11:40am 2D+EM+NS+SS+TF-TuM12 Nonlinear Optical Spectroscopy of 2D Semiconductor Monolayers, *Xiaobo Yin*, University of Colorado Boulder **INVITED**

Transition metal dichalcogenide (TMDC) monolayers have recently emerged as an important class of two-dimensional semiconductors with potential for electronic and optoelectronic devices. Unlike semi-metallic graphene, layered TMDCs have a sizeable bandgap. More interestingly, when thinned down to a monolayer, TMDCs transform from indirect-bandgap to direct-bandgap semiconductors, exhibiting a number of intriguing optical phenomena such as valley-selective circular dichroism, doping-dependent charged excitons and strong photocurrent responses. Using nonlinear optical spectroscopy, we probe experimentally the evidence of a series of excitonic dark states as well as structural symmetry in single-layer WS2 and MoS2.

Applied Surface Science
Room: 212D - Session AS+NS-TuM

Chemical/Molecular Information from Sub-micron Features and Materials

Moderator: Carl Ventrice, Jr., SUNY Polytechnic Institute, David Carr, Physical Electronics USA

8:40am AS+NS-TuM3 ASSD 30th Anniversary Speaker: Defect Detection and Characterization in Wafer Processing and Magnetic Storage Technologies – Then, Now and (maybe) the Future., *Christopher Brundle*, C R Brundle and Asociates **INVITED**

Some 30 years ago defects ("particles") in wafer processing were unacceptable for sizes in the um range. Today the specification is 23nm and will soon be 19nm. These numbers are, of course, directly related to the ever decreasing dimensions of semiconductor devices. This paper gives a historical overview of the evolution of the techniques used in defect detection and characterization for both Development and Manufacturing over this period, and what might be needed in the future.

In Magnetic Storage key dimensions have decreased at a similar pace and similar defect and quality control issues obtain. Some of these will also be discussed, if there is time.

Examples are presented where possible, but there is an understandable difficulty in obtaining release for real examples of defects concerning current forefront technology!

9:20am AS+NS-TuM5 Characterisation of Glass-To-Metal Interfaces using FIB and STEM, *Paul Yates*, University of Surrey, UK

Components needing electrical feed through seals are frequently made with glass-to-metal seals and have been for many years. They are often made with stainless steel and silicate glasses but, in order to save weight or for biomedical uses, titanium components are sometimes required. Silicate free glasses are required due to the deleterious reaction that occur between titanium and silicate glasses. The reactions in these systems are not fully understood. When characterising the interfaces and assessing interface quality the standard approach is to use cross sections and characterise with scanning electron microscopy and energy-dispersive x-ray spectroscopy. Although this can reveal micrometer scale processes it can not reveal the nano scale reactions that determine the bonding across the interface in many cases. In this work focussed ion beam milling and scanning transmission electron microscopy are used to attain nano scale information about selected areas of the interface between titanium and a strontium boroaluminate glass-ceramic. Additionally, reactions between the glass-ceramic and Kovar (Fe-29Ni-17Co), a common glass sealing alloy, are characterised. Oxidation of the Kovar surface creates an oxide, characterised with x-ray photoelectron spectroscopy and x-ray diffraction, that improves bonding across the interface compared to the native oxide.

9:40am AS+NS-TuM6 X-ray Structural Analysis of Self-assembled Nano-Dielectrics, *Li Zeng, A. Walker*, Northwestern University, *R. Turrisi*, University of Milano-Bicocca, Italy, *M.C. Hersam, T.J. Marks, M.J. Bedzyk*, Northwestern University

Organic thin-film transistors (OTFTs) are viewed as the new generation thin-film transistors (TFT) for future low-cost, printable, structural flexible electronics, and related processable solution-based organic and inorganic semiconductors. However, one major limitation of OTFTs is that the organics semiconductors exhibit relatively low carrier mobility, which requires high operating voltage in order to achieve an operational drain current. One route to reduce the operation voltage is to increase the capacitance of the dielectric layer as the drain current increases linearly with respect to the dielectric capacitance for constant operating voltages and channel dimensions. A class of materials called self-assembled nano-dielectrics (SAND) with phosphoric acid-functionalized organic precursors sandwiched between ultrathin layers of high-k inorganic oxide materials has been synthesized and applied in the TFT field. These materials show exceptionally large capacitance, excellent insulating properties, and are also

suitable for ambient atmosphere fabrication. The hybrid nature of these materials utilizing the distinct properties of both the organic and inorganic components can be incorporated into the low-operating voltage semiconductor-based OTFTs to enhance the performance.

Despite the impressive performance and flexibility of SANDs, some fundamental aspects of dielectric behavior remain unexplored. Particularly, the behavior of the Br^- counteranions that are paired with the phosphonic acid-based -electron (PAE) cationic building blocks are poorly understood. It is believed that the location, distribution of the Br^- counteranions, as well as their response to applied AC and DC electric fields, are critical to the behavior of the dielectric in device-like environments. Therefore, long-period X-ray Standing Wave (LP-XSW), which is a powerful technique sensitive to heavy atom distributions, was used to characterize a three-layer SAND structure deposited on synthetic Si/Mo multilayer substrates. The elemental distributions of Br and reference elements were extracted from the analysis of XSW data. These accurate measurements are important for better understanding counteranion distributions, charge transport, dipole-semiconductor interactions, and future device modeling and engineering.

11:00am AS+NS-TuM10 Multimodal Imaging for Physical and Chemical Surface Characterization using a Combined Atomic Force Microscopy-Mass Spectrometry Platform, *Olga Ovchinnikova*, Oak Ridge National Laboratory **INVITED**
The functionality of materials is largely determined by the mechanisms that take place at sub-micron length scales and at interfaces. In order to understand these complex material systems and further improve them, it is necessary to measure and map variations in properties and functionality at the relevant physical, chemical, and temporal length scales. The goal of multimodal imaging is to transcend the existing analytical capabilities for nanometer scale spatially resolved material characterization at interfaces through a unique merger of advanced scanning probe microscopy, mass spectrometry and optical spectroscopy. Combining atomic force microscopy (AFM) and mass spectrometry (MS) onto one platform has been demonstrated by our group as a method for high resolution spot sampling and imaging of substrates. To advance this basic approach and to expand its capabilities we now have incorporated Band-Excitation (BE) to allow us to measure nanomechanical properties of a sample by measuring the contact resonance frequency shift. In this presentation, I will discuss the benefits of a multimodal imaging system and demonstrate our results for polymeric systems, biological plant and animal tissue, and bacterial colonies. I will also talk about future developments to incorporate spectroscopic measurements into the platform.

This work was supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, United States Department of Energy. ORNL is managed by UT-Battelle, LLC for the U.S. Department of Energy under contract DE-AC05-00OR22725.

11:40am AS+NS-TuM12 Understanding the TERS Effect with On-line Tunneling and Force Feedback Using Multiprobe AFM/NSOM with Raman Integration, *A. Lewis,* The Hebrew University of Jerusalem and Nanonics Imaging Ltd, Israel, *Rimma Dekhter, P. Hamra, Y. Bar-David, H. Taha,* Nanonics Imaging Ltd, Jerusalem, Israel
Tip enhanced Raman scattering (TERS) has evolved in several directions over the past years. The data from this variety of methodologies has now accumulated to the point that there is a reasonable possibility of evolving an understanding of the underlying cause of the resulting effects that could be the origin of the various TERS enhancement processes.

The objective of this presentation is to use the results thus far with atomic force microscopy (AFM) probes with noble metal coating, etching, transparent gold nanoparticles with and without a second nanoparticle [Wang and Schultz, ANALYST 138, 3150 (2013)] and tunneling feedback probes [R. Zhang et. al., NATURE 4 9 8, 8 2 (2013)]. We attempt at understanding this complex of results with AFM/NSOM multiprobe techniques. Results indicate that TERS is dominated by complex quantum interactions. This produces a highly confined and broadband plasmon field with all k vectors for effective excitation. Normal force tuning fork feedback with exposed tip probes provides an excellent means to investigate these effects with TERS probes that we have shown can circumvent the vexing problem of jump to contact prevalent in conventional AFM methodology and permit on-line switching between tunneling and AFM feedback modes of operation.

12:00pm AS+NS-TuM13 High Resolution CREM for Electrical Characterization of Thin Oxide Layers, *Hagai Cohen*, A. Givon, Weizmann Institute of Science, Israel
The chemically resolved electrical measurements technique (CREM) has already been proven very useful in studies of nanometric layered structures. CREM exploits the chemical contrast across a studied system to probe the local, domain specific, electrostatic potential in a non-contact manner. As

such, its spatial resolution is usually determined by the studied structure itself, other than the probe size; a fact imposing severe limitations when nm, or even sub-nm, resolution is requested. In the present work we show that this inherent limitation can be overcome. Improved CREM resolution is established, with which a principal progress is demonstrated in the access to fine details of the electrical properties of nanometric SiO_2 layers grown on SiC substrates.

Nanometer-scale Science and Technology
Room: 212B - Session NS+SP-TuM

Nanoscale Imaging and Materials Characterization
Moderator: Mehmet Z. Baykara, Bilkent University

8:00am NS+SP-TuM1 Influence of Focused Electron Beam on Electrical Characterization of Advanced MOSFETs, *Jonghyuk Kang, S.H. Lee,* Samsung Electronics Co., LTD., South Korea, *B.D. Choi,* Sungkyunkwan University, Republic of Korea
The focused electron beam based inspection instruments such as Scanning Electron Microscope (SEM) have become widespread in the semiconductor manufacturing and failure analysis of scaled devices. Also, nano-probing systems with SEM guidance have become important in the failure analysis area to evaluate the localized device in the actual LSI [1] . However, electron beam leads to device degradation [2] and its damage are increasing with the scaling. As CMOS scaling is going to be sub-10nm regime [3], electron beam damages are becoming critical issue in performing electrical characterization at the contact level in integrated devices using nano-probe technique. To avoid the electron damage, the acceleration voltage should be lower. However, the lower acceleration voltage of electron beam leads to lower resolution of image created by SEM guidance.

In this work, we evaluated NMOS FinFET in SRAM cells manufactured in a 10nm CMOS process with Atomic Force Microscopy (AFM) based nano-probing system. AFM based nano-probing system has no electron beam damage because it uses topography image created by AFM instead of SEM for guidance at contact level [4] . After deprocessing the samples to the contact level, we irradiated electron beams to samples to investigate a dependency of the device characteristics on electron beam acceleration voltage. Compared to a non-exposed reference transistor, the exposure of electron beam on the target transistor lead to significant changes on device characteristics such as saturation current (I_{DS}), sub-threshold voltage (V_{TH}) and sub-threshold swing (S). This might be due to trapped charges in the gate oxide and interface state [5] . Our studies show that it is critical to avoid electron beam exposure before electrical device characterizations are carried out at the contact level using nano-probe system since electron beam induced device parameter changes are not negligible in the failure analysis of sub-10nm devices.

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8:20am NS+SP-TuM2 *In Situ* Synthesis and Characterization of Core-Shell Nanoparticle Arrays Using Dynamic Transmission Electron Microscopy, *Joseph McKeown*, Lawrence Livermore National Laboratory, *Y. Wu,* University of Tennessee, *J.D. Fowlkes,* Oak Ridge National Laboratory, *P.D. Rack,* University of Tennessee, *G.H. Campbell*, Lawrence Livermore National Laboratory
Core-shell nanoparticles have attracted much attention due to their unique and tunable properties relative to bulk structures of the same materials, making them candidates for a variety of energy- and catalysis-related applications. Intriguing magnetic behavior can be tailored by variation of size, interface, crystal orientation, and composition, and core-shell nanoparticles with noble-metal shells yield novel optical responses and enhanced electrocatalytic activity. The immiscible Co-Cu alloy system is of particular interest, because it combines a strong magnet (Co) with an

effective conductor (Cu) that also has a tunable plasmonic resonance. The ability to monitor and characterize these dewetting processes in situwhile the system is evolving can potentially lead to increased control and directed self-assembly. However, in situcharacterization of the dynamics of self-assembly processes has proven extremely challenging, particularly in materials systems that utilize metallic nanoparticles as the dynamics of these processes evolve extremely fast over very small spatial scales. Here, we present a method to synthesize Co@Cu nanoparticles via pulsed-laser-induced dewetting of Co-Cu alloy thin films. We show that this technique effectively synthesizes Co@Cu core-shell particles with controllable sizes ranging from tens to several hundred nanometers. The assembly dynamics during pulsed-laser-induced dewetting of Co-Cu alloy films were revealed using the high spatiotemporal resolution of the dynamic transmission electron microscope (DTEM) at Lawrence Livermore National Laboratory.

8:40am NS+SP-TuM3 Investigation of Nickel-assisted Growth of Silicon Carbide Nanowires, *Lunet E. Luna*, *R. Maboudian, C. Carraro*, University of California at Berkeley

Silicon carbide (SiC) based electronics hold promise for pushing past the limits of current technology to achieve small, durable devices that can function in high-temperature, high-voltage, corrosive, and biological environments. SiC is an ideal material for such conditions due to its high mechanical strength, excellent chemical stability, and its biocompatibility. Consequently, SiC nanowires have attracted interest in applications such as biological sensors, field emission cathodes, and energy storage devices. To realize SiC nanowire based devices for large-scale use, the growth mechanism must be further understood to enable strict control of nanowire crystal structure and orientation. Here we report on recent studies to understand the growth mechanism of Ni-assisted silicon carbide nanowires using single-source precursor methyltrichlorosilane. The effects of growth parameters, such as temperature and precursor flow rate, on the structure and morphology of the resulting nanowires will be presented. This study identifies the key parameters that may be varied to tailor nanowire growth for various applications.

9:00am NS+SP-TuM4 Homogeneous Nucleation and Characterization of Nanodiamonds Synthesized in an Atmospheric-Pressure Microplasma, *Jonathan Cole*, *R.M. Sankaran*, Case Western Reserve University

Nanodiamonds possess striking properties such as exceptional mechanical and chemical stability, low cytotoxicity, tunable active surface chemistry, and tunable photoluminescence-inducing color centers, but their synthesis remains a challenge. At normal temperature and pressure, graphite is the thermodynamically stable phase of bulk carbon, while the diamond phase requires high temperatures and pressures. Nanodiamonds have thus been produced via high-pressure, high-temperature (HPHT) conversion of graphite in the presence of carbonaceous precursors and via detonation of carbon-containing explosives. Alternatively, nanocrystalline diamond films have been deposited at low pressure (~1 Torr) by chemical vapor deposition (CVD). Supporting theoretical predictions[1] have shown that at the nanoscale, hydrogenated forms of carbon prefer sp^3 bonding, even at normal conditions, up to a certain size.

Here, we present a study of a plasma process for the synthesis of nanodiamonds at low temperature (<1000 ºC) and atmospheric pressure. C-H-O-containing vapor precursors diluted in Argon are continuously fed into a DC hollow cathode plasma discharge. Nanoparticles nucleate from radical moieties such as C_2 and CH, whose radiative transitions (specifically, C_2 516 nm vibrational band and CH 431 nm electronic band) are monitored by optical emission spectroscopy (OES). Particles are carried as an aerosol to either a filter for *ex situ* materials analysis or an *in situ* scanning mobility particle sizer system (SMPS). SMPS measurements confirm particle formation and allow us to correlate particle yield and size distribution with OES results. Specifically, we have compared results for ethanol and methanol precursors and find that C_2 formation is favored by ethanol, while CH formation is favored by methanol, and that an increase in both radical populations (measured as the aforementioned peak intensities normalized to Ar 750 nm intensity) increase with both particle number density and average diameter.

Analogous to CVD of diamond films[2], we find from TEM analysis that the selectivity of diamond phase is dependent on the C-H-O atomic ratio of the precursor. Specifically, methanol is found to produce a significant amount of sub-5 nm nanodiamonds, while ethanol mostly yields larger amorphous and graphitic carbon. We suggest that the radical chemistry observed via OES (i.e., C_2 versus CH populations) plays an important role in such observations, and we demonstrate that addition of H_2 gas to ethanol vapor will recover the results given by methanol.

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9:20am NS+SP-TuM5 Chemically-specific Intramolecular Imaging with Atomic Force Microscopy, *Ozgur Sahin*, Columbia University
INVITED

Atomic force microscopy (AFM) is a powerful tool for imaging and chemical characterization of biological samples at molecular resolution in physiologically relevant environments. However, the localized tip-sample interactions limit high-resolution images to the topmost layer of surfaces. Consequently, characterizing the three-dimensional (3-D) inner structures of molecules has been a challenge. Here we demonstrate three-dimensional localization of chemical groups within a protein complex using AFM. We employ short DNA sequences to label specific chemical groups inside the protein complex. T-shaped cantilevers functionalized with complementary probe DNAs allow locating each label with sequence specificity and sub-nanometer resolution. We measure pairwise distances between labels and reconstruct the 3-D loci of the target groups using simple geometric calculations. Experiments with the biotin-streptavidin complex showed that the 3-D loci of carboxylic acids of biotins are within 2-Angstroms of their respective 3-D loci in the corresponding crystal structure, suggesting AFM may complement existing structural biological techniques in solving structures that are difficult to study due to their size and complexity.

11:00am NS+SP-TuM10 Time-Resolved Small-Angle X-ray Scattering of Detonating Composition B-3 at the Advanced Photon Source, *Rachel Huber*, *D. Podlesak*, Los Alamos National Laboratory (LANL), *M. Bagge-Hansen*, Lawrence Livermore National Laboratory (LLNL), *D. Dattelbaum, M. Firestone*, LANL, *T. Graber*, Washington State University, *R. Gustavsen*, LANL, *R. Hodgin*, LLNL, *B.J. Jensen*, LANL, *L.M. Lauderbach*, LLNL, *P. Rigg*, Washington State University, *B. Ringstrand*, LANL, *S. Seifert*, Argonne National Laboratory, *N. Sinclair*, Washington State University, *E. Watkins*, LANL, *T.M. Willey, T. van Buuren*, LLNL

High explosive (HE) detonations drive chemical reactions under extreme conditions, in which explosive molecules are rapidly converted to small molecular products such as carbon, H_2O, CO_2 and N_2. Solid carbon products are known to be comprised of several allotropes including amorphous carbon, graphite, onion-like graphitic carbon, fullerenes, and nanodiamonds (NDs). The formation of different allotropes arises from the temperatures and pressures conditions on the nanocarbon phase diagram accessed during the detonation. Previously, only the starting explosive samples, and post-mortem soot were available for structural analysis. However, a fundamental understanding of how carbon particles form and evolve during a detonation must occur in real-time on the nanosecond timescale. New developments in *in-situ* time-resolved small angle X-ray scattering (TR-SAXS) has allowed for the measurement of multiple SAXS spectra of detonating Composition B-3 (60% TNT, 40% RDX) at the Dynamic Compression Sector (Sector 35-B) at the Advanced Photon Source (Argonne National Laboratory). The TR-SAXS measurements coupled to the detonation on the ns-timescale are the first of their kind in the United States. Through Guinier and Porod analysis of the TR-SAXS data, we are able to determine the size, morphology, and phase of the carbon allotropes at time delays behind the detonation front.[1,2] In addition, electron microscopy, X-ray photoelectron spectroscopy, and static SAXS were used to study the carbon solids in the post-detonation soot. By understanding the formation of solid carbon behind the detonation front, an improved theoretical framework may be applied to modeling the products equation of state for explosives.

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11:20am NS+SP-TuM11 LEEM Imaging of Growth of Au on Ge(110), *Bret Stenger*, *A. Dorsett, M.S. van Zijll, C.A. Gabris, C.K.B. Paw U, S. Chiang*, University of California, Davis

The growth of Au on Ge(110) was observed with Low Energy Electron Microscopy (LEEM). The objectives of this study were to control the growth of low-dimensional nanostructures and understand the collective diffusion behavior observed. Ge(110) was heated to 800°C and dosed with 0.5 ML of Au. During deposition, islands grew to ~1-2 microns in width and ~2-3 microns in length, all oriented along the same direction. The islands were observed to move and change shape over a short period of time (< 1s) indicating the rapid collective movement of ~$4x10^7$ atoms. As the temperature decreased, the island behavior was also studied and revealed rapid island contractions which left traces on the Ge(110) surface. This island growth is similar to that previously observed for Ag on Ge(110), although the Ag islands are typically a factor of 10 narrower and often 3 to 5 times longer.

11:40am NS+SP-TuM12 Strength and Fracture of Graphene Oxide Nanosheets, *C. Cao*, University of Toronto, Canada, *M. Daly, B. Chen, C.V. Singh, Y. Sun*, University of Toronto, *Tobin Filleter*, University of Toronto, Canada

Graphene oxide (GO) is a layered material comprised of hierarchical features which possess vastly differing characteristic dimensions. GO has been applied as a good candidate for paper-like materials, robust fibers, and reinforcement elements in composites. The use of GO in these materials has been motivated in large part by the predicted high mechanical properties of individual GO monolayers. Recent experiments performed in our research group have measured the strength of GO monolayers to be ~25 GPa [1], which is in good agreement with previously theoretical predictions [2]. Macroscopic papers and fibers synthesized using GO, however, typically exhibit strengths on the order of 10-100's of MPa's. GO nanosheets represent the critical hierarchical structure that bridges the length-scale of these monolayer and bulk material architectures.

In this study, the strength and fracture behavior of GO nanosheets were examined *in situ* with a micro-tensile device operated inside scanning and transmission electron microscopes (SEM/TEM) [3]. The tensile strength of GO nanosheets was measured to be as high as 12 ± 4 GPa, approaching the intrinsic strength of monolayer GO, and orders of magnitude higher than bulk GO papers. During mechanical failure, the nanosheets were observed to undergo intraplaner brittle fracture in highly localized regions through the cross-section of nanosheets due to interlayer load transmission via a hydrogen bond networks as reveled by complimentary Molecular Dynamics simulations.

GO nanosheets were found to exhibit variations in strength that were strongly correlated with the effective volume. This is consistent with Weibull statistics, such that larger GO nanosheets are more likely to possess larger planar defects and adversely impact strength. Furthermore, the Young's modulus was inversely correlated to sample thickness, and approached that of monolayer GO (~380 GPa) for thin samples. These trends provide strong evidence of the scaling effects on the mechanical properties of GO materials, and help to bridge the understanding of the mechanical behavior of hierarchical GO materials which will ultimately guide application as GO papers and coatings.

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12:00pm NS+SP-TuM13 Low-Temperature Atomic Layer Deposition of Crystalline Platinum Nanoclusters on Graphene Nanoplatelets Using (Methylcyclopentadienyl)-Trimethylplatinum and Oxygen, *Hao Van Bui*, Delft University of Technology, Netherlands, *R. Bevaart, F. Grillo*, Delft University of Technology, *J.R. van Ommen*, Delft University of Technology, Netherlands

The thermal atomic layer deposition of platinum using (methylcyclopentadienyl)-trimethylplatinum (MeCpPtMe₃) and oxygen has been investigated for more than a decade and performed on various supports, including flat surfaces [1, 2], nanoparticles [3], nanowires [4] and carbon-based nanomaterials [5, 6, 7, 8]. It has been demonstrated and widely accepted that this ALD process has a lower limit of deposition temperature of 200 °C. Here, we demonstrate the thermal Pt ALD on graphene nanoplatelets using MeCpPtMe₃ and dry air (20% wt. O₂), and show that highly dispersed and crystalline Pt nanoparticles can be obtained at a temperature as low as 80 °C. The feasible low-temperature deposition is

attributed to the role of the graphene support that can activate molecular oxygen to form O_2^- anions [9], which consequently enhances the oxidation reactions in ALD. Importantly, the low deposition temperatures (*i.e.*, 80 °C and 100 °C) can prevent the ripening of nanoparticles and hinder the formation of new nuclei during the ALD, allowing for better control in particle size and distribution. In contrast, at higher temperatures (150-250 °C), the ripening occurs, and new nuclei are constantly formed during the deposition, resulting in a broader particle size distribution.

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Surface Science
Room: 112 - Session SS+AS+EN+NS-TuM

Nanostructures, Nanoplasmonics and Surface Reactions
Moderator: Bruce Koel, Princeton University

8:20am SS+AS+EN+NS-TuM2 ENDOM: A Simple Method to Deposit Nanostructures from Nanowires to Nanopores, *Ashley Ellsworth*, *A.V. Walker*, University of Texas at Dallas

A key challenge in the practical application of nanostructures is their effective integration through assembly, patterning and alignment on technologically relevant substrates. We have recently demonstrated a new technique, electroless nanowire deposition on micropatterned substrates (ENDOM), by which to simultaneously synthesize and place nanowires on chemically patterned substrates. The nanowires can be precisely oriented on the surface in arbitrary shapes, such as an arch and around a right angle bend. In ENDOM, the shape of the deposit is controlled by the substrate pattern while its width is controlled by the reaction conditions. By employing longer deposition times and the appropriate substrate patterns, nanopores and nanochannels can be produced. However for sensing and nanoelectronic applications, free standing nanopores and nanochannels are generally employed. We have observed that the nanostructure adhesion to the surface is dependent upon the reagent concentrations. For example in Cu ENDOM, upon reduction of triethanolamine (complexing agent and buffer) concentration, nanowires no longer adhere strongly to the substrate and can be transferred to another substrate. In this presentation, we shall discuss the mechanisms of adhesion, transfer of these nanostructures to other substrates and proof-of-concept studies to synthesize free-standing nanostructures.

8:40am SS+AS+EN+NS-TuM3 Chemical Reaction on Photo-excited Plasmonic Nanostructures, *Sulio Linic*, University of Michigan **INVITED**

We will also show that plasmonic silver nanoparticles, optically excited with low intensity visible light, exhibit direct photo-catalytic activity in a number of oxidation reactions.1 We will discuss underlying mechanisms associated with these phenomena and predictive models that can capture the outcome of chemical transformations on these materials.[2,3,4] We propose that this new family of plasmonic metal photo-catalysts could prove useful for many heterogeneous catalytic processes that cannot be activated using conventional thermal processes on metals or photo-catalytic processes on semiconductors. I will show an example of such a process.[5]

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9:20am SS+AS+EN+NS-TuM5 Structured Noble Metal Nanosurfaces for Biosensing and Bioanalysis (4): TLC-SERS and *In Situ* Monitoring of Surface-Adsorbed Target Molecules, *Hiroyuki Takei*, J. Saito, K. Watanabe, Toyo University, Japan, T. Okamoto, Riken, Japan, H. Vieker, A. Beyer, A. Gölzhäuser, Bielefeld University, Germany

Surface-enhanced Raman spectroscopy, SERS, is a powerful technique for in-situ characterization of chemical species. Requisite noble metal nanosurfaces can be prepared with a variety of techniques, ranging from simple vacuum deposition of a metal followed by annealing to intricate processing by electron beam lithography. Some commercial SERS plates are now available, and it is sometimes possible to detect signals from even single molecules if pure. However, in real-world applications, target molecules are often found in mixtures, either containing other Raman-active chemical species or a background material that can overwhelm the target molecule. It can also happen that one might be interested in directly obtaining SERS spectra of chemical species adsorbed on a solid surface.

When faced with a mixture sample, we can carry out separation before SERS measurement. To do so, we incorporated a SERS layer into a thin layer chromatographic plate. While a number of workers have reported applying noble metal nanoparticles after separation with a conventional TLC plate, we feel that such an additional step is cumbersome and does not guarantee uniformity in SERS signals. Our TLC-SERS is prepared with the following procedure; (1) adsorption of 100 nm diameter SiO_2 nanospheres as a dense monolayer on a glass slide, (2) evaporation of gold or silver with thicknesses up to 100 nm, and (3) spreading of chromatography silica gels. Steps (1) and (2) give rise to surface-adsorbed cap-shaped noble metal nanoparticles. We demonstrate that the TLC-SERS can actually separate mixture samples and provide in-situ SERS spectra. Two examples will be used to demonstrate the utility of our TLC-SERS plates. One deals with a mixture of roughly equal portions of Raman-active chemical species, rhodamine 6 G, crystal violet and BPE. The other is skim milk to which a trace amount of melamine has been added. We show that the three-component mixture could be separated and SERS spectra of all three components could be obtained separately and that melamine added to skim milk could be detected after separation but not before.

For detection of surface-adsorbed chemical species, we prepared silver nanoparticles on a PDMS sheet, using the same protocol as above. The PDMS sheet can be made less than 1 mm thick so that with an appropriate pressurization system, pressure can be applied to the PDMS sheet in order to press the silver nanoparticles against a near-by solid surface to which target molecules are adsorbed. Such a system can be utilized to detect, for example, residual pesticides on agricultural produces. We will demonstrate direct detection of ferbam on a grapefruit.

9:40am SS+AS+EN+NS-TuM6 Growth and Intercalation of Cu and Dy on the Basal Plane of Graphite, *Patricia A. Thiel*, D. Appy, E.J. Kwolek, D. Shao, M. Wallingford, M.C. Tringides, J.W. Evans, Y. Han, Iowa State University, H. Lei, Institute of Solid State Physics, CAS, China, C.-Z. Wang, Iowa State University

Graphite, and surface processes on graphite, serves as a valuable benchmark for carbon-based materials such as graphene. We have studied copper and dysprosium on graphite, deposited by an e-beam evaporator in UHV and imaged with STM, to determine the characteristic features of nucleation and growth of metal islands. One of the fundamental questions that arises naturally is whether metal nucleates homogeneously on the terraces or whether it nucleates heterogeneously at defect sites. To answer this question we employ several tools, especially a comparison between high-level van der Waals theory for single atom diffusion, and measured island density. We also present evidence for unexpected metal intercalation at the surface of graphite, after treatment at elevated temperature.

11:00am SS+AS+EN+NS-TuM10 Surface-Mediated Self-assembly of a Flexible Nucleoside Analogue into Micron-sized Hydrogen-bonded Polymers, *Jun Wang*, P. Bonnesen, Oak Ridge National Laboratory, E. Rangel, E. Vallejo, A. Sanchez-Castillo, Universidad Autónoma del Estado de Hidalgo, Mexico, H.J. Cleaves, Tokyo Institute of Technology, Japan, A.P. Baddorf, B. Sumpter, M. Pan, P. Maksymovych, M. Fuentes-Cabrera, Oak Ridge National Laboratory

We report on an extraordinary large-scale surface-mediated molecular self-assembly of a flexible nucleoside analogue into a well-organized hydrogen-bonded polymer on Au(111). The nucleoside analogue is (*RS*)-N^9-(2,3-Dihydroxypropyl)Adenine (*R,S*-DHPA), and it consists of the Adenine nucleobase and a tethered glycol group. Employing scanning tunneling microscopy and density functional theory calculations we show that the polymer primarily self-assembles along the Au(111) herringbone reconstruction pattern and extends to the micrometer scale and beyond. The profound propensity toward self-assembly in this case arises from the properties of the glycol moiety of the *R,S*-DHPA molecule: it is linear and flexible, and these features, together with the specific ways in which the glycol and the Adenine moieties can hydrogen bond, confer *R,S*-DHPA with a superior self-assembly ability. Our results suggest that nucleoside analogues with flexible acyclic groups could provide the means for synthesizing substrate-supported mesoscale hydrogen-bonded polymers.

11:20am SS+AS+EN+NS-TuM11 Nanowire Kinking during Vapor-liquid-solid Growth: Experiments and Simulations, *Yanming Wang*, Y. Li, Stanford University, S. Ryu, Korea Advanced Institute of Science and Technology, P.C. McIntyre, W. Cai, Stanford University

Nanowires (NWs) are promising components for next-generation electronic and optical devices, and the vapor-liquid-solid (VLS) growth is a widely studied method for NW fabrication. However, many fundamental questions regarding the VLS mechanism are still not understood, such as NW kinking during growth. Kinking, a sudden change in axial orientation of nanowires during growth, is a common defect that complicates the directed synthesis of these nanocrystals. Understanding such defects is important for better control of the NW orientation, yield and quality required for applications.

Experimental studies of coherent kinking of germanium nanowires detect two different kinking structures. One structure, which is most pronounced for Ge NW's of diameter close to 20 nm, involves kinking from a vertical <111> to <110> growth axis on Ge (111) single crystal substrates. The other involves kinking from the vertical [111] axis to an inclined <111> growth direction for NWs of > 30 nm diameter.

The balance of capillary forces driving these two modes of kinking are analyzed quantitatively. We developed a 3D multi-phase field model for VLS NW growth. The model captures the NW tapering and sidewall facets in good agreement with experimental observations. The model predicts the steady-state NW growth velocity is a linear function of the vapor chemical potential and the inverse of catalyst diameter, providing a confirmation of the Gibbs-Thomson effect in nanowire growth. With anisotropic interfacial energies, the model shows the NW growth orientation dependence on catalyst diameter and hence it provides an explanation of the NW kinking in the steady-state growth regime. In this model, we introduce a perturbation force to induce the NW structural transition and the free energies are evaluated at different stages during the droplet movement. It enables us to discuss the instability of the catalyst droplet for different pedestal structures, which is important for understanding the onset of the kinking at the NW base.

11:40am SS+AS+EN+NS-TuM12 Adsorption of Water and Bromine on Gold Nanoclusters Investigated by Neutralization in Low Energy Alkali Ion Scattering, *Christopher Salvo*, J. Keagy, J.A. Yarmoff, UC Riverside

Small gold (Au) nanoclusters have been heavily studied because of their intriguingly high catalytic activity, especially when compared to bulk gold. We employ a specialized method of Low Energy Ion Scattering (LEIS) to probe the electronic properties of nanoclusters prepared with a variety of methods. The experiments measure the neutralization probability of singly scattered alkali ions, which is acutely sensitive to the local electrostatic potential a few Å's above the surface. Because the Au atoms are much more massive than the substrate atoms, this method allows the signal from the nanoclusters to be separated from that of the substrate so that the neutralization reflects the local properties of the cluster surfaces. Earlier work had demonstrated that the neutralization is a function of cluster size, and that it is enhanced for the smallest clusters presumably because they are negatively charged [1]. The work presented here investigates the adsorption of water and Br on Au nanoclusters grown on TiO_2 or SiO_2. There are multiple factors that can contribute to a change in the neutralization of the scattered ions, such as the cluster size, shape, or charge state. When Br attaches to a nanocluster, the neutralization decreases presumably due to charge transfer from the cluster to the electronegative Br atom. Surprisingly, it is found that the neutralization of scattered K^+ ions increases in the presence of adsorbed water at liquid nitrogen temperatures. Furthermore, the increase of neutralization for adsorbed water is independent of whether the water or the Au is deposited first. Possible explanations for these observations will be discussed.

[1] G.F. Liu, Z. Sroubek and J.A. Yarmoff, Phys. Rev. Lett., **92**, 216801 (2004).

12:00pm SS+AS+EN+NS-TuM13 Optical Constants Measured for Fe, Ni and Pd by Reflection Electron Energy-Loss Spectroscopy Spectra, *H. Xu, B. Da, S.F. Mao,* University of Science and Technology of China*, J. Toth, K. Tokesi,* Institute for Nuclear Research, Hungarian Academy of Sciences (ATOMKI)*, **Zejun Ding**,* University of Science and Technology of China

The energy loss function (ELF), which is directly related to optical constants of a solid, dominates the energy loss process of an electron moving inside or flying nearby a solid. It is therefore able to obtain optical constants by surface electron spectroscopy technique. Accurate measurement of optical data by optical methods in a photon energy range up to 10^2 eV is still insufficient; delicate experimental conditions are required when measuring data in vacuum ultraviolet region (20-50 eV). Fortunately, such information is essentially contained in and, therefore, can be extracted from a reflection electron energy loss spectroscopy (REELS) spectrum due to the shorter information depth of signal electrons compared with that of photons.

In the present work, reflection electron energy loss spectra of transition metals, Fe, Ni and Pd, were measured at several primary energies ranging from 0.5 keV up to 5 keV and in a wide energy-loss range. Prior to the measurements in situ cleaning of the sample surface was performed using Ar+ ion sputtering with proper current density and time. Vacuum was kept as 1.5×10^{-9} mbar in the measurement chamber during the REELS measurements. Surface cleanness was checked by XPS in several cases after the REELS measurements. An improved reverse Monte Carlo simulation for determination of optical constants via accurate description of electron inelastic transport process was performed. ELF of those metals were extracted from experimental REELS spectra. The accuracy of the obtained optical data has been confirmed by f-sum and ps-sum rules. Comparisions of our data with other sources from either experimental measurements or density functional theory calculation are given.

Tuesday Afternoon, October 20, 2015

2D Materials Focus Topic
Room: 212C - Session
2D+EM+MC+MI+NS+SP+SS+TF-TuA

Electronic and Magnetic Properties of 2D Materials
Moderator: Thomas Mueller, Vienna University of Technology, Austria, Xiaobo Yin, University of Colorado Boulder

2:20pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA1 Direct Capacitive Probe of Isospin Order in Graphene Bilayers**, *Andrea Young*, University of California at Santa Barbara **INVITED**
Bilayer graphene is a highly tunable electronic system in which electric fields can be used to control both the carrier density as well as the electronic structure. Like its monolayer cousin, the bilayer graphene Landau levels are characterized by approximate spin and valley degeneracy; unlike monolayer, however, the three dimensional structure of the bilayer allows control of the sublattice splitting with a perpendicular electric field. This feature has been used extensively to probe the phase diagram of interacting electrons, particularly within the zero energy Landau level, revealing a number of interacting states characterized by spin and/or valley order. Typically, however, the spin or valley order is inferred indirectly by varying conjugate fields and inferring the order from the resulting changes in conductivity. Here I will describe a technique capable of resolving layer-polarization directly through high sensitivity capacitance measurements. The measurements confirm the known features of the bilayer graphene phase diagram, while revealing several new phases and a series of sharp features associated with phase transitions between states of different layer polarization. These features suggest a new mechanism for inversion symmetry breaking in Bernal stacked bilayer graphene.

3:00pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA3 Patterning Hydrogenated Graphene via Electron Beam Irradiation**, *Woo-Kyung Lee*, K.E. Whitener, J.T. Robinson, P.E. Sheehan, Naval Research Laboratory
We demonstrate that electron-beam irradiation selectively removes hydrogen atoms from hydrogenated graphene (HG) prepared by the Birch reduction.[1] Hydrogen removal can pattern the surface with two different functionalities. First, we show that partially-hydrogenated graphene (Phg) on a SiO_2 substrate is ferromagnetic, and that the local magnetic strength can be tuned using e-beam irradiation. An e-beam lithography system enables us to modulate or eliminate the permanent magnetization over a large area to produce a patterned magnetic array. Secondly, since removal of the hydrogens converts the highly electrically insulating HG back into conductive graphene, we can write chemically isolated, dehydrogenated graphene nanoribbons (GNR) as narrow as 100 nm. These GNRs have a low sheet resistance ($\geq$ 31.5 Kω/$\square$), only 10x that of the pristine graphene, and their Dirac points before and after e-beam irradiation appear at comparable gate voltages.

1. *W.K. Lee et al., Advanced Materials, 27, 1774 (2015).*

3:20pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA4 Large-Area Low-Pressure Synthesis of Single-Layer MoS₂ Films and Schottky-Barrier Formation upon Metal Deposition**, *Michael Gomez*, J. Martinez, M. Valentin, L. Bartels, UC Riverside
Using a high vacuum CVD process we are able to synthesize large are monolayer MoS_2 films. Organic chalcogen precursors are released into the growth chamber and react with a Mo filament creating films up to $2cm^2$ in size that are uniform and free of oxides. The films have pronounced photoluminescence intensity and are in Raman spectroscopy indistinguishable from exfoliated material. Metal contact formation to these films was investigated under UHV conditions utilizing X-Ray Photoelectron Spectroscopy . These measurements permit us to follow the formation of a Schottky Barrier with increasing metal film thickness on the Angstrom scale. We utilize core level spectroscopy to indicate the evolution of the MoS_2 valence band under metal deposition.

4:20pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA7 Accelerating the Discovery of Alternative Fuel Catalysts through Intelligent Computational Framework**, *Altaf Karim*, COMSATS Institute of Information Technology, Pakistan **INVITED**
In today's modern world of high performance computing, properties of materials can be predicted with high accuracy before these materials are ever made. In this scenario my focus has been on the development of state of the art computational framework based on intelligent/ smart self-learning algorithms for the design and discovery of catalytic materials. By giving some examples, I will describe how this enterprise of the predictive multi-scale modeling/simulation has been passing through the stages of its evolution and how these complex algorithmic species integrated themselves into an intelligent python, which is helping scientists design & discover new materials for alternative fuel catalysis. In practice, our computational framework develops databases of candidate catalysts. Further this framework enables a set of algorithms to screen across a broad range of multi metallic catalytic materials with variable reactivity, selectivity, and stability while searching for materials with desired combination of properties required for the optimal catalytic performance for alternative fuel production. I would also explain that how our computational tools in catalyst design deal with the multi-component microstructures of catalysts composed of multi-element nano chunks. In order to tune up the rate limiting processes we can take advantage of the multi-element nano chunks. For example, on many catalytic surfaces the diffusion is rate limiting process for larger organic molecules. To enhance the diffusion such molecules on such surfaces, nano chunks of other materials (on which the diffusion of the organic molecules is comparatively higher) can be integrated in the catalyst's surface, which improves the overall performance of the catalyst in terms of overall reactivity and also selectivity. In addition to that our tools also help us to filter out, from the databases, stable multi-component microstructures of artificially engineered catalysts.

5:00pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA9 Probing Massive Dirac Electrons in Bilayer Graphene**, *Feng Wang*, University of California at Berkeley **INVITED**
Electrons in monolayer graphene are described by massless Dirac electrons, which exhibit unique quantum phenomena due to the pseudospin and Berry phase of the massless electrons. In this talk, I will discuss our effort in probing massive Dirac electrons in gapped bilayer graphene. In particular, I will discuss the topologically protected 1D conducting channel at the domain boundary of AB-BA bilayers, which can be attributed to the quantum valley Hall edge states in gapped bilayer graphene.

5:40pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA11 Combining Photoemission and Photoluminescence Microscopy to Study Substrate Transfer Process Effects in Chemical Vapor Deposited MoS₂ Monolayers**, *Olivier Renault*, M. Frégnaux, Univ. Grenoble Alpes/ CEA, LETI, MINATEC Campus, France, *J. Bleuse*, Univ. Grenoble-Alpes & CEA-INAC, France, *H. Kim*, Univ. Grenoble Alpes/ CEA, LETI, MINATEC Campus, France, *D. Voiry, M. Chhowalla*, Rutgers University
Within the perspective of integrating two-dimensional transition metal dichalcogenides (2D TMDs) such as molybdenum disulfide (MoS_2), into devices, it becomes of utmost importance to assess the influence of each step of the device fabrication process on the optical and transport properties of the MoS_2 single layer (1L) domains. Particularly at the deposition stage the properties may be influenced by substrate effects [1], and later, transfer processes may further alter the desired properties of TMDs. This requires effective microscopic characterization techniques.

We present a characterization method combining photoemission microscopy (XPEEM and Kpeem) and photoluminescence microscopy to compare the structural, optical and electronic properties of both as-deposited and transferred MoS_2 1L domains onto different substrates. XPEEM is used with laboratory sources in both direct space imaging for work function and core-level mapping [2] and particularly in the momentum microscopy mode (k-PEEM) to perform parallel angular imaging and retrieve the band structure in a one shot experiment [3]. Micro-photoluminescence spectroscopy at low (5K) and room temperature is used to detect the specific radiative recombination that occurs in MoS_2 1L (direct band gap semiconductor behavior) and to evidence the eventual presence of midgap states caused by process-induced defects. The results of both characterization techniques will be presented for MoS_2 1L domains transferred onto silica and gold substrates highlighting the roles of substrate nature (metal or insulant), surface roughness, and the presence of structural defects whether induced by the preparation process or intrinsic such as grain boundaries.

[1] Jin et al. Phys. Rev. Lett. 111 (2013), 106801.

[2] Kim, Renault, et al. Appl. Phys. Lett. 105 (2014) 011605.

[3] Mathieu et al., PRB 83 (2011) 235436.

Energy Frontiers Focus Topic
Room: 211B - Session EN+EM+NS+SE+SS+TF-TuA

Batteries and Supercapacitors
Moderator: Elijah Thimsen, Washington University, St. Louis, Andrew C. Kummel, University of California at San Diego

2:20pm EN+EM+NS+SE+SS+TF-TuA1 Behavior of Layered Cathode Materials: A Route to Higher Energy Density for Li-Ion Batteries, *Marca Doeff, F. Lin,* Lawrence Berkeley National Laboratory, *I. Markus,* Lawrence Berkeley Lab, University of California, Berkeley **INVITED**
The most promising cathode materials for Li-ion batteries geared towards vehicular applications are the so-called NMCs ($LiNi_xMn_yCo_zO_2$), based on cost and performance considerations. NMCs exhibit a slightly sloping voltage profile in lithium half-cells, with typical utilizations significantly lower than the theoretical capacity of about 280 mAh/g. An attractive strategy for increasing the energy densities of devices meant for traction applications would be to cycle NMCs to a higher potential than is currently used (usually about 4.3V vs. Li^+/Li) so that more lithium can be extracted and cycled. For this approach to be viable, the cathodes must exhibit excellent structural stability and good reversibility over a wide composition range. Our recent work has been directed towards understanding the high-potential behavior of NMCs, using an array of synchrotron x-ray techniques as well as transmission electron microscopy. These techniques show that surface reconstruction to rock salt and spinel phases occur during high voltage cycling, and result in impedance rises and apparent capacity losses. The degree to which this occurs is a function of how the material is made and its electrochemical history. Partial substitution of Ti for Co in NMCs not only increases the capacities obtained during cycling to 4.7V in lithium half-cells compared to baseline materials, but appears to improve the cycling behavior as well. First principles calculations show that the aliovalent substitution lowers the voltage profile slightly. This allows a greater amount of lithium to be extracted and cycled below 4.7V, resulting in higher practical capacities. The Ti-substitution also delays the formation of rock salt during charging, resulting in better capacity retention. These observations suggest that optimizing the synthesis and judicious substitution can mitigate deleterious structural changes of the NMCs due to high potential operation in Li-ion cells. These strategies should be combined with those designed to prevent side reactions with electrolytic solutions during high potential operation, such as new electrolytic solutions with improved oxidative stability, or atomic layer deposition coatings on electrode surfaces, to further ensure stable cycling.

3:00pm EN+EM+NS+SE+SS+TF-TuA3 Next-Generation Electrolytes for Lithium-Ion Batteries, *Sarah Guillot,* University of Wisconsin - Madison, *M. Usrey, A. Pena-Hueso,* Silatronix, Inc., *R.J. Hamers,* University of Wisconsin-Madison and Silatronix, Inc.
Current-generation electrolytes for lithium-ion batteries are limited in electrochemical stability and thermal stability. Over the last several years, researchers at University of Wisconsin and at Silatronix, inc. have developed several new generations of electrolytes based upon incorporation of organosilane groups into the molecular structure. A recently developed class of compounds shows unprecedented enhancements in performance, including the ability to cycle full cells over 400 times at 70 degrees C, and the ability to reduce or eliminate "gassing" at cathode surfaces. In this talk we will discuss the molecular structure of these organosilane-based compounds, quantitative measurements of the decomposition pathways, and the resulting mechanistic insights into the molecular properties that gives rise to their outstanding performance characteristics.

3:20pm EN+EM+NS+SE+SS+TF-TuA4 Physico-Chemical Properties of Polyamidoamine Dendrimer-Based Binders for Carbon Cathodes in Lithium-Sulfur Batteries, *Manjula Nandasiri, P. Bhattacharya, A. Schwarz, D. Lu,* Pacific Northwest National Laboratory, *D.A. Tomalia,* NanoSynthons LLC, *W.A. Henderson, J. Xiao,* Pacific Northwest National Laboratory
Lithium-sulfur (Li-S) batteries are one of the most promising energy storage systems, offering up to five-fold increase in energy density as compared with state-of-the-art lithium-ion batteries to meet the growing demand for environmentally benign energy storage devices with high energy density, low cost, and long life time. For practical applications, high sulfur (active material) loading (> 2 mg/cm^2) within the carbon cathode in Li-S batteries is essential. Most reports on engineered cathode materials for Li-S batteries are based upon low sulfur loadings (typically ~1 mg/cm^2), which are impractical and often give misleading results. It is unknown how these novel engineered cathodes behave under high sulfur loading conditions. The binder is perhaps the most critical material in achieving a high sulfur loading in carbon cathodes. We have recently used dendrimers with various surface chemistries as functional binders in Li-S cells with SuperP-carbon/S as the cathode material. Even without engineering the cathode, very favorable cycling stability and electrolyte wetting were obtained with these binders. It was attributed to the high density of surface functional groups on the dendrimers, high curvature of the binder and its porosity, and the interactions between the large number of basic nitrogen and oxygen atoms on the dendrimers and lithium polysulfides.

Here, we will discuss the fundamental properties of dendrimers as aqueous binders for Li-S battery cathodes and compare their performance with other aqueous, commonly used linear polymeric binders such as styrene butadiene rubber (SBR) and sodium carboxyl methyl cellulose (CMC). Specifically, generation 4 polyamidoamine (PAMAM) dendrimers with hydroxyl (OH), 3-carbomethoxypyrrolidinone (CMP), and sodium carboxylate (COONa) surface functional groups served as good, electrochemically stable binders at high S loadings (~3-5 mg/cm^2) with high initial capacities (> 1000 mAh/g). In comparison to CMC-SBR binder-based electrodes which failed at high C-rates (0.2C) after 40 cycles, dendrimer-based binders showed a capacity retention of >85% for more than 100 cycles. It was also observed that acidic groups and all-NH$_2$ surface groups are poor binders, whereas binders with COO$^-$ and neutral surface groups (OH, CH$_3$) show better performance. X-ray photoelectron spectroscopy was used to identify different surface functional groups in these dendrimers and understand their interactions with SuperP-carbon/S cathode. In addition, a detailed physico-chemical characterization using IR spectroscopy and XANES/EXAFS will be presented to substantiate the superior dendrimer-carbon/S interactions.

4:20pm EN+EM+NS+SE+SS+TF-TuA7 The Road beyond Lithium Batteries is Paved — In Three Dimensions — With Rechargeable, Dendrite-Free Zinc, *Debra Rolison, J.F. Parker, C.N. Chervin, I.R. Pala, M.D. Wattendorf, J.W. Long,* U.S. Naval Research Laboratory **INVITED**
Lithium-ion batteries dominate the energy-storage landscape, but do so with the ever-present threat of thermal runaway and conflagration courtesy of flammable electrolytes and oxygen-releasing electrode materials. Fortunately, Zn-based batteries offer a compelling alternative grounded in the innate safety and cost advantages of aqueous electrolytes augmented by the high earth-abundance of Zn and the high energy density of Zn-based batteries (comparable to Li-ion). Traditional Zn-based batteries provide suboptimal utilization of the zinc (typically <60% of theoretical capacity) and poor rechargeability—thanks to the complex dissolution/precipitation processes that accompany Zn/Zn^{2+} cycling of conventional powder-bed Zn electrode structures in alkaline electrolyte. We address these limitations by redesigning the zinc anode as a porous, 3D-wired "sponge" architecture. Zinc sponge electrodes achieve >90% Zn utilization when discharged in primary Zn–air cells, retaining both the 3D framework of the Zn sponge and an impedance characteristic of the metal thanks to an inner metallic core of 3D zinc. When cycled in Ag–Zn and Ni–Zn cells, the Zn sponges retain monolithicity and reveal uniform deposition of charge/discharge products at the external and internal surfaces, even to deep depth-of-discharge of the zinc. These results show that all Zn-based chemistries can now be reformulated for next-generation rechargeable, Li-free batteries

5:00pm EN+EM+NS+SE+SS+TF-TuA9 Porous Silicon Electrochemical Capacitor Devices for Integrated On-Chip Energy Storage, *Donald Gardner, C.W. Holzwarth III, Y. Liu, S. Clendenning, W. Jin, B.K. Moon, Z. Chen, E.C. Hannah, T.V. Aldridge,* Intel Corp, *C.P. Wang, C. Chen,* Florida International University, *J.L. Gustafson,* Intel Corp
Integrated on-chip energy storage is increasingly important in the fields of internet of things (IoT), energy harvesting, and sensing. Silicon is already the materials of choice for the integrated circuits found in every IoT device; however, the efforts to integrate electrochemical (EC) capacitors on a silicon die have been limited. Unlike batteries, EC capacitors are electrostatic devices and do not rely on chemical reactions enabling cycle lifetimes of >1M. This is especially important for off-power-grid IoT devices where difficulty associated with regularly replacing the batteries of billions of devices is prohibitive. This work demonstrates electrochemical capacitors fabricated using porous Si nanostructures with extremely high surface-to-volume ratios and an electrolyte. Devices were fabricated with tapered channels sized from 100 nm at the top to 20 nm and with aspect ratios greater than 100:1. Surface coatings were necessary for long-term stability because unpassivated silicon structures react with the electrolytes. To obtain uniform coatings using stop-flow atomic layer deposition (ALD), efficient surface reactions are needed between high volatility, low molecular weight, small molecular diameter precursors without chemical vapor deposition side reactions. $TiCl_4$ and NH_3 precursors were found to coat porous Si with TiN uniformly. Measurements of coated P-Si capacitors reveal that an areal capacitance of up to 6 mF/cm^2 can be achieved using 2 μm deep pores, and scales linearly with depth with 28 mF/cm^2 measured for

12 μm deep pores. Three-terminal CV measurements with EMI-BF$_4$ ionic electrolyte were used to examine the stability of different pore sizes and TiN coating thicknesses. Pores with an average 50 nm width and 100:1 aspect ratio were stable to ±1.2 V when cycled at 10 mV/s and stable to ±1.0 V when cycled at 1 mV/s. Different ionic liquids were studied to determine the ionic liquid best suited to TiN coated porous Si including TEA-BF$_4$/AN, EMI-BF$_4$, EMI-Tf, and a 3M EMI-BF$_4$/propylene carbonate (PC) mixture. Using impedance spectroscopy, the time constant for a 2 μm deep porous Si EC capacitor with a high conductivity TiN coating was found to be 17.6 ms which is fast enough that this can be used for applications involving AC filtering for AC-DC conversion. Measurements of volumetric energy density versus power density of porous Si devices versus other devices show several orders of magnitude higher energy density than electrolytic capacitors with a similar voltage range. These results are also between one to two orders of magnitude higher than other studies utilizing porous silicon and are comparable to commercial carbon-based EC capacitors.

5:20pm EN+EM+NS+SE+SS+TF-TuA10 Investigations of Magnesium Stripping and Deposition using *Operando* Ambient Pressure X-ray Photoelectron Spectroscopy, *Yi Yu*, Lawrence Berkeley National Laboratory, *Q. Liu*, Shanghai Tech University, China, *B. Eichhorn*, University of Maryland, College Park, *E.J. Crumlin*, Lawrence Berkeley National Laboratory

Since the first demonstration of rechargeable magnesium battery, magnesium metal has been considered as an attractive battery anode due to its high volumetric energy density, high negative reduction potential, natural abundance in the earth crust, and relatively good safety features due to its dendrite-free formation. Although it is well accepted that the dissolution and plating of metal plays an important role in the electrochemical properties related to the discharge and charge of the battery, the nature of metal-electrolyte chemical and electrochemical interaction is still not fully established. In an effort to elucidate the interfacial electrochemical mechanisms, we present the studies of magnesium deposition and stripping using *operando* ambient pressure X-ray photoelectron spectroscopy (AP-XPS). Synchrotron X-rays at the Advanced Light Source, Lawrence Berkeley National Laboratory and our 'tender' X-ray AP-XPS endstation allow for probing the liquid-solid interface at pressures up to 20 Torr. Cyclic voltammetry is employed to examine the reversibility of electrochemical magnesium deposition. This talk will provide details on how *operando* AP-XPS coupled with electrochemistry allows for studying electrochemical processes of magnesium deposition and stripping at the liquid-solid interface and yields chemical information relevant to real-world applications.

5:40pm EN+EM+NS+SE+SS+TF-TuA11 Atomic Layer Deposition of Solid Electrolytes for Beyond Lithium-Ion Batteries, *Alexander Kozen*, *G.W. Rubloff*, University of Maryland, College Park **INVITED**
Solid Li-based inorganic electrolytes offer profound advantages for energy storage in 3-D solid state batteries: (1) enhanced safety, since they are not flammable like organic liquid electrolytes; and (2) high power and energy density since use of the 3D geometry can maximize the volume of active material per unit area, while keeping the active layer thickness sufficiently small to allow for fast Li diffusion. The quality of thin solid electrolytes is currently a major obstacle to developing these solid state batteries, restricting electrolyte thickness to >100 nm to control electronic leakage, consequently slowing ion transport across the electrolyte and impeding 3-D nanostructure designs that offer high power and energy.

Furthermore, the ion-conducting, electron-insulating properties of solid electrolytes are promising for their use as protection layers on metal anodes (e.g., Li, Na, Mg) and on cathodes in proposed "beyond-Li-ion" battery configurations such as Li-NMC, Li-O$_2$, and Li-S to prevent electrolyte breakdown.

Atomic layer deposition (ALD) is well suited to the challenge of solid electrolytes, providing ultrathin, high quality films with exceptional 3-D conformality on the nanoscale. We have developed a quaternary ALD processes for the solid electrolyte LiPON, exploiting *in-operando* spectroscopic ellipsometry and *in-situ* XPS surface analysis for process development. ALD LiPON has tunable morphology, and a nitrogen-dependent tunable ionic conductivity as high as 3.5x10^{-7} s/cm.

We explore the potential of ALD solid electrolytes for the fabrication of solid, 3D microbatteries, as we as the use of thin ALD solid electrolyte coatings on metal anodes to improve interfacial stability against organic electrolytes and thus prevent SEI formation. We demonstrate and quantify protection of lithium metal anodes with low ionic conductivity ALD Al$_2$O$_3$ coatings to prevent degradation reactions, and probe the surface chemistry and morphology of these anodes. Finally, we demonstrate that protection of Li metal anodes using ALD protection layers can improve the capacity of

Li-S batteries by 60% by preventing anode corrosion by dissolved sulfur species in the electrolyte.

This work has implications beyond the passivation of lithium metal besides its focus and greatest impact on the Li-S battery system, as ALD protection layers could also be applied to other promising metal anode battery systems such as Mg and Na, and other beyond Li-ion technologies such as Li-NMC or- Li-Air where similar reactivity issues prevent adoption.

Nanometer-scale Science and Technology
Room: 212B - Session NS+EN+SS-TuA

Nanophotonics, Plasmonics, and Energy
Moderator: David Wei, University of Florida

2:20pm NS+EN+SS-TuA1 Subnanoscale Exciton Dynamics of C$_{60}$-based Single Photon Emitters Explored by Hanbury Brown Twiss Scanning Tunneling Microscope, *Pablo Merino Mateo*, *C. Grosse*, *A. Rosławska*, *K. Kuhnke*, *K. Kern*, Max-Planck-Institut für Festkörperforschung, Germany
Electron-hole pair (exciton) creation and annihilation by charges are crucial processes for technologies relying on efficient charge-exciton-photon conversion. Photoluminescence has been instrumental for this purpose with near-field techniques approaching 20 nm spatial resolution. However, molecular resolution is still out of reach and individual charge carriers cannot be addressed with these methods. In the present contribution we show how to overcome these limitations by using scanning tunneling microscopy (STM) to inject current at the atomic scale and Hanbury Brown-Twiss (HBT) interferometry to measure photon correlations in far-field electroluminescence.

Quantum systems like molecules or quantum dots cannot emit two photons at the same time which results in an antibunching of the emitted photon train and a dip in the photon-photon correlation function. Such single photon emitters are key elements for quantum cryptography and their miniaturization to the nanoscale would be desirable. This requires reproducible emitter separations typically below the optical diffraction limit and has imposed strong limitations on suitable structures and materials.

Using our HBT-STM setup on localized trap states in C$_{60}$ multilayers we were able to study single photon emission at the ultimate molecular scale. Controlled injection allows us to generate excitons in C$_{60}$ and probe them with charges one by one. We demonstrate electrically driven single photon emission and determine exciton lifetimes in the picosecond range. Monitoring lifetime shortening and luminescence saturation for increasing carrier injection rates provides access to charge-exciton annihilation dynamics with Ångstrom spatial resolution. Comparison with theory reveals exciton quenching efficiencies close to unity. Our approach introduces a unique way to study single quasi-particle dynamics on the ultimate molecular scale.

2:40pm NS+EN+SS-TuA2 Low-Damage Etching Process for the Fabrication of GaAs based Light-Emitting Devices, *Cedric Thomas*, *A. Higo*, Tohoku University, Japan, *T. Kiba*, Hokkaido University, Japan, *Y. Tamura*, Tohoku University, Japan, *N. Okamoto, I. Yamashita*, Nara Institute of Science and Technology, Japan, *A. Murayama*, Hokkaido University, Japan, *S. Samukawa*, Tohoku University, Japan
Fabrication of quantum dots (QD) and their use for optical devices are still facing big challenges, for instance a high-density and three-dimensional array of QDs is hardly achieved. We report here the fabrication of stacked layers of GaAs QDs (called nanodisks, NDs) of less than 20 nm in diameter by a top-down approach and their optical characteristics when embedding in light emitting device.

The fabrication process consists of a bio-template [1] used to create a high density etching mask coupled to a low-damage etching process using neutral beam (NB) [2]. The bio-template is realized by a self-assembled monolayer (SAM) of proteins called ferritins (cage like proteins) of 12 nm outside diameter with a 7 nm iron oxide core. The proteins are functionalized with poly-ethylene glycol (PEG) to control the ferritin-to-ferritin distance and avoid any ND coupling after fabrication. After removing the protein shell by oxygen based treatment, a high-density (ca. 1x10^{11} cm^{-2}) nano-pattern of cores is used as etching mask. The NB etching consists of an inductively couple plasma chamber separated from the process chamber by a carbon electrode with a high aspect-ratio aperture array. Therefore, the charged particles are efficiently neutralized and the UV photons from the plasma almost completely screened

Stacks of GaAs and AlGaAs layers were grown by metalorganic vapor phase epitaxy (MOVPE), with a GaAs cap layer of a few nanometer thick. SAM of ferritins was done by spin-coating. After removing protein shell by

oxygen annealing in vacuum, a hydrogen radical treatment was performed to remove to remove the oxide layer. Etching was then realized by pure chlorine NB. Regrowth of AlGaAs barrier was done by MOVPE. Finally, temperature dependence of photoluminescence emission and ND light emitting diode were measured and results discussed [3].

[1] I. Yamashita et al., Biochim. Biophys. Acta 1800 (2010) 845

[2] S. Samukawa et al., Jpn. J. Appl. Phys. 40 (2001) L997

[3] A. Higo et al., Sci. Reports 5 (2015) 9371

3:00pm NS+EN+SS-TuA3 Surface Plasmon-Mediated Selective Deposition of Au Nanoparticles on Ag Bowtie Nano-Antennas, *Jingjing Qiu*, *D. Wei*, University of Florida
Utilizing intrinsic surface properties to selectively direct and control nanostructure growth on a nanostructure is fundamentally interesting and holds great technological promise. We observed a surface plasmon resonance (SPR)-induced selective deposition of gold nanoparticles (Au NPs) at the tip of a silver (Ag) bowtie nanostructure using 532 nm laser excitation. Nanoscale secondary ion mass spectrometry (NanoSIMS) was applied to chemically image the distribution of elements after deposition, reaching a spatial resolution of ~50 nm and an elemental analysis sensitivity of 50 ppm. Possible mechanisms underlying this selective deposition were proposed based on the experimental evidence and theoretical discrete dipole approximation (DDA).

3:20pm NS+EN+SS-TuA4 Broadband Light Trapping in Nanopatterned Substrates for Photovoltaic and Photonic Applications, *Carlo Mennucci*, Department of Physics, University of Genova, Genova, Italy, *C. Martella, M.C. Giordano, D. Repetto, F. Buatier de Mongeot*, University of Genova, Italy
Here we report on self-organised nanofabrication method applied to substrates of relevance in the field of optoelectronic and photonics in view of light trapping applications. We demonstrate the optical functionalization of glass [1], crystalline semiconductor (GaAS and Si [2]) and TCO substrates recurring to a self-organised pattern formation based on low-energy Ion Beam Sputtering (IBS). High aspect ratio nanoscale features are formed recurring to defocused IBS through a self-organised sacrificial Au nanowire stencil mask. Ion-beam irradiation at grazing angle leads to the formation of quasi-periodic one-dimensional nanostructures with a characteristic lateral size in the range of 200nm and a root-mean-square roughness (σ) of the surface, measured by Atomic Force Microscope, ranging from 80 to 150nm.

These nanostructures confer broadband anti-reflective bio-mimetic functionality to crystalline semiconductor substrates (GaAs and Si [2]) as well as to glass and TCO substrates in the Visible and Near Infra-Red part of the spectrum. In fact, suppression of the reflected light intensity is due to high aspect ratio sub-wavelength features which leads to a progressive transition of the refractive index from the value of air to that of the substrate (index grading) analogous to that observed in the corneas of nocturnal moths. At the same time the patterned substrates have shown enhanced broadband light scattering due to the extended vertical dynamic of the surface corrugations with lateral size comparable or bigger than light wavelength. Moreover, Angular Resolved Scattering measurements has recently proved that nanostructured glasses can scatter light in the Visible and Near Infra-Red range of spectrum more efficiently and at wider angles with respect to standard Ashai-U substrates commonly used in optoelectronic device applications.

In order to asses the light trapping effect, identical amorphous thin film silicon solar cells (p–i–n single junctions) are grown on nano-patterned and on reference flat glass superstrates.Their performance is assessed by measuring their I–V characteristic and EQE under standard AM1.5g test conditions. The first encouraging results demonstrated that solar cells grown on patterned substrates with RMS roughness σ around 80 nm exhibit a 15% relative enhancement in photocurrent.

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4:20pm NS+EN+SS-TuA7 *In Situ* **Visualization of Intercalation-Driven Nanoparticle Phase Transitions using Plasmon-EELS**, *Jennifer Dionne*, Stanford University **INVITED**
A number of energy-relevant processes rely on nanomaterial phase transitions induced by solute intercalation. However, many of these phase transitions are poorly understood, since observing them in nanomaterials – and in particular in individual nanoparticles – can be extremely challenging. This presentation will describe a novel technique to investigate intercalation-driven phase transitions in individual nanoparticles, based on *in-situ* environmental transmission electron microscopy (TEM) and plasmon electron energy loss spectroscopy (EELS). As a model system, this presentation will focus on the hydrogenation of palladium nanoparticles. We use the plasmon-EEL signal at varying hydrogen pressures as a proxy for hydrogen concentration in the particle. First, we investigate the hydriding properties of single-crystalline particles, free from defects and grain boundaries, and free from elastic interactions with the substrate. We obtain single particle loading and unloading isotherms for particles ranging from approximately 10 nm to 100 nm, allowing us to address outstanding questions about the nature of phase transitions and surface energy effects in zero-dimensional nanomaterials. We find that hydrogen loading and unloading isotherms of single crystals are characterized by abrupt phase transitions and macroscopic hysteresis gaps. These results suggest that thermodynamic phases do not coexist in single-crystalline nanoparticles, in striking contrast with ensemble measurements of Pd nanoparticles. Then, we extend our single-particle techniques to explore the hydriding properties of polycrystalline and multiply-twinned nanoparticles, including Pd nanorods and icosahedra. In contrast to single crystalline nanoparticles, these particles exhibit sloped isotherms and narrowed hysteretic gaps. Based on these results, we develop a model to deconvolve the effects of disorder and strain on the phase transitions in nanoscale systems. Lastly, we describe techniques to generate high-resolution plasmon-EELS (and hence phase) maps of nanoparticles. These mapping studies promise unprecedented insight into the internal phase of nanomaterials, and can be complemented with diffraction and dark-field imaging studies. We will discuss how these results could be used to interpret the thermodynamics of Li-ion insertion in battery electrodes, hydrogen absorption in state-of the-art metal hydride catalysts, or ion exchange reactions in quantum dot syntheses.

5:00pm NS+EN+SS-TuA9 Pulsed Laser-Induced Self-Assembly of Noble Metal Nanoparticles and an EELS Characterization, *Yueying Wu*, University of Tennessee, *G. Li*, University of Notre Dame, *C. Cherqui, N. Bigelow*, University of Washington, *J.P. Camden*, University of Notre Dame, *D. Masiello*, University of Washington, *J.D. Fowlkes,* Oak Ridge National Laboratory, *P.D. Rack*, University of Tennessee
Controlled nanoscale synthesis of plasmonic nanostructures based on noble metals is critical for realizing many important applications such as surface-enhanced Raman spectroscopy (SERS), subwavelength waveguides, plasmonically enhanced photovoltaics, and photocatalysis. Recently pulsed laser induced dewetting (PLiD) has been shown to be an intriguing self and directed assembly technique for elemental and alloyed metallic nanoparticles. The liquid-phase assembly takes place in single to tens of nanoseconds and is governed by liquid phase instabilities and hydrodynamics of liquid thin films which produce arrays of random or highly ordered nanoparticles. In our recent studies, the PLiD of un-patterned, as well as nanolithographically pre-patterned thin films of various shapes and sizes was investigated for the purpose of understanding how initial boundary conditions facilitate precise assembly. The resultant ultra-smooth and metastable nanoparticles (~20nm to 1μm) are expected to be ideal building blocks for plasmonic applications. Based on this, we present a study on the self-assembly of gold and silver alloy thin films and also provide a comprehensive characterization of the resultant nanoparticles using electron energy loss spectroscopy (EELS) and through simulation using full-wave electron-driven discrete-dipole approximation (e-DDA). The study provides for the first time a thorough mapping of the plasmonic modes of synthesized Au-Ag alloy nanoparticles over a large size range.

5:20pm NS+EN+SS-TuA10 Flexible, Adaptive Optoelectronic Camouflage Skins Using Concepts Inspired by Cephalopods, *Cunjiang Yu*, University of Houston
Octopus, squid, cuttlefish and other cephalopods exhibit exceptional capabilities for visually adapting to or differentiating from the coloration and texture of their surroundings, for the purpose of concealment, communication, predation and reproduction. Long-standing interest in and emerging understanding of the underlying ultrastructure, physiological control and photonic interactions has recently led to efforts in the construction of artificial systems that have key attributes found in the skins of these organisms. In spite of several promising options in active materials for mimicking biological color tuning, such as cholesteric liquid crystals, electrokinetic and electrofluidic structures, colloidal crystals and plasmonics, existing routes to integrated systems do not include critical capabilities in distributed sensing and actuation.

The results reported here show that advances in heterogeneous integration and high performance flexible/stretchable electronics provide a solution to these critical sub-systems when exploited in thin multilayer, multifunctional assemblies. The findings encompass a complete set of materials, components, and integration schemes that enable adaptive optoelectronic camouflage sheets with designs that capture key features and functional

capabilities of the skins of cephalopods. These systems combine semiconductor actuators, switching components and light sensors with inorganic reflectors and organic color-changing materials in a way that allows autonomous matching to background coloration, through the well-known working principle of each device.

Demonstration devices capable of producing black-and-white patterns that spontaneously match those of the surroundings, without user input or external measurement, involve multilayer architectures of ultrathin sheets of monocrystalline silicon in arrays of components for controlled, local Joule heating, photodetection and two levels of matrix addressing, combined with metallic diffuse reflectors and simple thermochromic materials, all on soft, flexible substrates. Systematic experimental, computational and analytical studies of the optical, electrical, thermal, and mechanical properties reveal the fundamental aspects of operation, and also provide quantitative design guidelines that are applicable to future, scaled embodiments.

5:40pm **NS+EN+SS-TuA11 Controlled Deposition of High Quality Nanocrystal Multilayer Structures for Optoelectronic Applications**, *Sara Rupich, A.V. Malko, Y.N. Gartstein, Y.J. Chabal*, University of Texas at Dallas

In order to meet the world's growing energy demand, harvesting energy from the sun is necessary. While silicon-based solar cells remain the industry standard, hybrid Si/nanocrystal (NC) structures exhibit significant promise for the development of the next generation of photovoltaic devices. In most current NC-based photovoltaics, photons are absorbed, separated and extracted in the NC layer; however, conversion efficiencies are limited by interface quality and carrier mobility. Hybrid Si/NC structures offer an alternative approach. In these structures, light is absorbed in the NC layer and transferred via efficient excitonic radiative (RET) and non-radiative (NRET) energy transfer into the underlying Si substrate where charge extraction and collection occurs. In order to utilize such structures, the controllable deposition of tens of layers of NCs needs to be realized where the composition of each layer can be varied. While many techniques exist to deposit NCs on substrates (i.e. spin coating, dropcasting), these methods result in thick films with limited control over the composition. Composition controlled structures need to be built up one layer at a time.

Here, we present the controllable deposition of dense, NC multilayer structures on Si and SiO$_2$ substrates via evaporation-driven self-assembly at the air-liquid interface. Using a layer-by-layer approach, CdSe/ZnS NC multilayers were assembled, up to 15 layers in thickness. Extensive spectroscopic (UV-vis absorbance, photoluminescence (PL), ellipsometry) and microscopic (scanning electron microscopy and atomic force microscopy) characterization provided evidence for the successful deposition of high quality NC multilayers in each cycle. Additionally, the NCs were found to retain their quantum yields in the multilayers structures indicating that the deposition process does not introduce additional interface trapping centers and showing their promise for integration into optoelectronic devices. Using time-resolved PL measurements, a gradual increase in the average measured NC PL lifetime was observed as a function of layers for NC multilayers on Si surfaces. This behavior was confirmed by theoretical modeling and is indicative of the gradual reduction in ET efficiency as a function of distance and.

As this process is applicable to NCs of different size, shape and composition, the fabrication of band gap graded multilayers structures is possible, which would enable energy harvesting schemes based on directed energy flows.

6:00pm **NS+EN+SS-TuA12 Efficient Coupling of Visible Light to Thin Film Waveguides; FDTD Field Model Results for Nanometer Scale Graded Index/Waveguide Structures.**, *Adam Lambert, E. Demaray*, AVS

Previous work utilizing Finite Difference Time Domain (FDTD) models with 20 nm resolution demonstrated normal incident plane wave AM 1.5 solar light could be coupled and concentrated into modes of a lateral duct with ~ 91% efficiency for tapered concentrator with spatially uniform refractive index. However, for efficient coupling and mode compression into high index waveguides in advanced devices, continuously graded index films on the order of 150-200nm with nonlinear profiles have been shown to be near ideal anti-reflective coatings which Antropy Technology can now produce at high volume using modern sputter coating processes. Such devices could be revolutionary not only in the field of photonics, but could also open the path for an wide variety of green energy and advanced lighting applications. This presentation focuses on current advances in the parametric investigation of nonlinear refractive index profiles and related sputter coating production processes. The FDTD problem solving framework provides the fully resolved time dependent propagation of the electromagnetic field, accounting for the nonlinear influence of subwavelength structures and allowing for detailed design of the thin film product. We are reporting resolution capabilities are in the 1-5nm range depending on the relevant length scales for the process. Quantification of power, absorption/heat, and other variables relevant to R&D can easily be extracted during post processing. Parallel Monte Carlo simulations predict the refractive index profile resulting from dual source, inline, biased pulse DC sputter coating. The combination allows for highly accurate feasibility studies and front end process design. Both quantified numerical results as well as qualitative animations of the influence of the subwavelength devices are presented for both processes, as well as a detailed overview of the potential applications.

Nanometer-scale Science and Technology
Room: Hall 3 - Session NS-TuP

Nanometer-scale Science and Technology Poster Session

NS-TuP1 Characterization of Nanodiamonds with Nitrogen Vacancy Centers for Optically Detected Magnetic Resonance in Biological Applications, *Molly May*, University of Colorado at Boulder, *K. Briggman*, National Institute of Standards and Technology (NIST)
The unique chemical, optical, and spin properties of nitrogen vacancy centers in nanodiamonds make them a promising new material for biological sensing. They exhibit strong, stable fluorescence at room temperature and can be used to interrogate the spins of local molecules via optically detected magnetic resonance (ODMR) in biological environments. Successful implementation of ODMR requires control of the size and surface chemistry of the nanodiamonds as well as determination of the numbers and locations of the nitrogen vacancy centers. We report a process for disaggregating commercially available detonation nanodiamonds and we characterize and modify their surface chemistries. Furthermore, we measure the fluorescence and spin properties of the nitrogen vacancy centers and describe our progress toward constructing a multimodal (optical with microwave) platform for performing ODMR using nanodiamonds in living cells.

NS-TuP2 Understanding the "Click Chemistry" Approach to Achieve High-Coverage, High-Precision Nanostructures Deposited on Solid Surfaces, *Mackenzie G. Williams*, *A.V. Teplyakov*, University of Delaware
The use of layered nanostructures as a platform for surface reactions requires the ability to maintain precise control over the architectural structure and surface chemistry. The use of a copper(I)-catalyzed cycloaddition between azide and alkyne moieties to build such structures has been amply reported. This "click reaction" allows selective covalent attachment but the development of a layered structure in which each layer consists of a single layer with a coverage close to 100% has yet to be reported. In the present work, gold substrates were functionalized with terminal azide groups and silica nanoparticles of different sizes were functionalized with either alkyne or azide groups. This approach allows for a simple verification of a full monolayer deposition via microscopy. In a sonication-assisted "click reaction", a monolayer of the alkyne-terminated nanoparticles was attached to the substrate. The formation of the monolayer was confirmed by scanning electron microscopy (SEM) and the calculated surface coverage, close to 95% compared to the absolute maximum, was much higher than those reported in literature for similar systems. Atomic force microscopy (AFM) was used to verify that a single layer of nanoparticles was produced instead of a well-ordered stack of multiple layers. A focused ion beam (FIB) was used to cut into the sample and confirm the nanoparticle layer height by SEM. Subsequent "click reactions" with alternating alkyne- and azide-modified silica particles formed high-coverage multilayer structures. In a separate set of experiments, iron oxide nanoparticles were modified with alkyne groups and were "clicked" onto a gold substrate. The chemical attachment was followed by attenuated total reflectance infrared (ATR IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) and compared to predicted spectra obtained through density functional theory (DFT) calculations to confirm completion of the "click reaction". The improved control and surface coverage over previously-reported systems is thought to result in part from the sonication-assisted attachment, in contrast to typical procedures that include stirring or dip-coating to promote attachment. The mechanism of attachment, specifically the catalyst intermediate, is also thought to play a role in the nanoparticle attachment density. DFT investigations into the stability of the intermediate were used to determine how the functionalization scheme of the starting materials may affect surface coverage. This work outlines modifications to a commonly-practiced attachment procedure that provide unparalleled surface coverage and control over individual layers of the nanostructures produced.

NS-TuP3 FIB Technique for PVTEM Sampling of MESH Capacitor, *Sungho Lee*, Samsung Electronics, Republic of Korea, *C.W. Yang*, Sungkyunkwan University, Republic of Korea
As the semiconductor device feature size continues to be scaled down, the aspect ratio of the capacitor becomes higher to satisfy the high capacitance requirement for cell operation. The higher the height of capacitor, the more storage node bent. Therefore, we adopt the Mechanically Enhanced Storage node for virtually unlimited Height (MESH) [1] process to prevent storage node's bending nowadays. However, even with this process, there are failure problems and the yield is still less than 100%. To find methods to prevent these problems, the failures should be analyzed. Normally physical failure analysis (PFA) needs a site specific transmission electron microscopy (TEM) sample which is vertically cross-sectioned by using focused ion beam (FIB) [2], but sometimes a plan-view TEM (PVTEM) sample [3] is also required to clarify the exact cause of failure .

The nodes do not stand in a line after conventional FIB work for PVTEM sampling. The node may fall off a TEM thin foil sample in the worst case. In order to overcome this problem, we developed new FIB technique for PVTEM sampling of MESH capacitor. The new FIB technique comprises four major steps:

Step 1 : '1' shape marking at the target height

Step 2 : milling a top part of capacitor

Step 3 : carbon deposition to fill the space between nodes

Step 4 : milling a bottom part of capacitor

Conventional FIB work consists of step1, 2, and 4. We add a carbon deposition step right after the 2nd step of the top part milling. We found that the nodes seem to move during the 3rd step milling (mill a bottom part) because of the void between nodes.

We adopted this modified milling method to the TEM sampling of a real failure case and obtained a PFA result of a 2 bit failure using plan-view TEM image. The new modified milling method turned out to be very effective and can be adopted in a mass production.

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NS-TuP5 A Simple Fabrication of Nano-Pillar Structures by Contact Block Copolymer Technique, *Hwasung Kim*, Samsung Electronics, Republic of Korea, *J.W. Park, D.H. Yun, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea
Recently, the formation methods of nano-structured materials are intensively investigated for next-generation devices such as chemical sensor, optical sensor, field effect transistor, and solar cell. The diameter, spacing, and shape of the nano-structured materials are very important in the devices because they control the device performance such as the electrical and optical properties. In this study, the silicon nano-pillar structures were fabricated by a contact block copolymer (BCP) technique which is a potential technique for the fabrication of self-aligned nanoscale structures. For the contact BCP technique, a nanometer scale BCP pattern such as hole and line pattern was formed on the silicon surface and the BCP masked silicon was exposed to nitrogen ion beam for the surface nitriding. Using the nitride surface, after the removal of the BCP mask, the silicon nano-pillar structures could be successfully fabricated using chlorine-based ion beam. This technique provided a method of forming a silicon nanostructure using simplified process steps by removing additional step of the mask deposition and etching. Especially, due to the extremely low thickness of the nitride mask layer, precise transfer of the mask dimension to silicon was possible. The use of low-energy ion beam could minimize the damages on the nano-pillar silicon surface in addition to the increase of etch selectivity.

NS-TuP6 A Calculation of the Virtual Source Size of Electron Gun using Digital Image Processing Techniques, *Cheolsu Han*, Korea Basic Science Institute, Republic of Korea, *B. Cho*, Korea Research Institute of Standards and Science, Republic of Korea, *J.-M. Jeong, J-G. Kim*, Korea Basic Science Institute, Republic of Korea
An electron microscope (EM) such as a scanning electron microscope or a transmission electron microscope are powerful tools in nanometer science and technology.[1,2] There are important parameters such as a resolution and a probe current in the EM.[2] The optical parameters of an electron source such as a virtual source size and a brightness are strongly relate to the parameters and a performance of the EM. These parameters can be used to design the optical system of EM such as a condenser and an objective lenses and calculate a magnification and a probe current. In order to design an optical system, we have to find the optical parameters of the electron gun. In this work, we describe how to calculate the virtual source size.

To calculate the virtual source size, a homebuilt electron gun testing system (HEGTS) have been developed. Electron beam images have been obtained

by the HEGTS which includes an electron gun with tungsten hairpin filament, a movable aperture, and imaging system with CCD camera. Digital image processing techniques such as a noise rejecting filter, a binary image, a pixel operation method, and etc. have been used to calculate the virtual source size.[3] And a shadow-image technique also have been used.[4] An apparent edge sharpness of the shadow image is determined by the source size. A distance between 25% and 75% of a maximum intensity of electron beam profile can be used to calculate the size.

To obtain the electron beam images by CCD camera (1,600x1,200 pixels), we used a W hairpin filament at a vacuum pressure of 5.5×10^{-5} Pa. In order to accelerate the generated electron beam, the electron gun system is floated at -10 kV and the filament is heated by adjusting the current flow. A virtual source position was obtained by the movable aperture (100 um) and the beam images. Finally, we calculated the virtual source size of 44.2 um under the conditions.

We demonstrate how to calculate the virtual source size using the homebuilt electron gun testing system without a scanning coil and a secondary electron detector.

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NS-TuP7 Transport Properties of Ge Nanocrystals Embedded within a SiO$_2$ Matrix Produced by RF Sputtering, *A. Hernandez-Hernandez,* Universidad Autonoma del Estado de Hidalgo, Mexico, *A. Garcia-Sotelo, E. Campos,* **Salvador Gallardo-Hernandez,** Cinvestav-IPN, Mexico, *J.L. Enriquez-Carrejo, P.G. Mani-Gonzalez, J.R. Farias-Mancilla,* Universidad Autónoma de Ciudad Juárez-IIT, Mexico, *M. Melendez-Lira,* Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Mexico

The characteristics of germanium, mainly its compatibility with silicon technology, and the sensitivity of its band structure to confinement confer a high attractive to the synthesis of germanium nanostructures. The samples were prepared on p-type Si (1 1 1) substrates by reactive sputtering. Structural characterization was carried out by grazing angle X-ray diffraction. Surface roughness was quantified by atomic force microscopy and correlated with micro Raman spectroscopy imaging. X-ray diffraction showed the amorphous characteristics of the heterostructures. Micro-Raman mapping allow to obtain the Ge nanocrystals distribution. XPS indicates that there is a transition layer with a gradual composition around Ge nanocrystals. SIMS results are well correlated with the Ge depth distribution observed by micro-Raman imaging. IvsV and spectral response results are correlated with the size and spatial distribution of Ge nanocrystals.

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NS-TuP8 Nanoparticles Produced by Laser Ablation in Liquid Enviroment, *LuisAlberto Hernández-Hernández,* Instituto Politécnico Nacional, Mexico, *A. Hernández-Hernández,* Universidad Autónoma del Estado de Hidalgo, Mexico, *F. De Moure-Flores,* Universidad Autónoma de Querétaro, Mexico, *J.G. Quiñones-Galván,* Universidad de Guadalaja, Mexico, *M. Meléndez-Lira,* CINVESTAV-IPN, Mexico

The formation of ZnS, ZnO, Ge, Si and SiGe alloy nanoparticles under laser ablation of solid targets in liquids environment is reported. The use of an Nd:YAG laser allow high rate of nanoparticles formation as a solution. The nanoparticles are characterized by X-ray diffraction (XRD), UV-Visible transmission spectroscopy and transmission electron microscopy (TEM). The nanoparticles size dependence on both the laser fluence and the nature of the liquid is studied. In some cases, nanoparticles of compounds are formed via reaction of the target whit the liquid.

NS-TuP9 Enhanced Photoresponse of a Metal-Oxide-Semiconductor Photodetector with Germanium Nanocrystals Embedded in the Silicon Oxide Layer, *Arturo Hernández-Hernández,* Universidad Autónoma del Estado de Hidalgo, México, *L.A. Hernández-Hernández,* Escuela Superior de Física y Matemáticas del Instituto Politécnico Nacional, Mexico, *F. De Moure-Flores,* Universidad Autónoma de Querétaro, México, *J.G. Quiñones-Galván,* Universidad de Guadalajara, Mexico, *B. Marel Monroy, G. Santana-Rodríguez,* Universidad Nacional Autónoma de México, *M. Melendez-Lira,* Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Mexico

In this work we report a two-terminal metal-oxide-semiconductor photodetector for which light is absorbed in a capping layer of germanium nanocrystals embedded in a silicon oxide matrix grown on p -type silicon substrates. Operated at direct and reverse bias photoresponse from 900 to 1300 nm was observed. Also, we report on the effect of nanocrystal size on the photocurrent. The highest optoelectronic conversion efficiency was observed in samples with smaller germanium nanocrystals. This effect were explained by a transistorlike mechanism, in which the inversion layer acts as the emitter and trapped positive charges in the dielectric layer assist carrier injection from the inversion layer to the contact, such that the primary photocurrent could be amplified.

NS-TuP11 Clarifying the Role of Surface Chemistry in Fabrication of Large Nanostructured Surfaces using Ion Irradiation, *Kayla Steeves Lloyd, I.L. Bolotin, M. Majeski,* University of Illinois at Chicago, *M. Schmeling,* Loyola University Chicago, *L. Hanley, I. Veryovkin,* University of Illinois at Chicago

Formation of hexagonally ordered nanodots on GaSb surfaces during ion sputtering in the late 1990s has invigorated interest in using low energy ion irradiation for nanostructuring and functionalization of material s surfaces. However, the underlying physical phenomena behind this technique remain poorly understood, leaving many questions about the mechanisms of nanostructure formation via ion irradiation unanswered. This dearth of understanding stems in part from the fact that research in this area has focused thus far primarily on surface structure, and not surface chemical composition. A surge of interest toward the role chemical processes play in forming morphology of surfaces irradiated by ion beams is evidenced by a series of recent works on surfactant sputtering and silicide induced ion beam patterning. In view of this growing interest, we report herewith experimental results on surface nanostructuring of Si via irradiation by low energy inert gas ions in various arrangements featuring co-deposition of impurity atoms on irradiated surfaces in order to "seed" the formation of nanostructures. These atoms were sputtered from smaller targets of various geometries placed close to Si samples. Such arrangements allow for controllable variation of the fluence, impact energy, and incidence angle of bombarding ions as well as of the surface concentration of impurity atoms. Instead of focusing on previously well studied fine nanoripple and nanodot patterns, this work concentrates on courser surface morphologies obtained at fluences nearing 10^{19} ions/cm^2. These ion-irradiated nanostructured samples have been comprehensively characterized by structure-sensitive (SEM, AFM and XRD) and composition-sensitive (XPS and TXRF) experimental techniques in order to better understand the interplay between chemical composition and structure of their surfaces. It has been confirmed that the nanostructured surfaces were much easier obtainable via the "seeding" approach. Moreover, using Si as the "seeding" target failed, in contrast to Cu and stainless steel targets that helped produce feather-like arrays of tilted amorphous nanopillars/nanocones homogeneously covering large surface areas exceeding 100 mm^2. This necessity of using certain metal surfactants for nanostructure formation proved the importance of surface chemistry in formation of the surface structure under ion irradiation. Experimental results on surface processing with low energy ion beams and compositional-versus-structural characterization obtained in this work will be discussed and interpreted in our presentation at the Meeting.

NS-TuP13 Nitrogen Vacancies in Nanodiamond As Nanoscale Probes in Complex Environments, *Margaret Robinson, J. Ng, H. Zhang, Z. Ma, R. Goldsmith, R.J. Hamers,* University of Wisconsin-Madison

The unique optical properties of nitrogen vacancies (N$_V^-$) in nanodiamond offer an opportunity to probe charge, spin, and other local properties in complex environments at the single-particle level. The intensity of fluorescence from N$_V^-$ centers can be modulated by the application of a microwave field. In complex, heterogeneous systems this ability to selectively modulate the intensity of N$_V^-$ centers using microwaves can be used to discriminate between fluorescence due to nanodiamonds and fluorescence arising from other sources. Here, we describe experiments aimed at understanding the factors that control the ability to read out N$_V^-$ center fluorescence and reject background fluorescence. We have characterized the optical response of N$_V^-$ centers in diamond nanoparticles having different diameters and bearing different numbers of N$_V^-$ centers using photoluminescence, fluorescence lifetime, and single-particle

microscopy. Results of N_v-center modulation via applied microwave fields will be described, along with an analysis of the signal-to-noise parameters for optimization of N_V^- centers as probes of the charge, spin, and other local properties in complex materials systems.

NS-TuP14   Dielectrophoresis (DEP)-Aligned Carbon Nanotubes for Fabricating Electronic Devices, *John Elike*, *Z. Xiao*, Alabama A&M University

We report the fabrication of carbon nanotube field-effect transistors (CNTFETs)-based inverter and ring oscillator electronic circuits. The dielectrophoresis (DEP) method was used to align and deposit single-walled carbon nanotubes for fabricating the electronic devices. The electrical property of fabricated CNTFET-based devices was measured. The CNTFET-based inverter shown excellent electrical transfer characteristics, while the CNTFET-based ring oscillator demonstrated oscillation characteristics, denoting that the CNTFET-based circuits can function well for the application of electronic circuits.

NS-TuP15   Preparation, Characterization, and Optical properties of Al Doped Vanadium Pentoxide Nanowires, *Chen-Chuan Chang*, National Tsing Hua University, Taiwan, Republic of China, *M.W. Huang*, Chinese Culture University, Taiwan, Republic of China, *H.C. Hsih*, National Chung Hsing University, Taiwan, Republic of China

Al doped Vanadium pentoxide nanowires were synthesized via a rheological phase reaction on Si (100) substrate by self-assembled process using solid precursors of vandium powders (V2O2 99.5%) in an Ar atmosphere (5×10^{-2} Torr, 10 sccm) at 800 °C in a horizontal quartz tube furnace. The nanowires with high yields were obtained in the whole substrate, have a length of several micrometers and diameter of 50 and 100 nm. XRD and TEM analysis show an orthorhombic crystal structure growing along direction [020] with sharp diffraction peaks at (010) and (020). XPS patterns showed three conspicuous binding energy peaks of nanorods is characteristics of vanadium in the +5 oxidation state which is well consistent with the value of V2O5 structure. Micro-Raman spectroscopy was also used to investigate the vibrational modes of the nanowires. Thermal CVD process can be expected to serve as a practical and general method to synthesize metal oxide nanowires in a large scale.

NS-TuP16   Formation of Ag Nano-net for Application to Flexible Electronics, *J.W. Fang, J.K. Wu, Dung-Ching Perng*, National Cheng Kung University, Taiwan, Republic of China

Electronics built on flexible substrate creates a wide range of exciting consumer products. Many of the developed or under developed flexible electronics, such as displays, sensors, solar cells and artificial electronic skin, are based on very thin organic or polymer substrates and some may suitable for roll-to-roll manufacturing. The ability of bending, rolling, and elastically stretching defines the electronics' degree of flexibility. The structure of a generic electronics is composed of a substrate, back-electrode, active layers, front-electrode, and encapsulation. To make the structure flexible, all components must bendable to some degree without losing their function. However, in-organic thin film materials used for building the device layers are rigid and brittle. They often result in peeling, cracking or rupture when devices are subjected to mechanical strain and/or thermal stress. In the case of flexible CuInSe2-based solar cells, one of the challenge tasks is to improve cracking or rupture issues of the Mo back-contact. In our previous studies, the Mo layer deposited on polyimide (PI) substrate showed that the Mo layer will not crack until the PI substrate curving to 20 mm in diameter either tensile or compressive stress applied.

Silver possesses the highest electrical conductivity of any element and the highest thermal conductivity of any metal. Silver is also a very ductile and malleable element. Its plasticity properties capable of extent or deform without fracture. Embedded Ag nanowires (NWs) into transparent conducting oxide (TCO) films, such as AZO or ITO, has been intensively studied recently. However, the Ag NWs are just stacked together, the junction resistance of the two Ag NWs is larger than 1G ohms. Lower junction re-sistance and junction reliability need to be further improved for its application to reliable flexible electronics.

Ag atoms can migrate easily from (100) to (111) surface to lower its surface energy upon annealing. The Ag NWs are fused at the junctions after thermal annealing. The surface migration can happen as low as 90ºC. The Ag NW splits into several dome-shaped Ag nano-particles if over-annealing is performed. Conditions for forming Ag nano-net (NN)with fused junctions are studied using tube furnace and rapid thermal annealing systems. NW density, temperature, and annealing time are the key factors affecting Ag NN's formation. When embedding in Al2O3-doped ZnO film, a 40-80% (dep. on NW density) further reduction in film resistivity can be achieved as compare fused NW junctions to that of non-fused junctions. Developing of Ag NN and all other detailed results will be presented in the conference.

NS-TuP17   Nichrome Nano-Pillars formed by using Plasma-Assisted GLAD, *Dean Walters*, Argonne National Laboratory

Glancing angle deposition has already made a place for itself by being a simple process for making 1-D nano-structures such as rods and pillars. Since the structures are formed as an array built up on a substrate they can be directly applied to applications such as battery anodes, electron emitters, and gas sensors. Why this technique is applicable to a variety of metals and compounds this study focuses on Nichrome A which is an alloy of 80% nickel and 20% chromium which has useful deposition characteristics at room temperature.

The resulting structures that are made by using magnetron sputtering with the addition of plasma assistance will be presented. The purpose of the plasma assistance will be to assess its ability to alter the surface migration of adatoms with the goal of changing the width of the pillar by a means other than temperature. SEM and other results comparing nano-pillars made with and without plasma assistance will be presented.

NS-TuP18   A New Alternative for Silicon Thinning using NH4OH Solution Wet Etching for 3D MOS Transistors, *G.M.B. Soares, A.R. Silva, F.H. Cioldin, L.C.J. Espíndola, J.G. Filho, Ioshiaki Doi, J.A. Diniz*, University of Campinas, Brazil

Tetramethylammonium hydroxide (TMAH) aqueous solutions, which are the silicon orientation-dependent wet etching, have been used for silicon thinning to get silicon nano (SiNWs) or sub-micron (SiSMWs) wires. These wires can be used as the conduction channel for three-dimensional (3D) Metal-Oxide-Silicon (MOS) transistors, such as FinFETs and JunctionLess, respectively. In this work, instead of TMAH, ammonium hydroxide (NH4OH) solutions (concentration of 9% wt) are used to get SiNWs and SiSMWs, because also these solutions are silicon orientation-dependent wet etching. Furthermore, NH4OH solutions are cheaper and fully compatible with CMOS technology. Silicon wafers with (100) crystallographic orientation were used. On these wafers, after RCA cleaning, 330 nm thick SiO2 layer was grown using thermal oxidation. Lithography, SiO2 etching (using HF solution) and organic cleaning (to remove photoresist) steps were carried out to define lines of SiO2 (masking oxide) with width of 3 μm and spacing of 7 μm between lines. Reactive Ion Etching with SF6 plasma was carried out, resulting in silicon three-dimensional (3D) mesa structures under SiO2 lines. The 3D mesa sidewalls are the <110> planes and the Si surface between the mesa structures are the <100> plane. After anisotropic etching using NH4OH solution, Optical (OM) and Scanning Electron (SEM) Microscopy analysis were used to get images of top and side views of samples. The results presented that the <111> planes of Si surface with (100) crystallographic orientation between the mesa structures (spacing of 7 μm) were exposed, resulting a V-groove shape, while, the lateral etching under SiO2 of <110> plane mesa sidewalls occurred, with consequent thinning of these 3D structures. Using the etching process time and 3D structure measurements extracted from OM and SEM , the lateral etch rate under SiO2 of <110> plane mesa sidewalls of 110 nm/min was obtained. It is important to notice that the sidewalls are smooth, which is a mandatory requirement to fabricate SiNWs and SiSMWs for 3D conduction channel for FinFETs and JunctionLess transistors. Thus, using our method to get silicon thinning with NH4OH solution, both devices have been fabricated on Si and SOI wafers, with (100) crystallographic orientation surfaces, respectively. On both wafers, the lateral etch rate under SiO2 of <110> plane 3D mesa sidewalls of 110 nm/min was repeated and SiNWs and SiSMWs were obtained, indicating that our NH4OH solution is a new alternative to get 3D nanostructures on Si substrates. The electrical characteristics of these devices are going to present in the conference.

NS-TuP19   Design and Development of a Microfluidic Device for the Synthesis of Bioconjugated Lipidpolymer Hybrid Nanoparticles, *Eri Takami*, San Jose State University

In recent years, lipid -polymer hybrid nanoparticles have gain attention as an efficient drug delivery device to treat various diseases, including cardiovascular disease, tuberculosis, and cancer. To synthesize lipid-polymer hybrid nanoparticles in a simple, efficient manner, we designed and developed a microfluidic device that utilizes a three channel pathway and a mixer channel. We prepared the microfluidic wafer using soft lithography techniques; with a negative masked designed with AutoCAD, we exposed UV light onto photoresist on a silicone wafer to outline the channels of the device. We then molded the microfluidic device using polydimethlsiloxane (PDMS) as the primary material for the fluid flow channels. The PDMS mold of the device was bonded to glass using plasma bonding in a vacuum chamber. The prepared microfluidic device can be customized to synthesize nanoparticles of different size, different encapsulated drug, and different surface functionalization. The production of higher quality nanoparticles in an efficient manner using our microfluidics device can expedite the research and development process of drug delivering lipid polymer hybrid nanoparticles.

NS-TuP20 Integration of Fe3O4 Nanoparticles on Graphene Oxide Assisted by Ultrasound for Electrochemical Supercapacitors, *Jeseung Yoo, Y.-S. Seo*, Sejong university, Republic of Korea

Fe_3O_4-reduced graphene oxide (rGO) composite has been developed for electroactive materials for supercapacitor due to its synergistic effects between them. Integration of Fe_3O_4 nanoparticle on GO has been usually done based on by precipitation, chemical binding, and charge interaction. In the process, oxygen-containing functional groups on GO act as a template for binding the nanoparticles. Therefore rGO prepared by low temperature or chemical methods for supercapacitor electrodes applications would inevitably possess some part of oxygen, which reducing supercapacitor performance because of charge transfer resistance. Here we developed an integration method assisted by ultrasound where hydrophobic nanoparticle forms hydrophobic bonding to hydrophobic part on graphene oxide. Chemical structure of the composite was confirmed by UV-vis spectrometer, FTIR, and Raman scattering, and its morphology was monitored by TEM, SEM, and XRD. We tested the stability of the composite by cathodic potential cycling and defined the specific capacitance.

NS-TuP21 Graphene Quantum Dot-Titania Nanoparticle Composite As Photoanode in Photoelectrochemical Cells, *Sowbaranigha Chinnusamy Jayanthi, R. Kaur, F. Erogbogbo*, San Jose State University

A composite material is synthesized using graphene quantum dots (GQDs), titania nanoparticles (TiO2) and Polyvinyl alcohol (PVA) as the binder. A thin film of the hybrid paste is spin coated on an ITO substrate. The GQDs are synthesized by wet chemical method using bird charcoal and are non-toxic and inexpensive. The effect of concentration, pH, and size of the GQDs on the photo catalytic properties of titania are studied. GQDs exhibit optical absorptivity; photoluminescence and band gap tunability depending on the size and have the potential to enhance the photocatalytic properties of titania. In particular the hybrid combination is expected to decreases the recombination of charge carriers, increases mobility of the charge carriers and helps to improve the overall photo-conversion efficiency. The size and structure of the composite material are studied using analytical characterizations techniques such as Scanning Electron Microscope (SEM) image, Atomic force microscope (AFM) and X-ray diffraction patterns (XRD). Electrical/electronic performance of the composite photocatalyst is studied using photocurrent density measurements that are obtained from Photoelectrochemical cell (PEC) experiment. Photoluminescence (PL) spectrum, and UV-vis transmission spectrum results aid in understanding the optical-electrical properties. The use of this combination of materials is novel in photo electrochemical (PEC) water splitting application and has implications for efficient and cost effective solar fuel cells.

2D Materials Focus Topic
Room: 212C - Session 2D+MN+NS+SP+SS+TF-WeM

Mechanical and Thermal Properties of 2D Materials
Moderator: Oleg Yazev, Ecole Polytechnique Fédérale de Lausanne (EPFL), Petra Reinke, University of Virginia

8:00am 2D+MN+NS+SP+SS+TF-WeM1 Mechanical Properties of Polycrystalline Graphene, *Joseph Gonzales*, University of South Florida, *R. Perriot*, Los Alamos National Laboratory, *I.I. Oleynik*, University of South Florida
Experimental investigation of mechanical properties indicates that the polycrystalline graphene grown by chemical vapor deposition is as strong as pristine. The microscopic characterization of graphene samples using Atomic Force microscopy (AFM) nano-indentation is limited in the sense that the detailed mechanical characteristics such as stress and stain distributions under the indenter, elastic moduli and breaking strength are not available directly from experiment. Using accurate description of interatomic interactions provided by novel screened environment-dependent bond order, (SED-REBO) potential, we performed large-scale molecular dynamics investigations of mechanical properties of polycrystalline graphene under conditions mimicking nano-indentation AFM experiments. The atomically resolved characterization of the stress and strain distributions under indenter are used to understand detailed mechanisms of graphene strength and failure. The breaking strength, the crack initiation and propagation are investigated as a function of the grain boundary structure and the grain size distribution as well as the position of the indenter – at the center of the grain, at the a single grain boundary and at the junction of three or more grain boundaries.

8:40am 2D+MN+NS+SP+SS+TF-WeM3 Lévy Flights Found in Freestanding Graphene, *Paul Thibado*, University of Arkansas, *M. Neek-Amal, F. Peeters*, University of Antwerp, Belgium
Local, long-time evolution measurements of the height fluctuations of a 2D membrane allows examination of the fundamental foundations of statistical mechanics in soft condensed matter. However, such measurements have proved elusive, thereby forcing critical theoretical assumptions in the best models. We report sub-nanometer, high-bandwidth height measurements of freestanding graphene using constant-current, point-mode scanning tunneling microscopy, as a follow-up to our previous related works [1-2]. By tracking atoms directly, the ability to measure dynamic events is increased by a factor of 1000 over the present state-of-the-art membrane imaging technology. Surprisingly, the membrane velocities follow the Cauchy-Lorentz distribution consistent with a Lévy process, rather than the expected Maxwell-Boltzmann distribution. We introduce a new theoretical approach using fractional-stochastic calculus.

Acknowledgements:

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9:00am 2D+MN+NS+SP+SS+TF-WeM4 Multilayer Graphene Strength Characterization, *Joseph Rowley*, N. Boyer, K. Berry, R.C. Davis, Brigham Young University, *R. Creighton, J. Abbott, S. Cornaby, M. Harker*, Moxtek Inc., *R. Vanfleet*, Brigham Young University
Although there are many examples in the literature of multilayer graphene fabrication and electrical characterization, there is a lack of data on the mechanical properties of multilayer graphene, especially many layer. Conversely there is data about the mechanical properties of single layer graphene, and limited information about bilayer and few layer, but little about many layer. Multilayer Graphene was fabricated using chemical vapor deposition on a Nickel catalyst. Different flow rates and cooling rates were investigated to produce many layer films. Due to the high strength in graphene, these films were able to be suspended over millimeter size openings and have a differential pressure applied. This allowed for the characterization of the strength of these membranes using bulge testing.

9:20am 2D+MN+NS+SP+SS+TF-WeM5 Nanoelectromechanical Systems Based on 2D Materials beyond Graphene -- Effects from Geometry, Nonlinearity, and Anisotropy, *Zenghui Wang*, Case Western Reserve University **INVITED**
Investigating and manipulating the mechanical degree of freedom in two-dimensional (2D) nanostructures present unique challenges and opportunities: such effort demands advanced fabrication and measurement schemes, and offers new insight into the physical properties of 2D materials. I will present our explorations and findings in mechanical processes at the nanoscale, through studying resonant nanoelectromechanical systems (NEMS) based on 2D materials beyond graphene (*e.g.*, molybdenum disulfide, black phosphorus, etc.). I will discuss the implications of geometrical irregularities on the nanomechanical responses of 2D-material-based resonators; impacts of device and material parameters on the mechanical nonlinearity and motional noise in 2D resonant transducers; and effects of material anisotropy in nanomechanical resonators based on new types of highly anisotropic 2D materials. These findings open new pathways towards nanomechanical coupling and tuning of the physical properties in 2D nanomaterials, and offer opportunities for building novel devices with new multimode functions.

11:00am 2D+MN+NS+SP+SS+TF-WeM10 Phonon Spectroscopy of Graphene Field Effect Devices with the STM, *Fabian Natterer, Y. Zhao, J. Wyrick*, NIST/CNST, *W.Y. Ruan, Y.-H.C. Chan, M.-Y.C. Chou*, Georgia Institute of Technology, *N.B. Zhitenev, J.A. Stroscio*, NIST/CNST
Phonon spectroscopy of graphene by inelastic electron tunneling spectroscopy with the STM has been elusive in previous measurements [1–3]. The difficulty lies within the weak phonon signatures that are buried by other dominant spectral features that inhibit a clear distinction between phonons and miscellaneous excitations. Utilizing a back gated graphene device that permits continuous adjustment of the global charge carrier density, we employ an averaging method where individual tunneling spectra at varying charge carrier density are condensed into one representative spectrum [4]. This method improves the signal for inelastic transitions that appear at constant threshold, while it broadens and thereby suppresses dispersive spectral features. We use this method to demonstrate the mapping of the total graphene phonon density of states, in good agreement with density functional calculations. Using the knowledge about the phonons thusly obtained, we closely examine our gate resolved spectra and observe a surprising and abrupt change in the phonon intensity when the graphene charge carrier type is switched through a variation of the back gate electrode potential. This sudden variation in phonon intensity is asymmetric in carrier type, depending on the sign of the tunneling bias. We invoke a resonance mediated tunneling process that relies on the presence of tip-induced quasi-bound state resonances in graphene, resembling whispering gallery modes for electrons and holes [5]. Our tip-sample system thereby mimics a giant molecular state and shares analogies with resonant enhanced excitations of molecular vibrational or rotational modes [6–9].

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11:20am 2D+MN+NS+SP+SS+TF-WeM11 Edge-state-induced Stabilization of Dopants in Graphene, *Yuuki Uchida*, A. Akaishi, J. Nakamura, The University of Electro-Communications (UEC-Tokyo) and JST CREST, Japan
Impurity doping is an efficient way to modify electronic properties of graphene. Several groups have reported the stability of dopants in graphene, especially near edges of graphene: Impurity atoms prefer to locate at the zigzag edge of graphene rather than the armchair one[1]. It has also been

reported that the electronic properties are strongly dependent upon the location of dopants, which is derrived from the non-equivalence of the two sublattice[2]. It is well-known that the edge-localized state emerges at the zigzag edge[3], which is specific for the so-called bipartite lattice. However, it has not been clarified yet how the edge-state affects the dopant stability depending on the sublattice. In this study, we investigate the role of the sublattice-dependent edge-state on the stabilization of impurities. We evaluate the dependence of the structural stability on the distance of impurity atoms from the zigzag edge using first-principles calculations within the density-functional theory. We have employed two types of graphene nanoribbons (GNRs) with the armchair- (AGNR) or the zigzag-(ZGNR) edge.

For AGNR, the formation energy of dopants does not change neither systematically nor monotonically as a function of the distance from the edge. On the other hand, for ZGNR, the formation energy is lower than that for AGNR and decreases with decreasing distance from the edge. In addition, two types of tendencies are confirmed for odd- and even-numbered sites from the zigzag edge, corresponding to the different sublattices of the bipartite lattice.

Such peculiar behavior as for of the formation energy can be explained as follows : The doped N atom donates its electron to the unoccupied-edge-state just above the Fermi level, resulting in the lowering of the one-electron energy of this state. The smaller the distance of N atoms from the zigzag edge is, the larger the electrostatic attraction between electrons of edge-localized states and positively-charged ion-shell at the N site becomes. Further, N atoms are much more stabilized at the odd-numbered site, because the edge-state has finite amplitude only at the odd-numbered sites.

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11:40am **2D+MN+NS+SP+SS+TF-WeM12 Exploring the Thermal Stability of Two-Dimensional Black Phosphorus**, *Xiaolong Liu, J.D. Wood, K.-S. Chen, E. Cho, M.C. Hersam*, Northwestern University

Two dimensional (2D) black phosphorus (BP) has attracted significant attention due to its superlative electronic and optical properties. Unlike graphene, its intrinsic and thickness-dependent band gap makes it feasible for direct application in electronic and optoelectronic devices.[1] However, before 2D BP can be effectively employed in such applications, it is necessary to establish the thermal stability of 2D BP since annealing is a key element in most device fabrication processes. Towards this end, we have utilized *in situ* scanning/transmission electron microscopy and spectroscopy methods to characterize the thermal decomposition process of mechanically exfoliated 2D BP.[2] The decomposition is observed to occur at ~400 °C in the form of sublimation, compared to the 550 °C of bulk BP. This decomposition initiates *via* eye-shaped cracks along the [001] direction and then continues until only a thin, amorphous red phosphorous-like skeleton remains. *In situ* electron energy loss spectroscopy, energy-dispersive X-ray spectroscopy, and energy-loss near-edge structure changes provide further quantitative insight into this chemical transformation process.

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12:00pm **2D+MN+NS+SP+SS+TF-WeM13 Gas Permeation Through 1 nm Thick Carbon Nanomembranes**, *A. Beyer, M. Ai,* Bielefeld University, Germany*, S. Shishatskiy, J. Wind,* Helmholtz-Zentrum Geesthacht, Germany*, X. Zhang, V. Chinaryan, Y. Yang,* **Armin Gölzhäuser**, Bielefeld University, Germany

The gas permeation characteristics of 1 nm thick carbon nanomembranes (CNMs) from self-assembled monolayers are reported. The assembly of CNMs onto polydimethylsiloxane (PDMS) support membranes allows determination of gas permeation characteristics. Single layer and triple layer CNMs were investigated in respect to permeation of hydrogen, helium, carbon dioxide, oxygen, nitrogen, argon, methane and ethane. In addition, the CNM-PDMS composites were characterized by X-ray photoelectron spectroscopy, helium-ion microscopy as well as atomic force microscopy. A careful analysis about the contribution of the PDMS support membranes to the gas permeation allowed an estimate of the intrinsic CNM permeances. These values indicate a molecular sieve-like property of CNMs which is attributed to molecular-sized channels in CNMs. As an example, hydrogen and carbon dioxide gas molecules display an order of magnitude higher permeance values for single layer CNMs in comparison to oxygen and nitrogen, which possess larger kinetic diameters.

Nanometer-scale Science and Technology
Room: 212B - Session NS-WeM

Nanodiamond for Optical and Biomedical Applications

Moderator: Huan-Cheng Chang, Academia Sinica, Olga Shenderova, Adámas Nanotechnologies Inc.

8:20am **NS-WeM2 Time- Resolved Luminescence Nanothermometry with Nitrogen-Vacancy Centers in Nanodiamonds**, *O.C. Chen, Pei-Chang Tsai*, Academia Sinica, Taiwan, Republic of China

We have developed FNDs into a nanoscale luminescence thermometer for both temporally and spatially resolved temperature sensing with hosted NV⁻ centers, time-resolved luminescence nanothermometry was demonstrated with 100-nm FNDs spin-coated on a glass substrate and submerged in gold nanorod solution heated by a near-infrared laser, a pump-probe-type experiment that enables the study of nanoscale heat transfer with a temporal resolution of better than 10 μs. Moreover, we present a three-point sampling method that allows real-time monitoring of the temperature changes over ±100 K, an advantage of this three-point method is that it possesses a built-in ability for self-correction of signal fluctuation. To verify the validity of these measurements and to understand the heat transfer in the nanometer and microsecond scales, we carried out heat transfer numerical simulations. The simulated time constants for single exponential decays are $\tau = 20$ μs at r = 1.0 μm and $\tau = 25$ μs at r = 1.5 μm, compared with our experimental observations of 12 and 18 μs, respectively. Finally, the present study represents the first demonstration of thermometric investigation at the nanometric length scale with microsecond time resolution. It adds an important new dimension to the use of NV⁻ centers in diamond for quantum sensing applications.

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8:40am **NS-WeM3 Nanoscale Measurement and Diagnostics using Diamond Quantum Probes**, *Jörg Wrachtrup*, Universit of Stuttgart, Germany **INVITED**

Diamond defects are a novel class of nanoscale quantum sensors. They are capable of measuring forces, pressure, temperature, magnetic and electric field with high accuracy on length scales of a few nano meters. The nano sensors function under various environmental parameters including ambient conditions. Diamond defect can be either enclosed in nanocrystals 1D or 2D materials depending on the application purpose. The talk will highlight various applications comprising precision measurement of magnetic, electric field and pressure with application in energy management systems and bioimaging.

9:20am **NS-WeM5 Measurement of Carbon Condensates Using Small-Angle X-ray Scattering During Detonation of High Explosives**, *Trevor Willey, M. Bagge-Hansen, L.M. Lauderbach, R. Hodgin, S. Bastea, L. Fried, A. Jones, D. Hansen, J. Benterou, C. May,* Lawrence Livermore National Laboratory*, T. Graber,* Washington State University*, B.J. Jensen, D. Dattelbaum, R. Gustavsen, E. Watkins, M. Firestone,* Los Alamos National Laboratory*, J. Ilavsky,* Argonne National Laboratory*, T. van Buuren,* Lawrence Livermore National Laboratory

Detonation is one of the primary methods to produce nanodiamond. A new small-angle x-ray scattering (SAXS) end station has been developed by LLNL for use at the new Dynamic Compression Sector at the Advanced Photon Source to observe carbon condensation during detonation of high explosives. The beamline and endstation are capable of synchronously initiating detonation and then acquiring up to four SAXS patterns from single x-ray pulses, which in 24-bunch mode at the APS are < 100 ps and arrive every 153.4 ns. Timescales are ideal: detonation investigation and model validation requires data regarding processes occurring at nanometer length scales on time scales ranging from nanoseconds to microseconds. The endstation and beamline have now demonstrated unprecedented fidelity in SAXS data during detonation; for the first time the data contains a clear Guinier knee and high-fidelity power law slope, giving information about the size and morphology of the resultant nanoparticles. We have commenced investigating HNS which is an explosive known to produce copious graphitic soots, RDX/TNT mixtures similar to what is commonly used to produce nanodiamond, and DNTF, a hydrogen-free, nitrogen rich, hot, and high velocity explosive. HNS produces carbon particles with a radius of gyration of 3 nm in less than 400 ns after the detonation front has

passed, and this size is constant over the next several microseconds. The power-law slope is about -3, consistent with a disordered, irregular, or folded sp^2 structure. Comp B, a 60% RDX, 40% TNT mixture, produces 3 nm particles also within a few hundred ns, and has a power law that is around -3.7, consistent with 3D nanodiamond particles. DNTF produces larger, 7 nm particles with a power law that is -4 over the first few hundred ns and then decreases to -3.8, ultimately also consistent with 3D diamond nanoparticles. In all three cases, particles are produced in the first few hundred ns, and then do not appreciably grow over the next several microseconds, which is in direct contradiction to previous pioneering work on RDX/TNT mixtures, TATB, and several other explosives, where observations indicate significant particle growth (50% or more) continues over several microseconds.

9:40am NS-WeM6 Surface Functionalization of Nanocarbons Formed from Detonating High Explosives, *Bryan Ringstrand, R.C. Huber, D. Podlesak, D. Dattelbaum, R. Gustavsen, M. Firestone*, Los Alamos National Laboratory

High explosive detonation is an exothermic process where CHNO molecules are transformed into, but not limited to, H_2O, CO, CO_2, N_2, and solid carbon (i.e. soot). The type and quantity of carbon allotrope present depends on the explosive formulation and the temperature and pressure of the detonation. The carbon allotropes that form during a detonation include nanodiamond, graphite, and amorphous carbon; however, nanodiamonds are the most interesting. Due to their chemical inertness and biocompatibility, nanodiamonds have garnered interest in biomedical and electronic applications.[1]

The nature of a detonation event produces soot that is contaminated with metals, metal oxides, and other carbon phases (i.e. sp^2 carbons). Removal of these species is essential to obtaining pristine nanodiamond. Metals and metal oxides are removed using mineral acid treatments; whereas, sp^2 species are thermally oxidized above 400 °C.[2] Although acid treatment and thermal oxidation generate pristine nanodiamond, these methods damage the characteristic markers that provide information about the processes and conditions that give rise to nanodiamond as a carbon allotrope.

Another benign approach could be surface functionalization of the soot followed by separation of functionalized and non-functionalized components. Carbon nanotubes have been known to de-aggregate and disperse in ionic liquids.[3] A similar approach was demonstrated for pristine nanodiamond using an imidazolium based ionic liquid covalently bound to its surface. These functionalized nanodiamonds showed increased dispersibility in polar solvents and formed stable gels in other ionic liquids.[4]

Our efforts to adapt ionic liquids for the surface functionalization of nanocarbons produced by high explosive detonation will be discussed. Specifically, imidazolium based ionic liquids incorporating decyl chains through various coupling strategies will be reviewed. The functionalized nanocarbons could then be dispersed in solvents, allowing for individual component isolation and size fractionation. The isolated products were characterized using a range of techniques including SEM, TEM, powder X-ray diffraction, X-ray scattering, and XPS.

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11:00am NS-WeM10 Quantum Sensing in Biology using the Nitrogen-Vacancy Centre in Diamond, *L.J. Hollenberg, David Simpson*, University of Melbourne, Australia **INVITED**

The nitrogen-vacancy (NV) defect centre in diamond can be used as a single spin quantum probe for nanoscale magnetometry. Optically, it possesses a broad absorption band from 512-560 nm, sustained fluorescence from 630-750 nm, is chemically inert and bio-compatible, making it ideal for room-temperature applications. The populations in the spin-1 sublevels of the NV ground state, which are sensitive to local magnetic fields, can be measured and polarised optically, and controlled via resonant microwave fields (~ 3 GHz). Through various quantum control schemes the NV centre has been used to detect static (DC), sinusoidal (AC) and fluctuating (FC) magnetic fields. This talk will briefly review some of the overall progress and applications of the NV centre in the detection of electronic and nuclear spins at the nanoscale, including our own work on the quantum measurement of nanodiamond-NV centres in a living cell, detection of Gd spin labels in a lipid bi-layer, and T1-based electron spin resonance techniques for the non-invasive detection of magnetic species.

11:40am NS-WeM12 Large Scale Production of Fluorescent Nanodiamond Particles, *Olga Shenderova, N.J. Nunn, G.E. McGuire*, Adámas Nanotechnologies Inc.

Nanodiamond (ND) particles have recently emerged as a key platform for many sectors of nanoscience and nanotechnology due to their outstanding mechanical performance, biocompatibility and distinctive optical properties, a combination of assets not often met in the nanoworld. Particularly production of ND particles containing nitrogen-vacancy (NV) color centers exhibiting stable luminescence and unique spin properties have brought ND particles to the forefront of materials research. Based on the SBIR award from National Institute of Health (NIH), Adámas Nanotechnologies developed a large scale production of ND containing NV color centers in hundreds of grams batches. While nitrogen is an intrinsic impurity in diamond, vacancies must be created by high energy irradiation. Variety of factors play a role in creation of a high density ensemble of NV centers in NDs including density of substitutional nitrogen, size of starting particles that undergo irradiation, irradiation dose and temperature, post irradiation processing including fragmentation to the smaller sizes. In the paper, role of these factors will be discussed. Production of fractions of NDs with median sizes ranging between 10 and 100 nm was demonstrated, exceeding by an order of magnitude brightness of a relevant typically used organic dye for NDs with sizes exceeding 50nm. The brightness of fluorescent nanodiamonds and an organic dye was compared side-by-side under identical conditions using total internal reflection fluorescence microscopy (TIRFM) measurements at NIH.

Scanning Probe Microscopy Focus Topic
Room: 212A - Session SP+AS+NS+SS-WeM

Advances in Scanning Probe Microscopy
Moderator: An-Ping Li, Oak Ridge National Lab, Saban Hus, Oak Ridge National Laboratory

8:00am SP+AS+NS+SS-WeM1 Designer Electrons: Quantum Information and New Particles in Atomically Assembled Matter, *Hari Manoharan*, Stanford University **INVITED**

The observation of massless Dirac fermions in monolayer graphene has propelled a new area of science and technology seeking to harness charge carriers that behave relativistically within solid-state materials. Using low-temperature scanning tunneling microscopy and spectroscopy, we show the emergence of Dirac fermions in a fully tunable condensed-matter system—molecular graphene—assembled via atomic manipulation of a conventional two-dimensional electron system in a surface state. We embed, image, and tune the symmetries underlying the two-dimensional Dirac equation into these electrons by sculpting the surface potential with manipulated molecules. By distorting the effective electron hopping parameters into a Kekulé pattern, we find that these natively massless Dirac particles can be endowed with a tunable mass engendered by the associated scalar gauge field, in analogy to the Higgs field. With altered symmetry and texturing of the assembled lattices, the Dirac fermions can be dressed with gauge electric or magnetic fields such that the carriers believe they are in real fields and condense into the corresponding ground state, as confirmed by tunneling spectroscopy. Using these techniques we ultimately fabricate a quantum Hall state without breaking time-reversal symmetry, in which electrons quantize in a gauge magnetic field ramped to 60 Tesla with zero applied laboratory field. We show that these and other chiral states now possible to realize have direct analogues in topological insulators, and can be used to guide or confine charge in nontrivial ways or to synthesize new particles [1,2].

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8:40am SP+AS+NS+SS-WeM3 Scanning Quantum Dot Microscopy, *Ruslan Temirov, C.W. Wagner, M.F.B.G. Green, P.L. Leinen*, Forschungszentrum Juelich GmbH, Germany, *T.D. Deilmann, P. Krueger, M.R. Rohlfing*, Muenster University, Germany, *F.S.T. Tautz*, Forschungszentrum Juelich GmbH, Germany

Interactions between atomic and molecular objects are to a large extent defined by the nanoscale electrostatic

potentials which these objects produce. Consequently, a tool for nanometre scale imaging and quantification of

local electrostatic fields could help in many areas of nanoscience research. In this contribution we introduce a

scanning probe technique that for the first time enables truly three-dimensional imaging of local electrostatic

potential fields with sub-nanometre resolution. Registering single electron charging events of a molecular

quantum dot attached to the tip of a tuning fork atomic force microscope operated at 5 K, we image the

quadrupole field of a single molecule adsorbed on a metal surface. To demonstrate quantitative measurements,

we investigate the Smoluchowski dipole field created by a single metal adatom adsorbed on a metal surface. We

show that because of its high sensitivity the technique can probe electrostatic potentials at large distances from

their sources, which should allow for the imaging of samples with increased surface roughness.

Reference

[1] C. Wagner, M. F. B. Green, P. Leinen, T. Deilmann, P. Krüger, M. Rohlfing, R. Temirov, F. S. Tautz

arXiv:1503.07738 (2015)

9:00am SP+AS+NS+SS-WeM4 Local Probing of the Photo-carrier Lifetime by Kelvin Probe Force Microscopy, *Nicolas Chevalier, S. Pouch, D. Mariolle,* Univ. Grenoble Alpes/ CEA, LETI, MINATEC Campus, France*, B. Grevin,* Univ. Grenoble Alpes/ CEA, INAC, SPrAM, LEMOH, France*, Ł. Borowik*, Univ. Grenoble Alpes/ CEA, LETI, MINATEC Campus, France

The photo-carrier lifetime plays a major role in the overall efficiency of a solar cell because it limits the proportion of photo-generated charges collected at the electrodes. This lifetime, which should be ideally as large as possible in an organic or inorganic solar cell, is rather difficult to measure in nanostructured materials or in more complex hybrid systems, indirect band-gap semiconductors, and ultra-thin layers. Identifying the losses mechanisms is one of the main objectives for increasing the performances of solar cells. Most of the experimental approaches developed so far consist in studying recombination by techniques such as transient photovoltage measurements or charge extraction. All these techniques average sample properties over macroscopic scales, making them unsuitable for directly assessing the impact of local heterogeneity on the recombination process. In this paper, we propose a steady method to measure the photo carrier lifetime by photo-modulated techniques based on Kelvin probe force microscopy (KPFM). [1] Additionally, KPFM technique provides a spatially resolved measurement, which is applicable on the overall of solar cells.

We will present the principle of this original method based on the measurement of the surface potential by KPFM under an illumination with a rectangular waveform light modulation. Photo-carrier lifetime down to µs scale is reachable with our experimental setup. The modulation-dependent surface potential is plotted as a function of the frequency. Assuming an immediate generation time under illumination and an exponential decay of the surface potential during the dark condition, the averaged surface potential over a cycle can be fitted as a function of the frequency by simple equation where the only fit parameter is the photocarrier-lifetime. [2] Instrumental aspects as well as data treatment will be reviewed. Measurements obtained on silicon nanocrystals embedded in 30 nm film of silicon dioxide [3] and on organic donor-acceptor blend (PBTFB and PCBM) [4] will be presented to illustrate the potential of the technique.

This work was supported by the French "Recherche Technologique de Base" Program and performed in the frame of the trSPV Nanoscience project. The measurements were performed on the CEA Minatec Nanocharacterization Platform (PFNC).

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9:20am SP+AS+NS+SS-WeM5 Nanoscale Capacitance-Voltage (C-V) Curves: Using Scanning Microwave Impedance Microscopy (sMIM) to Characterize Local Electrical Properties of Linear and Non-Linear Materials, *Stuart Friedman, Y. Yang, O. Amster,* PrimeNano, Inc.

Understanding and optimizing advanced materials frequently requires detailed knowledge of nanoscale electrical properties. Scanning probe techniques such as scanning tunneling microscopy (STM), conductive AFM (cAFM), scanning capacitance microscopy (SCM), and Kelvin probe force microscopy (KPFM) provide such nano-electrical measurements, but are generally limited in the classes of materials they can characterize or the properties they can measure. Scanning microwave impedance microscopy (sMIM) uses GHz frequency microwaves and shielded AFM probes to directly measure the impedance (capacitance and conductance) of the tip sample interface. As such sMIM is sensitive to the permittivity and conductivity of a wide variety of samples including dielectrics, conductors, and semiconductors.

When sMIM is applied to non-linear materials, changing the tip sample bias changes the local electric field thereby changing the local electrical properties of the sample just under the AFM tip. The electric field induced changes in the sample create changes in the tip-sample impedance that can be measured by sMIM. For example, when imaging doped semiconductor samples, the tip sample interface forms either a metal-semiconductor junction or a metal-insulator-semiconductor junction. Plotting the sMIM measured capacitance as a function of the tip sample bias voltage produces the equivalent of a typical capacitance-voltage curve, but from nanoscale regions selected from an AFM image. C vs V results from doped silicon samples that closely match theoretical calculations will be discussed. The talk will also present results from advanced and novel materials and devices, such as III-V semiconductors, 2D materials and 1D structures where sMIM data has been used to assess non-linear behavior and characterize dopant type and distribution.

9:40am SP+AS+NS+SS-WeM6 STM Study of the Correlation between Structural, Magnetic, and Electronic Properties of Co Nano-Islands on Cu(111), *Jewook Park, C. Park, M. Yoon, Z. Gai, A.P. Baddorf, A.-P. Li,* Oak Ridge National Laboratory

An epitaxially grown Co nano-island on Cu(111) surface is a model system to study the correlation between structural, magnetic, and electrical properties of nanophase materials. We carried out an extensive study on Co islands by using spin-polarized scanning tunneling microscopy and spectroscopy (SP-STM/S) at low temperatures (130 K and 38 K). Two structurally different island types are clearly distinguished, rotated by 180 about the surface normal due to a stacking fault in one type of the islands. The triangular Co islands are 5-20 nm wide and 4 Å high. Regardless of the structural asymmetry, both faulted and un-faulted Co islands possess two distinctive spin orientations. With Cr-coated W-tip as a spin-polarized probe, bias-dependent tunneling conductance maps are measured on Co islands. An antiparallel spin-orientation between magnetized tip and Co islands display higher conductance compared to a parallel relation at -400 meV and *vice versa* at around Fermi-level, which is verified by density functional theory calculations. Furthermore, by recording 23 hours of time-lapse images from the same Co islands, we demonstrate a time-dependent correlation between structural, magnetic, and electrical behaviors. We find that a contamination-induced structural change modifies the magnetic properties of Co islands and is confirmed by theoretical calculations.

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

11:00am SP+AS+NS+SS-WeM10 Probing Electrostatic Field Effect in Quantum Materials by Microwave Impedance Microscopy, *Keji Lai,* University of Texas at Austin **INVITED**

The research of complex quantum materials, in which a dazzling number of emergent phenomena take place in the nanoscale, is a major theme in modern condensed matter physics. For real-space imaging of complex systems, electrical impedance microscopy fills an important void that is not well represented by the existing local probes. Using shielded cantilever probes and sensitive microwave electronics, we can now perform non-invasive electrical imaging with sub-100nm resolution and sub-aF sensitivity.

Combining the cryogenic microwave impedance microscopy (MIM) and a spin-coated thin ionic gel layer, we are able to visualize the metal-insulator transition of functional materials in electrolyte-gated electric double-layer transistors. The microwave images acquired at different gate voltages clearly show the spatial evolution of channel conductivity and its local fluctuations through the transition. By applying a large source-drain bias above the glass transition temperature of the gel, an uneven conductance profile is established across the EDLT channel, which can be visualized by the MIM and further investigated by transport measurements and numerical simulations. The combination of ultra-thin ion-gel gating and microwave microscopy paves the way for studying the microscopic evolution of phase transitions in complex materials induced by electrostatic field effects.

11:40am SP+AS+NS+SS-WeM12 Subsurface Visualization of Soft Matrix using 3D-Spectroscopic Atomic Force Acoustic Microscopy, *Kuniko Kimura*, K. Kobayashi, A. Yao, H. Yamada, Kyoto University, Japan

Nondestructive visualization of subsurface features of various materials with nanometer-scale spatial resolution is strongly demanded in a wide variety of scientific research fields such as nanoelectronics, nanomechanics and life science. Recently, many research groups have demonstrated the visualization of nanometer-scale subsurface features using various techniques based on atomic force microscopy (AFM) [1-4]. (All references and figures are given in Supplement.) We recently demonstrated the imaging of Au nanoparticles buried under 900 nm from the surface of a polymer matrix by atomic force acoustic microscopy (AFAM), as shown in Fig. 1 [5]. In AFAM, the amplitude and phase of the cantilever vibration at the contact resonance frequency induced by the sample excitation are measured, which allows us the quantitative evaluation of surface stiffness [6]. The AFAM images in Fig. 1 show that the surface viscoelasticity of the soft matrix is affected by subsurface hard objects such as the Au nanoparticles buried even roughly 1 micro-meter below the surface. However, only from AFAM images, it is difficult to determine which the dominant mechanism for the subsurface imaging is viscosity variation or elasticity variation, because AFAM images were taken at a single excitation frequency near contact resonance.

In this presentation, we discuss the origin of the visualization of subsurface features in soft matrix based on spectroscopy of AFAM [7]. We recorded the amplitude and phase spectra at every pixel of the AFAM image as represented in Fig. 2, which we call 3-dimensional spectroscopic atomic force acoustic microscopy (3D-spectroscopic AFAM). A schematic diagram of the 3D-spectroscopic AFAM is shown in Fig. 3. After the tip was brought into contact with the surface, we first measured the contact resonance frequency (fc). Then we recorded the amplitude and phase spectra measured by a lock-in amplifier, while the tip was raster-scanned with the contact mode. At each scanning pixel, the excitation frequency was swept with the span of 25 kHz which was centering around fc, whose sweep time was 35 msec. The total acquisition time for 128 x 128 pixels took about 20 min.

Using this method, we can compare the frequency spectrum measured on the subsurface Au nanoparticle with that on another position having no subsurface particle, as shown in Fig. 4. We can also reconstruct AFAM images of arbitrary frequencies within the sweep frequency range, which is the meaning of "3-dimensional". Moreover, the 3D-spectroscopic AFAM enables us to characterize the amplitude and phase spectra and to detect the variation that may be caused by the nonlinear tip-sample interactions.

12:00pm SP+AS+NS+SS-WeM13 Quantifying the Effects of Cantilever Modes Shapes on Studies of the Liquid-Solid Interface, *Aleks Labuda*, M. Viani, D. Walters, R. Proksch, Asylum Research, an Oxford Instruments company

At the core of most AFM measurements is the assumption that the motion of the cantilever probe can be well quantified. However, most AFM systems use a "beam bounce" optical beam deflection (OBD) method which, because it is fundamentally an angular measurement, only provides accurate tip position information when the mode shape of the cantilever matches the calibration conditions. For example, if the OBD sensitivity is calibrated with a force curve, the calibration holds true only for experiments where the mode shape is similar to an end-loaded cantilever. This assumption is quickly violated when the cantilever is oscillated at frequencies different from the calibration. This is especially true in liquids, where Q~1 and the combination of significant base motion and hydrodynamic effects lead to a variety of different mode shapes that are strongly frequency dependent (see Figure). This clearly demonstrates that the sensitivity (nm/V) is actually a frequency dependent quantity. Worse, it may also drift with time. Another consequence is that the effective stiffness of the cantilever, which depends on mode shape, is also highly frequency dependent. Both of these effects cause quantitative misinterpretation of the tip-sample interaction and artifacts in imaging contrast. These problems affect both dynamic AFM modes (such as AM-AFM and FM-AFM) as well as sub-resonance modes such as fast force mapping and force modulation.

To quantify this effect, we present measurements based on Ref [1-2] using a modified commercial AFM that combines a standard OBD detector with an integrated laser Doppler vibrometer (LDV) system that directly measures displacement. As shown in the Figure, The OBD and LDV can be used simultaneously, such that the cantilever base motion or tip motion can be accurately monitored with the LDV during an AFM experiment – independent of the OBD and any feedback loops. In the Figure, the ~2 μm LDV laser spot was scanned along the cantilever for high-resolution in situ mapping of its dynamics across a wide spectrum of frequencies and showing significant deviations from ideal mode shapes over the entire frequency range.

The effects of these frequency-dependent mode shapes are then quantified by appropriate modeling for a variety of experimental conditions, and demonstrated experimentally using stiff levers for AM-AFM at the calcite-water interface and soft levers for fast force mapping of polymeric materials.

Surface Science
Room: 113 - Session SS+AS+NS-WeM

Metals, Alloys & Oxides: Reactivity and Catalysis
Moderator: John Russell, Jr., Naval Research Laboratory

8:00am SS+AS+NS-WeM1 Surface Chemistry of Single-Layer MoS₂, *Koichi Yamaguchi*, E. Li, L. Bartels, University of California - Riverside

Molybdenum disulfide (MoS$_2$) is a semiconducting transition metal dichalcogenide (TMD) that forms a stable monolayer 2D crystal structure similar to graphene. It is the key material for industrial hydrodesulfurization (alloyed with cobalt) and has shown promise in electrocatalytic water splitting. We present a study of MoS$_2$'s ability to bind small reactants and its stability when exposed to them at elevated temperature. We utilize a combination of thermally programmed desorption measurements and in-situ PL imaging. The latter permits us to study the film activity over a wide pressure range (high-vacuum to ambient).

8:20am SS+AS+NS-WeM2 On the Adsorption Behavior of a Porphyrin on Different Cu Surfaces: A Comparative Scanning Tunneling Microscopy Study, *Liang Zhang*, Universität Erlangen-Nürnberg, Germany, *M. Lepper*, Universität Erlangen-Nürnberg, Germany, *M. Stark, S. Ditze, H.-P. Steinrück, H. Marbach*, Universität Erlangen-Nürnberg, Germany

Self-assembly of functional molecular building blocks on well-defined surfaces is a promising approach for the bottom-up fabrication of two-dimensional nanostructures with outstanding properties. In this respect, porphyrins are particularly attractive because of their distinct chemical and physical properties.[1,2]

In this presentation, we investigate and compare the adsorption behaviour of 2H-5,10,15,20-Tetrakis-(3,5-di-tert-butyl)-phenylporphyrin (2HTTBPP) on different substrates, i.e., Cu(111),[3-5] Cu(110) and Cu(110)-(2X1)O, under ultra-high vacuum conditions by scanning tunneling microscopy (STM). At room temperature, supramolecular arrangements of 2HTTBPP are observed on Cu(111) and Cu(110)-(2X1)O, while on Cu(110) individual 2HTTBPP molecules are observed in a disorderd layer. Interestingly, the intramolecular conformations of the molecules are quite different on the investigated substrates, as determined by STM.[4] The corresponding findings are interpreted by accounting for specific molecule-molecule and molecule-substrate interactions. In addition, the so-called self-metalation of 2HTTBPP with Cu atoms will be reported and discussed.[4,5]

References:

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8:40am SS+AS+NS-WeM3 Redox-Active On-Surface Assembly of Metal-Organic Chains with Single-Site Transition Metals, *Steven Tait*, Indiana University **INVITED**

Programming the specific chemistry of single-site transition metal centers at surfaces by organic ligand design is a promising route to improve selectivity in surface catalysts. The chemical behavior of the surface and redox chemistry happening at the surface need to be further developed and understood. These studies benefit from interdisciplinary research into the programming of the growth, reactivity, and functionality of nano-scale systems in general and metal-organic complexes as surface catalysts in particular. Our group has recently demonstrated the formation of structurally ordered and chemically uniform single-site centers at surfaces by on-surface redox chemistry of metallic precursors including platinum, chromium, iron, and vanadium with organic ligands on a gold surface (*J. Am. Chem. Soc.* 2014, **136**, 9862-9865; *J. Chem. Phys.* 2015, **142**, 101913; and newly submitted work). The on-surface redox process relies on straightforward vapor deposition protocols and takes advantage of the catalytic role of the surface to show promise as an approach for the growth of inorganic complexes at surfaces. The ability to tune the reactivity and catalysis of these systems is a central question in this field. We report new results here that probe the extent of oxidation state control in these systems

using tailored tetrazine-based ligands and vanadium metal; vanadium is an excellent candidate for probing access to a variety of oxidation states. The oxidizing power of the tetrazine species is tuned by peripheral functional groups to access two and three electron oxidation processes, as determined by X-ray photoelectron spectroscopy (XPS). Platinum(II) centers have also been formed with these ligands. In each of these cases, the metal-ligand complexes take the form of nearly identical one-dimensional polymeric chains, resolved by molecular-resolution scanning tunneling microscopy (STM). These structures provide highly uniform quasi-square-planar coordination sites for the metal, which contributes to the well-defined chemical state of the metal. This strategy is also applied to earth-abundant metals such as iron and chromium using commonly available phenanthroline ligands and is allowing us to develop understanding of how to control and program single-site metal centers on surfaces for next-generation catalysis.

9:20am SS+AS+NS-WeM5 Ultra-thin Bi(110) Films on Si(111)√3x√3-B Substrates, *I. Kokubo, Y. Yoshiike, K. Shishikura, K. Nakatsuji, Hiroyuki Hirayama*, Tokyo Institute of Technology, Japan

Bismuth (Bi) takes the rhombohedral (A7) crystalline structure in bulk. However, it also takes the black phosphorous (BP) structure in ultrathin films. Theoretically, a few bilayer thick Bi(110) films with the BP structure were predicted to be a nontrivial two-dimensional topological insulator by removing the buckling at the surfaces [1]. In the meantime, ultrathin Bi(110) films with the A7 structure was suggested to realize the Dirac electron system at the surfaces [2]. From these viewpoints, the growth, structure, and electronic states of the Bi(110) ultra-thin films are of great interest. In this study, we investigated the details of the atomic arrangements and electronic states at the Bi(110) islands on the Si(111)√3 × √3-B substrate experimentally using scanning tunneling microscope (STM) [3] and angle-resolved photoelectron spectroscopy (ARPES) in a synchrotron radiation facility.

In the study, we found that atomically flat, long, narrow Bi(110) islands grew along specific orientations on the Si(111))√3 × √3-B substrate. The orientations belonged to one of the two sets of three-fold rotational axes, which differed by 26° each other. The preference of the specific orientations were reasonably attributed to the commensuration of the diagonal of the rectangular Bi(110) lattice to the √3 × √3 substrate unit cell. The islands grew as to make their edges parallel to the short side of the Bi(110) rectangular unit cell. The combination of the Bi domains of different orientations caused various types of boundaries on the wide terraces of the Bi(110) islands. In particular, the domains along ±87° from the {1-10} direction were found to be connected perfectly on the atomic scale at the straight boundary by inserting a local switching of the bond direction to the zigzag chains of the in-plane bonds. On the Si(111))√3 × √3-B substrate, both the odd layer thick A7 and even layer thick BP Bi(110) islands appeared. The dispersive surface bands and their Fermi surface mapping with characteristic electron and hole pockets were observed in ARPES spectra. Details will be reported in the presentation.

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9:40am SS+AS+NS-WeM6 STM Study of Growth Processes for Ir/Ge(111), *M.S. van Zijll, B.H. Stenger, C.H. Mullet, E.S. Huffman, D. Lovinger, W.F. Mann, Shirley Chiang*, University of California, Davis

Using scanning tunneling microscopy (STM), we have characterized the surface of clean Ge(111) dosed with 0.66 to 2.0 monolayers (ML) of Ir and then annealed to temperatures between 550 K and 800 K. We observed a broad range of surface formations, including Ir adatom clusters and various stages of island formation. Islands with winding, wormy shapes formed around 580K. As the annealing temperature increased above 650K, round islands formed. In addition, a new type of growth is observed in which the Ir gathers along the antiphase domain boundaries between competing surface domains of the Ge surface reconstruction; this gives the appearance of the Ir forming pathways interconnecting different Ir islands. The low energy electron diffraction (LEED) pattern for this surface shows domains with (√3 x √3)R30° reconstruction and becomes sharper as the temperature is increased. In the STM images, the Ge top layer reconstruction, the Ir adatom clusters, the pathways, and the Ir round islands all have √3-spacing between features. X-ray photoemission spectroscopy (XPS) was used to determine that the IR coverage was ~ 2.0 monolayers when low energy electron microscopy (LEEM) images showed completion of 1 overlayer of Ir grown on Ge(111) at 600C. We present a model consistent with our XPS and LEEM data that suggests that each Ir adatom cluster observed in STM images corresponds to three Ir adatoms. To model the surface-adsorption processes for the Ir/Ge(111) system, we used simple Monte Carlo simulations with pair-wise surface potentials and random walks of atoms to imitate surface diffusion. Particular parameter choices yielded growth along pathways between domain boundaries of the substrate, in agreement with the experimental data.

11:00am SS+AS+NS-WeM10 Gas Sensor Resistance Changes for Ar/O₂ and H₂O Plasma Modified SnO₂ Nanomaterials, *Erin Stuckert, C.J. Miller, E.R. Fisher*, Colorado State University

Although steps have been made to decrease toxic gas emissions globally, these emissions persistently cause detrimental health effects worldwide. Current household gas sensors are limited in their abilities to detect sensitively and selectively at or below relevant toxicity levels for many gases. Tin(IV) oxide (SnO_2) nanomaterials are well-equipped to address some of these limitations as a result of dual valency (Sn^{2+} and Sn^{4+}) and high surface area, thus creating diverse surface chemistry. These properties are advantageous for gas sensing devices because SnO_2 functions as a sensor via gas-surface interactions, facilitated by adsorbed oxygen species. By measuring changes in resistance upon gas exposure, sensitivity and selectivity are observed. To increase sensitivity through maximizing gas surface interactions, chemical vapor deposition-grown SnO_2 nanowires and commercial nanoparticles were treated with an Ar/O_2 and $H_2O_{(v)}$ plasma resulting in increased oxygen adsorption. Surface and bulk characterization throughout the plasma treatment process demonstrate an increase in adsorbed oxygen content over a 30 - 150 W applied power range regardless of plasma precursor, in addition to showing that tin reduction occurs upon $H_2O_{(v)}$ plasma treatment. Gas sensing performance was initially explored by exposing SnO_2 sensors to air at temperatures of 25-300° C to determine base resistance of the materials in an ambient atmosphere. The data show changes in resistance that are dependent upon nanomaterial architecture, plasma treatment conditions, and sensor temperature. Base resistance changes for specific plasma and sensor conditions will be discussed as well as sensor responses and selectivity upon exposure to toxic gases including benzene and carbon monoxide. By combining materials characterization with gas sensor responses, we can optimize sensor sensitivity and selectivity by tuning plasma modification conditions with aims for targeted gas sensing applications.

11:20am SS+AS+NS-WeM11 Enhanced Adsorption of CO₂ at Steps of Planar ZnO(0001) Grown on Au(111), *Xingyi Deng, D. Sorescu, J. Lee*, National Energy Technology Laboratory

In this work, we study the energetics of CO_2 adsorbed on the bi- and tri-layer ZnO(0001) grown on Au(111) using temperature programmed desorption (TPD) and calculations based on density functional theory (DFT). Both bi- and tri-layer ZnO(0001) on Au(111) adopt a planar, graphite-like structure via an inter-layer relaxation to minimize the surface dipole arising from alternating Zn^{2+} and O^{2-} layers. CO_2 is adsorbed weakly on these planar ZnO(0001) surfaces, desorbing between 125-130 K in TPD. Two other desorption peaks were also observed in TPD at ~ 150 and 280-320 K and are attributed to the CO_2 adsorption at the steps between the bi- and tri-layer ZnO(0001) surfaces. This enhanced adsorption of CO_2 at the steps is supported by DFT calculations: the computed energetics of CO_2 adsorbed on surfaces and at steps is indeed consistent with that estimated from the TPD experiments via the Redhead method. Implications of our fundamental results for ZnO based catalysts will be discussed.

11:40am SS+AS+NS-WeM12 Characterization of Band Gap and Lattice Constant of Ultrathin ZnO Layers on Au(111), *Junseok Lee, D. Sorescu, X. Deng*, National Energy Technology Laboratory

Ultrathin layers of ZnO grown on the Au(111) substrate have been characterized using low-temperature scanning tunneling microscopy (STM). Under reactive deposition condition, the ZnO layers have been found to grow by forming islands. Detailed analysis of electronic structure have been conducted using scanning tunneling spectroscopy (STS) and the density functional theory (DFT) calculations. The band gap of ultrathin layers of ZnO is found to be larger compared to the bulk ZnO wurtzite structure. The density functional theory calculations provides understanding of the increased band gaps of thin ZnO layers. The lattice constants of ultrathin ZnO layers on Au(111) are also found to be larger than that of the bulk lattice constant, which could be explained by the formation of graphitic-like ZnO layers.

12:00pm SS+AS+NS-WeM13 Submonolayer Water Adsorption on Stepped and Planar Pt Surfaces, *Rachael Farber,* Loyola University Chicago, *M.J. Kolb,* Leiden Institute of Chemistry, *J. Derouin,* Loyola University Chicago, *M.T.M. Koper, L.B.F. Juurlink,* Leiden Institute of Chemistry, *D.R. Killelea,* Loyola University Chicago

The adsorption of water onto metal surfaces yields a host of intricate adsorbate structures at

coverages less than a single layer. Complex adsorption structures arise due to the delicate balance

of hydrogen bonding between water molecules as well as attractive forces between water molecules

and the metal surface. Therefore, the complexity of the system provides an excellent opportunity to

refine models of water-water and water-surface interactions. Water molecules are largely confined

to a single plane and, as a result, the geometry of aligned water molecules gives rise to frustrated

hydrogen bonding. At low coverages of water on metal surfaces, these frustrated intermolecular

interactions result in the formation of structures other than the classic hexagons of bulk water. We

will report the results of a combined theory-experiment study of water adsorption on planar Pt(111)

and stepped Pt(553). Experimentally, temperature programmed desorption (TPD) and ultra-high

vacuum scanning tunneling microscopy (UHV-STM) were used to quantify water coverage and to

image the resultant surface structures. On Pt(111), 5, 6, and 7-membered rings were found to form

across the Pt surface, in agreement with previously reported experimental results and electronic

structure calculations. On Pt(553), however, tetragonal structures that have not been previously

observed were found to form across monatomic steps. These observations confirm DFT

calculations for submonolayer water coverage on Pt(553) and provide fine details as to how water-

water and water-surface interactions are balanced on active metal surfaces.

Wednesday Afternoon, October 21, 2015

2D Materials Focus Topic
Room: 212C - Session 2D+EM+IS+MC+NS+SP+SS-WeA

Dopants and Defects in 2D Materials

Moderator: Daniel Gunlycke, Naval Research Laboratory,
Zenghui Wang, Case Western Reserve University

2:20pm 2D+EM+IS+MC+NS+SP+SS-WeA1 The Effect of Defect Density on the Mechanical Properties of Graphene, *Jonathan Willman*, *J.M. Gonzales,* University of South Florida, *R. Perriot,* Los Alamos National Laboratory, *I.I. Oleynik,* University of South Florida
Recent experiments involving nanoindentation of graphene have demonstrated counterintuitive weakening of Young's modulus with increasing concentrations of point defects in graphene in contradiction to previous investigations. To fully resolve these inconsistencies we perform large-scale molecular dynamics simulations of nanoindentation under conditions of Atomic Force Microscopy (AFM) nanoindentation experiments. The reliable description of interatomic interactions is achieved by using recently developed screened environment-dependent bond order (SED-REBO) potential. The elastic properties of the defective graphene, the breaking strength and the mechanisms of fracture under indenter are investigated as a function of type of point defects as well as their concentration.

2:40pm 2D+EM+IS+MC+NS+SP+SS-WeA2 Investigation of Grain Boundaries in CVD Grown MoS₂, *Kolyo Marinov*, *D. Ovchinnikov, D. Dumcenco, A. Kis,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland
We present the characterization of grain boundaries in polycrystalline CVD-grown MoS_2 films. Epitaxial growth on sapphire substrates is achieved leading to preferred orientation of the domains, which is confirmed by transmission electron microscopy experiments. Using Scanning Kelvin probe microscopy the local potential drop across the three predominant types of grain boundaries in field effect transistors is investigated. These measurements demonstrate that the interfaces between single grains do not degrade the electrical conductivity, which is due to the well aligned growth of the single domains. Furthermore, the relatively high mobility of electrons in the polycrystalline material stays constant even in devices with channels of 80 µm containing multiple grains, separated by grain boundaries. Our approach is a step forward to fabrication of large-area, uniform and high quality single-layer CVD MoS_2.

3:00pm 2D+EM+IS+MC+NS+SP+SS-WeA3 Polycrystalline 2D Materials: Atomic Structure and Electronic Transport Properties, *Oleg Yazyev*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**
Grain boundaries and dislocations are intrinsic topological defects of polycrystalline materials, which inevitably affect their physical properties. In my talk, I will discuss the structure of topological defects in two-dimensional (2D) materials such as graphene and monolayer transition metal dichalcogenides (TMDCs) [1].

I will first introduce a general approach for constructing dislocations in graphene characterized by arbitrary Burgers vectors and grain boundaries covering the complete range of possible misorientation angles. By means of first-principles calculations we address the thermodynamic properties of grain boundaries revealing energetically favorable large-angle configurations as well as dramatic stabilization of small-angle configurations via the out-of-plane deformation, a remarkable feature of graphene as a two-dimensional material [2]. Both the presence of stable large-angle grain-boundary motifs and the out-of-plane deformation of small-angle configurations have recently been observed by scanning tunneling microscopy [3].

In the rest of my talk, I will focus on the electronic transport properties of polycrystalline 2D materials. Ballistic charge-carrier transmission across periodic grain boundaries is governed primarily by momentum conservation. Two distinct transport behaviors of such grain boundaries in graphene are predicted − either perfect reflection or high transparency with respect to low-energy charge carriers depending on the grain boundary periodicity [4]. It is also shown that certain periodic line defect structures can be engineered and offer opportunities for generating valley polarized charge carriers [5]. Beyond the momentum conservation picture we find that the transmission of low-energy charge carriers can be dramatically suppressed in the small-angle limit [6]. Unlike graphene, TMDCs combine a two-valley electronic band structure with strong spin-orbit effects. The latter can be employed for creating spin-polarized currents and adds yet another conservation law in the electronic transport across regular defects such as the frequently observed inversion domain boundaries [7,8].

* This work has been supported by the Swiss NSF, ERC and Graphene Flagship.

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4:20pm 2D+EM+IS+MC+NS+SP+SS-WeA7 Defects Compensation and Refining Optical Luminescence in Organic/Transition Metal Dichalcogenide Heterostructure, *J.H. Park,* UC San Diego, *A.M. Sanne, H.C.P. Movva,* UT-Austin, *S. Vishwanath,* Cornell University, *Il Jo Kwak,* UC San Diego, *H. Xing,* Cornell University, *J. Robertson,* University of Cambridge, UK, *S.K. Banerjee,* UT-Austin, *A.C. Kummel,* UC San Diego
Since layered transition-metal dichalcogenides(TMD) have demonstrated novel electronic and optoelectronic property, intense research has focused synthesis and integration into future electronic devices. Unlike graphene, TMD materials have band gaps, and these band structures can be tuned by thickness. However, in many cases, unintentional defects can be observed on TMD giving rise to the degradation of performance in the devices. Even for mechanical exfoliated TMD, there is a high density of defects, such as vacancies. For successful integration of TMD into devices, proper passivation of defects on TMD requires high stability in ambient conditions. In this study, a TiOPc monolayer was employed for passivation of defects to improve electrical and optical properties in TMD devices. Multilayer MoS_2 flakes were cleaved in ambient condition and transferred into the UHV chamber; afterwards. TiOPc monolayers were deposited on the MoS_2 surfaces by organic molecular beam epitaxy. After deposition, TiOPc forms a monolayer with only few defects, and the TiOPc monolayer structure has square lattice in a 1.5x1.5 nm grid. This crystal structure indicates that each TiOPc in the monolayer is directed outward to vacuum. The deposited TiOPc layer has very high thermal stability on MoS_2; the TiOPc layer on MoS_2 requires annealing above of 673K for desorption. This high thermal stability indicates there are strong interaction between TiOPc and MoS_2 surface. STS shows the band gap of the monolayer is 1.8 eV, while bulk MoS_2 has a 1.3eV band gap. Moreover, the Fermi level of TiOPc/bulk MoS_2 is shifted to the valence band, consistent with a P type shift. However, bulk MoS_2 surface, where less than monolayer of TiOPc was deposited, has Fermi level shifted towards the conduction band, consistent with N type doping. In the single layer MoS_2 deposited TiOPc monolayer, threshold bias is shifted from -30 V to near O V, indicating P-doping of MoS_2. It can be hypothesized that the work function transition of MoS2 is changed as a function of thickness. Before deposition of the TiOPc monolayer, the defects peak corresponded to S vacancy is displayed at 1.7 eV in photoluminescence. Conversely, the deposition of TiOPc monolayer almost completely suppresses S vacancy peak located 1.7 eV. Moreover, in the single layer MoS_2 FET, the on/off ratio is enhanced more than 2 orders magnitude. The similar charge transfer behavior also can be observed in TiOPc/WSe_2; on the bilayer WSe_2/HOPG, the TiOPc monolayer deposited on the first layer of WSe_2 shows the a conduction band shifted Fermi level, while a TiOPc monolayer deposited on the second layer of WSe_2 shows a valence band shifted Fermi level.

4:40pm 2D+EM+IS+MC+NS+SP+SS-WeA8 Reactivity and Wettability of PVD Metals on 2D Transition Metal Dichalcogenides, *Christopher Smyth,* *S. McDonnell, R. Addou, H. Zhu, C.L. Hinkle, R.M. Wallace,* University of Texas at Dallas
Transition metal dichalcogenides (TMDs) have been studied for years due to their tribological properties, but recent discoveries have illuminated unique opportunities for the use of single or few layer TMDs in electronics, specifically tunnel field effect transistors (TFETs). The properties of FETs fabricated with single and few layer TMDs have been investigated with some degree of success, but it has been shown via in-situ chemical analysis that interface interactions between certain contact metals and the underlying TMD are not fully understood[1,2].

In this study, the wettability and reactivity of various metals with a number of bulk TMDs (MoS_2, $HfSe_2$, $SnSe_2$, etc.) were investigated. Multiple samples were processed in parallel to ensure that all sample sets saw

identical metal depositions. The metal-TMD interface was monitored in-situ using X-ray photoelectron spectroscopy (XPS) and metal film topography was imaged using atomic force microscopy (AFM). For some low work function metals, noticeable differences in interface chemistry were found between samples that saw high vacuum rather than UHV metal e-beam depositions.

Significant variations in compatibility between contact metal and TMD were discovered. These variations were dependent upon the metal-TMD pair and the base pressure of the chamber prior to metal deposition. Au exhibits far superior wettability on $MoSe_2$, where uniform thin films were achieved, compared to $ReSe_2$, on which Au grows as clusters. Au wettability varies between that of thin films and clusters for the other TMDs studied. An Au thin film deposited on $SnSe_2$ results in the formation of reaction products such as Sn metal, as evidenced by the evolution of different chemical states in the Sn $3d$ spectrum after deposition. Reactions between MoS_2 and Sc producing Mo metal occur when Sc is deposited in UHV instead of HV. These results provide further understanding for the critical interface between Sc and TMD in high performance TFETs.

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5:00pm 2D+EM+IS+MC+NS+SP+SS-WeA9 Defects and Boundaries in 2D Materials: Correlating Electronic Properties to Atomic Structures, *An-Ping Li*, Oak Ridge National Laboratory **INVITED**
The quest for novel two-dimensional (2D) materials has led to the discovery of hybrid heterostructures of graphene and other 2D atomic films, which provide us fascinating playground for exploring defects and boundaries in a variety of atomic layers. Even in graphene itself, there usually exist large amount of extended topological defects, such as grain boundaries and changes in layer thickness, which divide graphene into grains and domains. These interfaces and boundaries can break the lattice symmetry and are believed to have a major impact on the electronic properties, especially the transport, in 2D materials.

Here, we report on the electronic and transport properties of two types of defects studied by STM and multi-probe scanning tunneling potentiometry with a focus on the correlations to their atomic structures. The first type of defect is the monolayer-bilayer (ML-BL) boundaries in epitaxial graphene on SiC. By measuring the transport spectroscopy across individual ML-BL graphene boundaries, a greater voltage drop is observed when the current flows from monolayer to bilayer graphene than in the reverse direction, displaying an asymmetric electron transport upon bias polarity reversal [1, 2]. Interestingly, this asymmetry is not from a typical nonlinear conductance due to electron transmission through an asymmetric potential. Rather, it indicates the opening of an energy gap at the Fermi energy. Another type of defect is 1D interface in hexagonal boron nitride (hBN) and graphene planar heterostructures, where a polar-on-nonpolar 1D boundary is expected to possess peculiar electronic states associated with edge states of graphene and the polarity of hBN [2]. By implementing the concept of epitaxy to 2D space, we grow monolayer hBN from fresh edges of monolayer graphene with lattice coherence, forming a 1D boundary [3]. STM/STS measurements reveal an abrupt 1D zigzag oriented boundary, with boundary states about 0.6 eV below or above the Fermi level depending on the termination of the hBN at the boundary [4]. The boundary states are extended along the boundary, and exponentially decay into the bulk of graphene and hBN. The origin of boundary states and the effect of the polarity discontinuity at the interface will be discussed.

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4 J. Park et al., *Nature Commun.* **5**, 5403 (2014).

5:40pm 2D+EM+IS+MC+NS+SP+SS-WeA11 Metal Ion Intercalated 2D Materials as Transparent Electrodes, *Jiayu Wan**, *W. Bao, F. Gu*, University of Maryland, College Park, *M. Fuhrer*, Monash University, Malaysia, *L. Hu*, University of Maryland, College Park
Transparent electrode materials are critical for optoelectronic devices such as touch screen and solar cells. Graphene has been widely studied as transparent electrodes for its unique physical properties. To further boost the performance of graphene based transparent electrodes, we novelized Li-ion intercalation in graphene, and achieved highest performance of carbon based transparent electrodes.[1] Transmission as high as 91.7% with a sheet resistance of 3.0 ohm/sq is achieved for 19-layer LiC_6, which corresponds to a figure of merit ($Sigma_{dc}/Sigma_{opt}$) at 1,400, significantly higher than any other continuous transparent electrodes. The unconventional modification of ultrathin graphite optoelectronic properties is explained by the suppression of interband optical transitions and a small intraband Drude conductivity near the interband edge. To achieve low cost, large scale graphene-based transparent electrodes, we further developed Na-ion intercalated printed reduced graphene oxide (RGO) film[2]. Unlike pristine graphene that inhibits Na-ion intercalation, the larger layer-layer distance of RGO allows Na-ion intercalation, leading to simultaneously much higher DC conductivity and higher optical transmittance. The typical increase of transmittance from 36% to 79% and decrease of sheet resistance from 83 kohms/sq to 311 ohms/sq in the printed network was observed after Na-ion intercalation. Compared with Li-intercalated graphene, Na-ion intercalated RGO shows much better environmental stability, which is likely due to the self-terminating oxidation of Na ions on the RGO edges. This study demonstrated the great potential of metal-ion intercalation to improve the performance of graphene-based materials for transparent conductor applications.

Reference
1. Jiayu Wan[a], Wenzhong Bao[a], et al., Nature communications, 2014,5, 4224. ([a] equally contribution)

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6:00pm 2D+EM+IS+MC+NS+SP+SS-WeA12 Oxygen Reduction Reaction on Nitrogen-doped Graphene, *Jun Nakamura*, The University of Electro-Communications (UEC-Tokyo), Japan, *A. Ichikawa, H. Matsuyama, A. Akaishi*, The University of Electro-Communications (UEC-Tokyo)
Recently, several groups have reported high oxygen reduction reaction (ORR) activities in nitrogen-doped carbon nanomaterials which are candidates of metal-free catalysts for ORR [1]. Lee et al. have successfully fabricated nitrogen-doped graphene with the high ORR activity in acid media [2]. It has been confirmed that local atomic configurations of dopants in nitrogen-doped graphene are classified into three functional groups (pyrrole-like, pyridine-like, and graphite-like configurations) [3,4]. However, the mechanism of the ORR on the nitrogen-doped graphene has not fully understood.

In this work, we examine the ORR on the nitrogen-doped graphene containing the graphite-like N in a basal plane using first-principles calculations. In general, the ORR occurs mainly two pathways: The two-electron pathway (2e-) that is reduced to hydrogen peroxide ($H2O2$), and the direct four-electron pathway (4e-) that reduces to water ($H2O$). Thermodynamic electrode potentials of each process at standard conditions are about 0.68V (2e-) and 1.23V (4e-), respectively. In case of the associative mechanism for the two- and four- electron reduction pathways, the electrocatalytic activity is governed by the stability of reaction intermediates like OOH*, OH*, and O* (where "*" refers to a surface site). Free energies of the reaction intermediates have been calculated based on the computational hydrogen electrode model suggested by Nørskov et al. [5]. We have taken account of effects of electrode potential, Ph of a solution, a local electric field in double layer, and water environment.

We have constructed energy diagrams at several electrode potentials on the basis of the first-principles calculations. It has been shown that the 2e- and 4e- reduction processes proceed at potentials up to about 0.5V and 0.8V, respectively. This means that we can control the reduction pathway for the nitrogen-doped graphene with the graphite-like N. Proton-electron transfer to OOH* (the 2e- pathway), and the formation of OOH* (the 4e- pathway) are confirmed to be the rate-limiting steps, respectively. Density dependence of N on the ORR activity will also be discussed in the presentation.

References
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In-Situ Spectroscopy and Microscopy Focus Topic
Room: 211B - Session IS+SS+NS+BI+VT+MN+AS-WeA

In situ Imaging of Liquids using Microfluidics
Moderator: Xiao-Ying Yu, Pacific Northwest National Laboratory, Stephen Nonnenmann, University of Massachusetts - Amherst

2:20pm   IS+SS+NS+BI+VT+MN+AS-WeA1   *In Situ* Multimodal Biological Imaging using Micro- and Nanofluidic Chambers, *James Evans*, *C. Smallwood*, Pacific Northwest National Laboratory   **INVITED**
Biological organisms have evolved a number of spatially localized and highly orchestrated mechanisms for interacting with their environment. Since no single instrument is capable of probing the entire multidimensional landscape, it is not surprising that one of the grand challenges in biology remains the determination of how dynamics across these scales lead to observed phenotypes.

Therefore, there is a need for in-situ correlative multimodal and multiscale imaging to fully understand biological phenomena and how chemical or structural changes at the molecular level impact the whole organism. We have been advancing new methods for both cryogenic and in-situ correlative analysis of biological samples using electron, ion, optical and x-ray modalities. Central to this work is the development of new micro- and nanofluidic chambers that enable in-situ observations within precisely controlled liquid-flow environments. In this talk I will review the design of these new chambers, highlight current science applications and outline our future goals for adding additional functionality and expanding the versatility of the devices to other disciplines.

3:00pm IS+SS+NS+BI+VT+MN+AS-WeA3 Glyoxal Aqueous Surface Chemistry by SALVI and Liquid ToF-SIMS, *Xiao Sui*, *Y. Zhou*, *Z. Zhu*, Pacific Northwest National Laboratory, *J. Chen*, Shandong University, China, *X.-Y. Yu*, Pacific Northwest National Laboratory
Glyoxal, a ubiquitous water-soluble gas-phase oxidation product in the atmosphere, is an important source of oxalic acid, a precursor to aqueous secondary organic aerosol (SOA) formation. Many recent laboratory experiments and field observations suggest that more complex chemical reactions can occur in the aqueous aerosol surface; however, direct probing of aqueous surface changes is a challenging task using surface sensitive techniques. The ability to map the molecular distribution of reactants, reaction intermediates, and products at the aqueous surface are highly important to investigate surface chemistry driven by photochemical aging. In this study, photochemical reactions of glyoxal and hydrogen peroxide (H_2O_2) were studied by a microfluidic reactor, System for Analysis at the Liquid Vacuum Interface (SALVI), coupled with Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Aqueous surfaces containing glyoxal and hydrogen peroxide were exposed to UV light at variable lengths of time and were immediately analyzed in the SALVI microchannel by in situ liquid ToF-SIMS. In addition, various control samples were conducted to ensure that our findings were reliable. Compared with previous results of bulk solutions using ESI-MS, our unique liquid surface molecular imaging approach provided observations of glyoxal hydrolysis (i.e., first and secondary products, dimers, trimers, and other oligomers) and oxidation products (i.e., glyoxylic acid, oxalic acid and formic acid) with sub-micrometer spatial resolution. We potentially provide a new perspective and solution to study aqueous surface chemistry as an important source of aqueous SOA formation of relevance to atmospheric chemistry known to the community.

3:20pm IS+SS+NS+BI+VT+MN+AS-WeA4 Investigating *Shewanella Oneidensis* Biofilm Matrix in a Microchannel by *In Situ* Liquid ToF-SIMS, *Yuanzhao Ding*, Nanyang Technological University, Singapore, *X. Hua*, *Y. Zhou*, *J. Yu*, *X. Sui*, *J. Zhang*, *Z. Zhu*, Pacific Northwest National Laboratory, *B. Cao*, Nanyang Technological University, Singapore, *X.-Y. Yu*, Pacific Northwest National Laboratory
Biofilms consist of a group of micro-organisms attached onto surfaces or interfaces and embedded with a self-produced extracellular polymeric substance (EPS) in natural environments. The EPS matrix, like the "house of the cells", provides bacteria cells with a more stable environment and makes them physiologically different from planktonic cells. *Shewanella*

oneidensis MR-1 is a metal-reducing bacterium, forming biofilms that can reduce toxic heavy metals. This capability makes *S. oneidensis* biofilms very attractive in environmental applications. To better understand the biofilm EPS matrix composition at the interface, in situ chemical imaging with higher spatial resolution and more molecular level chemical information is strongly needed. Traditionally, electron microscopy and fluorescence microscopy are common imaging tools in biofilm research. However, the bottlenecks in these imaging technologies face the limitations that it is difficult for them to provide chemical information of small molecules (e.g., molecule weight <200). In this study, we use an emerging technology liquid Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) to observe *S. oneidensis* biofilm cultured in a vacuum compatible microchannel of the System for Analysis at the Liquid Vacuum Interface (SALVI) device. Chemical spatial distributions of small organic molecules that are considered to be the main building components of EPS in live biofilms are obtained. Principal component analysis is used to determine differences among biofilms sampled along the microchannel. This new approach overcomes previous limitations in live biofilm analysis and provides more chemical information of the EPS relevant to biofilm formation. Better understanding of the biofilm matrix will potentially fill in the knowledge gap in biofilm surface attachment and detachment processes and improve the engineering and design of *S. oneidensis* biofilms with high efficiencies in heavy metal reduction.

4:20pm   IS+SS+NS+BI+VT+MN+AS-WeA7   Ultrafast Proton and Electron Dynamics in Core-Level Ionized Aqueous Solution, *Bernd Winter*, Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherring BESSY II, Germany   **INVITED**
Photo- and Auger electron spectroscopy from liquid water reveals a novel electronic de-excitation process of core-level ionized water in which a pair of two cations forms, either $H_2O^+ \cdot H_2O^+$ or $OH^+ \cdot H_3O^+$. These reactive species are the delocalized analogue to H_2O^{2+}, formed in a localized on-site Auger decay, and are expected to play a considerable role in water radiation chemistry. Both cationic pairs form upon autoionization of the initial ionized water molecule, and we are particularly interested in the situation where autoionization occurs from a structure that evolves from proton transfer, from the ionized water molecule to a neighbor molecule, within a few femtoseconds. The actual autoionization is either through intermolecular Coulombic decay (ICD) or Auger decay. Experimental identification of the proton dynamics is through isotope effects. A question that arises is whether such so-called proton-transfer mediated charge separation (PTM-CS) processes occur in other and similarly hydrogen-bonded solute molecules as well. This is indeed the case, and is illustrated here for ammonia and glycine in water, as well as for hydrogen peroxide in water, where characteristic differences are detected in the Auger-electron spectra from the light *versus* heavy species, *i.e.*, NH_3 in H_2O *versus* ND_3 in D_2O, glycine(H) in H_2O versus glycine(D) in D_2O, and H_2O_2 in H_2O versus D_2O_2 in D_2O. The important spectral feature here is the high-kinetic energy tail of the Auger spectrum, which has no gas-phase analogue, and hence reflects the participation of solvent water in the relaxation process. The probability of the proton dynamics, judged from the intensities of the electron signal and inferred from methods of quantum chemistry and molecular dynamics, is found to depend on hydrogen-bond strength and hence on the specific hydration configuration. Favorable configurations for hydrogen peroxide(aq) occur due to the molecule's flexible structure. In ammonia(aq) the PTM processes are found to be less probable than for water(aq), which is attributed to the planarization of the ammonia molecule upon core-level ionization. The effect is smaller for the neutral $-NH_2$(aq) group of glycine at basic pH, where intramolecular dynamics is less likely. Nature and chemical reactivity of the initial transient species and their role for radiation chemistry and for local reactions relevant for biological molecules in an aqueous environment are discussed for the different molecular hydrogen-bonded systems.

5:00pm   IS+SS+NS+BI+VT+MN+AS-WeA9   Water Dissociation in Metal Organic Frameworks with Coordinatively Unsaturated Metal Ions: MOF-74, *Kui Tan*, The University of Texas at Dallas, *S. Zuluaga*, Wake Forest University, *E. Fuentesf*, The University of Texas at Dallas, *H. Wang*, Rutgers University, *P. Canepa*, Wake Forest University, *J. Li*, Rutgers University, *T. Thonhauser*, Wake Forest University, *Y.J. Chabal*, The University of Texas at Dallas
Water dissociation represents one of the most important reactions in catalysis, essential to the surface and nano sciences. However, the dissociation mechanism on most oxide surfaces is not well understood due to the experimental challenges of preparing surface structures and characterizing reaction pathways. To remedy this problem, we propose the metal organic framework MOF-74 as an ideal model system to study water reactions. Its crystalline structure is well characterized; the metal oxide node mimics surfaces with exposed cations; and it degrades in water. Combining *in situ* IR spectroscopy and first-principles calculations, we

explored the MOF-74/water interaction as a function of vapor pressure and temperature. Here, we show that, while adsorption is reversible below the water condensation pressure (~19.7 Torr) at room temperature, a reaction takes place at ~150 °C even at low water vapor pressures. This important finding is unambiguously demonstrated by a clear spectroscopic signature for the direct reaction using D_2O, which is not present using H_2O due to strong phonon coupling. Specifically, a sharp absorption band appears at 970 cm^{-1} when D_2O is introduced at above 150 °C, which we attribute to an O-D bending vibration on the phenolate linker. Although H_2O undergoes a similar dissociation reaction, the corresponding O-H mode is too strongly coupled to MOF vibrations to detect. In contrast, the O-D mode falls in the phonon gap of the MOF and remains localized. First-principles calculations not only positively identify the O-D mode at 970 cm^{-1} but derive a pathway and kinetic barrier for the reaction and the final configuration: the D (H) atom is transferred to the oxygen of the linker phenolate group, producing the notable O-D absorption band at 970 cm^{-1},while the OD (or OH) binds to the open metal sites. Experimental data and theoretical modeling further shows that the reaction is facilitated by a cooperative effect of several H_2O molecules. This finding explains water dissociation in this case and provides insight into the long-lasting question of MOF-74 degradation. Overall, it adds to the understanding of molecular water interaction with cation-exposed surfaces to enable development of more efficient catalysts for water dissociation.

Ref: K. Tan, S. Zuluaga, Q. Gong, P. Canepa, H. Wang, J. Li, Y. J. Chabal and T. Thonhauser, *Chem. Mater.*, 2014, **26**, 6886-6895.

5:20pm IS+SS+NS+BI+VT+MN+AS-WeA10 Competitive Co-Adsorption of CO_2 with H_2O, NH_3, SO_2, NO, NO_2, N_2, O_2, and CH_4 in M-MOF-74 (M= Mg, Co, Ni): The Role of Hydrogen Bonding, *K. Tan,* The University of Texas at Dallas, *Sebastian Zuluaga,* Wake Forest University, *H. Wang,* Rutgers University, *Y. Gao,* The University of Texas at Dallas, *J. Li,* Rutgers University, *T. Thonhauser,* Wake Forest University, *Y.J. Chabal,* The University of Texas at Dallas
The importance of co-adsorption for applications of porous materials in gas separation has motivated fundamental studies, which have initially focused on the comparison of the binding energies of different gas molecules in the pores (i.e. energetics) and their overall transport. By examining the competitive co-adsorption of several small molecules in M-MOF-74 (M= Mg, Co, Ni) with *in-situ* infrared spectroscopy and *ab initio* simulations, we find that the binding energy at the most favorable (metal) site is not a sufficient indicator for prediction of molecular adsorption and stability in MOFs. Instead, the occupation of the open metal sites is governed by kinetics, whereby the interaction of the guest molecules with the MOF organic linkers controls the reaction barrier for molecular exchange. Specifically, the displacement of CO_2 adsorbed at the metal center by other molecules such as H_2O, NH_3, SO_2, NO, NO_2, N_2, O_2, and CH_4 is mainly observed for H_2O and NH_3, even though SO_2, NO, and NO_2 have higher binding energies (~70-90 kJ/mol) to metal sites than that of CO_2 (38 to 48 kJ/mol) andslightly higher than water (~60-80 kJ/mol). DFT simulations evaluate the barriers for H_2OàCO_2 and SO_2àCO_2 exchange to be ~ 13 and 20 kJ/mol, respectively, explaining the slow exchange of CO_2 by SO_2, compared to water. Furthermore, the calculations reveal that the kinetic barrier for this exchange is determined by the specifics of the interaction of the second guest molecule (e.g., H_2O or SO_2) with the MOF ligands. Hydrogen bonding of H_2O molecules with the nearby oxygen of the organic linker is found to facilitate the positioning of the H_2O oxygen atom towards the metal center, thus reducing the exchange barrier. In contrast, SO_2 molecules interact with the distant benzene site, away from the metal center, hindering the exchange process. Similar considerations apply to the other molecules, accounting for much easier CO_2 exchange for NH_3 than for NO, NO_2, CH_4, O_2, and N_2 molecules. In this work, critical parameters such as kinetic barrier and exchange pathway are first unveiled and provide insight into the mechanism of competitive co-adsorption, underscoring the need of combined studies, using spectroscopic methods and *ab initio* simulations to uncover the atomistic interactions of small molecules in MOFs that directly influence co-adsorption.

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6:00pm IS+SS+NS+BI+VT+MN+AS-WeA12 *In Situ* STM Observation of Pd(110) Under the Hydrogen Pressure Between 10^{-6} Pa and 10^{-3} Pa, *Jun Yoshinobu, H. Kikuchi, T. Koitaya, K. Mukai, S. Yoshiomoto,* University of Tokyo, Japan
Hydrogen adsorption and absorption on/in Pd and Pd alloys are vital processes for the hydrogen storage and hydrogen permeation materials. We investigated the Pd(110) surface under the hydrogen pressures between 10^{-6} Pa and 10^{-3} Pa at room temperature using in-situ atom-resolved scanning tunneling microscopy (STM). We observed missing-atom, missing-row and added-row structures and the number of atoms in these structures were quantitatively analyzed as a function of exposure time. Note that adatoms

were not detected probably because they were mobile in the present experimental conditions. At 10^{-6} Pa, the numbers of missing-row and added-row atoms increased up to ~20 L (langmuir) and after that they were gradually reaching the saturation (steady-state). On the other hand, the number of missing-atoms decreased gradually from the initial stage. With increasing the hydrogen pressures the number of missing-row atoms and added-row atoms increased, and the whole surface was covered with these reconstructed structures after large exposures (>1000 L). It has been known that not only hydrogen adsorption but also hydrogen absorption occur in such conditions. Thus, the missing-row and added-row reconstructed structures are inevitable for hydrogen absorption on Pd(110).

Nanometer-scale Science and Technology
Room: 212B - Session NS+EN+MG+SS+TF-WeA

Nanoscale Catalysis and Surface Chemistry
Moderator: Sidney Cohen, Weizmann Institute of Science, Israel

2:20pm NS+EN+MG+SS+TF-WeA1 Effects of γ-Al_2O_3 Support on the Geometry and Electronic Structure of H-covered Pt Nanoparticles, *Sampyo Hong, G. Shafai, T.S. Rahman*, University of Central Florida
We have studied the effects of γ-Al_2O_3(110) support on the geometry and electronic structures of H-coveredPt$_x$ (x=22,44) nanoparticles (NP) using density functional theory (DFT). We find that the unoccupied d-band center of γ-Al_2O_3(110) supported Pt NPs exhibits a blue shift with decreasing Pt size similarly as the measured XANES absorption peak energy of Pt NP samples. In fact, our DFT results reveal that the shift of the unoccupied d-band center of Pt NPs is dependent of surface hydroxylation level on γ-Al_2O_3(110). At higher hydroxylation the calculated unoccupied d-band center can even show red shift. Thus, consideration of hydroxylation level on γ-Al_2O_3(110) is needed to properly interpret support effect from XANES spectra. Overall, the strength of Pt- γ-Al_2O_3(110) binding seems to be a reasonable measure of the shift of unoccupied d-band center as a result of metal-support interaction: the stronger the interaction the more the blue shift. In the light of these results, it is plausible to postulate that the adsorption energy shift of XANES spectra represent the strength of metal-support interaction (support effect). A remarkable example of such hydroxylation tuned metal-support interaction is structural transition of Pt$_{22}$ from a biplanar to a 3D-like geometry as a function of support hydroxylation.

3:00pm NS+EN+MG+SS+TF-WeA3 Fabrication and SERS Activity of Metal-loaded TiO_2 Nanometer ScaleParticles, *Paolo Reyes, J.C. Hemminger*, University of California Irvine
Our current research focuses on the fabrication and study of metallic loaded titanium dioxide (TiO_2) nanoparticles supported by highly oriented pyrolitic graphite (HOPG). Highly dispersed TiO_2 particles are formed via physical vapor deposition (PVD) under high vacuum settings with an average pseudo-diameter of 11.6 ± 2.65 nm. Metallic loading is completed by an ex-situ photo-deposition method by exposure to precursor metal salt solutions under TiO_2 bandgap UV irradiation. We have attempted to fabricate Pt-, Ag-, Au-, and Pt-Au-TiO_2 particles and observed photocatalytic enhancement with the inclusion of Pt nanoparticles deposited onto TiO_2 surfaces. We believe this enhancement is a result of Pt nanoparticles harboring free excited electrons and preventing electron-hole recombination. We have developed a technique to increase the density of TiO_2 particles by creating site defects on the surface of HOPG through plasma mild oxygen plasma exposure. Highly dispersed TiO_2 nanoparticle distributions allow an increase of metal nanoparticle formation on TiO_2 for surface and intrinsic property observations. Ag nanoparticles have been fabricated in order to observe Surface Enhanced Raman Spectroscopy (SERS) Ag nanoparticles were observed to be an average pseudo-diameter of 2.6 ± 1.4 nm. A probe molecule was used to determine Raman intensity enhancement factor (EF) and we believe that the EF can be affected by the spacing and size of Ag-TiO_2 nanoparticles. We will present our studies of bi-metallic loading of TiO_2.

4:20pm NS+EN+MG+SS+TF-WeA7 Pyridine Coordination Chemistry for Molecular Assemblies, *Milko Van der Boom*, Weizmann Institute of Science, Israel **INVITED**

Many types of metal-ligand interactions have creatively been used in the chemical sciences since the description of coordination complexes. The rich coordination chemistry of pyridine-type ligands has contributed significantly to the incorporation of metal ions into functional materials on surfaces. We will discuss molecular assemblies formed with a variety of pyridine-based compounds. These assemblies are formed by layer-by-layer deposition from solution that allows for precise fitting of the assembly properties. The degree of intermolecular interactions can be controlled by varying the degree of π-conjugation and the availability of coordination sites. Unlike molecular assemblies that are constructed with organic ligands, assemblies with polypyridyl complexes are active participants in their own formation and amplify the growth of the incoming molecular layers. Such a self-propagating behavior for molecular systems is rare and the mechanism of their formation will be presented. Incorporating multiple metal complexes into a single assembly give rise to composite materials that exhibit unique electrochemical and electrochromic properties that are dependent on the arrangement of these metal complexes. We will also discuss the coordination chemistry of pyridine-based compounds with nanoparticles, the formation of metal-organic frameworks and their practical applications.

5:00pm NS+EN+MG+SS+TF-WeA9 Atomic Scale Iron Carbide Films on Au(111) and Cu(111) as a Iron Fischer-Tropsch Model Catalyst, *Gilbère Mannie*, X. Wen, Y.W. Li, SynCat@Beijing, China, *J.V. Lauritsen*, Interdisciplinary Nanoscience Center (iNANO), Denmark, *H.J.W. Niemantsverdriet*, SynCat@Beijing, China

Iron-based Fischer-Tropsch synthesis (FTS) is one of the most investigated catalytic systems in the world due to the ability to convert any form of hydrocarbons like coal, natural gas or biomass into diesel, gasoline and chemicals [1]. Although investigated for more than 50+ years, fundamental surface reactions involved in this process are not known or fully understood. Within the FTS community, iron carbide is seen as the active phase in the catalytic process but the atomic-scale surface structure and even the stoichiometry of the bulk phase is a matter of debate [1,2]. In order to fundamentally investigate the active phase, to for example verify molecular modeling studies on iron carbide surfaces (like [3,4]), we successfully synthesized highly-crystalline iron carbide monolayer islands (on Au(111)) and multilayer islands (on Cu(111)). Obtained carbidic films are suitable for analysis with scanning tunneling microscopy (STM) and other surface science techniques. Our atomically-resolved STM results, together with preliminary density functional theory (DFT) results show that we can characterize our iron carbide (Fe_xC_y) islands as iron layer with interstitial carbon atoms, based on the increase of the inter-atomic Fe-Fe distance [5]. During the synthesis of the Fe_xC_y islands we were able to record some STM movies showing the formation of the carbidic phase out of the metallic phase but we could also record movies during dosing experiments of several gasses (H_2, O_2) to the pure iron carbide islands. During the presentation we will explain how we synthesized these crystalline iron carbide films and how these films can act as a model system for fundamental Fischer-Tropsch catalyst research.

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5:20pm NS+EN+MG+SS+TF-WeA10 Fullerene Interaction with W Surfaces: Synthesis of Nanospheres with Tunable Bandgap, *Ehsan Monazami*, University of Virginia, *J.B. McClimon,* University of Pennsylvania, *P. Reinke*, University of Virginia

The interaction of f C_{60} molecules with metal surfaces is a topic of considerable interest and discussed in the context of molecular electronics and organic solar cell applications. Our work focuses on the interaction of C_{60} with W, which is a carbide forming transition metal. It has generally been assumed that the C_{60} cage breaks up readily on a W surface, but our observations reveal a more complex, temperature induced reaction sequence leading to the formation of nanospheres with variable bandgap, which has been studied with in-situ STM and STS analysis.

The nanospheres are synthesized by initiating the reaction between C_{60} deposited on a W-thin film surface grown on MgO(001) at about 450 K. In contrast to previous reports, the molecules do not collapse but the spherical shape is retained up to 800 K and the electronic structure changes gradually from wide bandgap C_{60} to fully metallic nanospheres. The size distribution of the nanospheres is centered at 1.5 nm (600 K) and shifts for higher temperatures to about 2 nm with a concurrent decrease in height resulting in an ellipsoidal shape. These nanoshères present an exceptional resistance to sintering which is a unique feature for metallic nanoparticles. The densely packed C_{60} and isolated C_{60} molecules show the same transition in shape and electronic structure which confirms that the transformation is controlled by the reaction with the W substrate.

The transition in the electronic structure progresses gradually from the wide-bandgap molecule (2.3 eV) to a bandgap of ~1eV at 700 K, and a metallic surface at 800 K. We will illustrate this progression with a series of ST spectra and maps. The bandgap variation offers for the first time a pathway to the formation of nanoscale clusters (nanospheres) with variable bandgap while retaining the surface curvature in narrow range. The detailed structure of the nanospheres is, however, still subject to discussion. We currently favor, based on our experimental results, a substitution model where the W-atoms from the substrate react with the C_{60} cage which acts as a scaffold. The W atoms are incorporated substitutionally forming a carbide type bonding, whose presence is indicated by XPS analysis. The variation in bandgap is then driven by the degree of substitution and the fullerene molecule acts as a scaffold. We predict that other carbon scaffolds such as nanotubes and carbide forming transition metals can react in the same manner leading to a new class of nanostructures with unique adaptability of the electronic structure. The nanospheres are an excellent testbed for the physics and chemistry of highly curved surfaces.

Supported by NSF-DMR Ceramics DMR-100580.

5:40pm NS+EN+MG+SS+TF-WeA11 Enantiomeric Separations of Chiral Pharmaceuticals using Chiral Tetrahexahedral Au Nanoparticles, *Nisha Shukla*, D. Yang, A.J. Gellman, Carnegie Mellon University

Chiral tetrahexahedral (24-sided) Au nanoparticles are tested for their use as chiral separators of pharmaceutical drugs in solution phase. Tetrahexahedral Au nanoparticles were chirally modified with either D- or L-cysteine. They show enantioselective adsorption of pharmaceuticals such as propranolol hydrochloride (used for anxiety and high blood pressure) from a solution of racemic propranolol hydrochloride, thus leaving an enantiomeric excess in the solution phase. This work suggests that chiral nanoparticles can be used for enantiomeric separation of real pharmaceutical drugs. A simple robust model has also been developed that allows extraction of the enantiospecific equilibrium constants for R- and S-propranolol hydrochloride adsorption on the chiral tetrahexahedral Au nanoparticles. The model obviates the need for experimental determination of the surface area of absorbent Au nanoparticles which is extremely difficult to measure.

6:00pm NS+EN+MG+SS+TF-WeA12 Electroreduction Catalysis with Defect-Rich Metal Nanoparticles, *Xiaofeng Feng*, M. Kanan, Stanford University

New design principles for electroreduction catalysts are essential for CO_2 recycling using renewable electricity. Au is one of the most active catalysts for CO_2 reduction to CO, and numerous efforts have been made to optimize Au catalysts by tuning the size, composition, and shape of Au nanostructures. Here we show that grain boundaries (GBs) in Au nanoparticles create highly active surface sites for CO_2 electroreduction (1). Defect-rich Au nanoparticles were synthesized by vapor deposition of Au onto a carbon nanotube thin film, which enables direct TEM characterization without further processing. We compared the CO_2 reduction activity of the as-deposited catalysts to those annealed at different temperatures. While the annealing process has little impact on the distribution of Au surface facets, it reduces the GB density, which is quantified by measuring GB lengths and particle areas from high-resolution TEM images. We found that the surface-area-normalized activity for CO_2 reduction is linearly correlated with GB density in Au nanoparticles in the low overpotential regime. Similarly, GB-density was also found to correlate with catalytic activity for the electroreduction of CO to multi-carbon oxygenates on Cu nanoparticles. Our studies show that grain boundary engineering is a general strategy for improving electrocatalytic activity for carbon fuel synthesis.

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Scanning Probe Microscopy Focus Topic
Room: 212A - Session SP+2D+AS+NS+SS-WeA

Probing Electronic and Transport Properties
Moderator: Tae-Hwan Kim, Pohang University of Science and Technology, Jewook Park, Oak Ridge National Laboratory

2:20pm **SP+2D+AS+NS+SS-WeA1 Geometric and Electronic Structures of Epitaxially Grown Pnictide 122, 111 and Cu$_x$Bi$_2$Se$_3$ Samples**, *Young Kuk*, Seoul National University, Republic of Korea **INVITED**
Order parameters were measured mainly on low-temperature cleaved, superconductor surfaces from their measured topographic images (constant current maps) and Fourier-transformed, measured density of states (energy dependent dI/dV map) in previous scanning tunneling microscopy (STM) studies. However, no direct evidence of coupling mechanisms has been given for these *high temperature* superconductors by these STM studies. We intend to study how homogeneity of a doped sample influences the superconducting property in an STM study. We were able to grow pnictide 111, 122, and Cu$_x$Bi$_2$Se$_3$ samples by molecular beam epitaxy. We found that surfaces of these grown samples are often terminated by alkali or alkaline atomic plane or non-superconducting metallic planes. These surfaces reveal distorted superconducting or non-superconducting properties. We adopted various ways to expose the superconducting planes in these samples. At the same time, we tried to grow samples homogeneously doped over the coherence lengths. Nodal structures were observed on these samples in their quasiparticle interference patterns. In this talk we will discuss the properties of the s±, s, d states as likely candidates pairing states for these materials.

3:00pm **SP+2D+AS+NS+SS-WeA3 Direct Measurement of Conductance from Topological Surface States in Topological Insulators**, *Corentin Durand*, X. Zhang, S. Hus, M. McGuire, I. Vlassiouk, A.-P. Li, Oak Ridge National Laboratory
Topological insulators (TI) with characteristic topological surface states (TSS) attract great interest for both fundamental physics and device applications. However, the unavoidable presence of defects in bulk single crystals usually dopes the material leading to a metallic behavior. Thus, the direct measurement of the TSS electronic transport properties is hard to achieve due to the dominant contribution from the bulk states. Here, we measure the transport properties of Bi$_2$Se$_3$ crystals by Four Probe Scanning Tunneling Microscopy (4P-STM) technique at different temperatures on fresh surfaces obtained by cleavage in Ultra-High Vacuum (UHV) (base pressure = $2x10^{-10}$ Torr). In contrast to conventional models that assume two resistors in parallel to count for both the TSS and bulk conductance channels, we show that this technique can be used to differentiate the 2D contribution of TSS to the transport from the 3D contribution (bulk) by considering the potential profiles across the interface. Our method allows quantitative determination of conductivities from both channels. We also compare our results with samples exhibiting pure 2D and 3D transport behaviors. Our results shows that our approach enables direct distinguishing and accessing electronic transport of TI surfaces surface states, which can be applied to the studies of 2D to 3D crossover of conductance in other complex systems.

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

3:20pm **SP+2D+AS+NS+SS-WeA4 Chiral Edge States of Topological Insulator in 1D**, *Tae-Hwan Kim*, Pohang University of Science and Technology, Republic of Korea, *S. Cheon, S.-H. Lee*, Institute for Basic Science, Republic of Korea, *H.W. Yeom*, Pohang University of Science and Technology and Institute for Basic Science, Republic of Korea
Chiral edge states are one of the most fascinating hallmark of topological insulators [1-4]. While chiral edge states are the vitally important feature of 2D and 3D topological insulators, no correspondence has yet been found in 1D. On the other hand, in 1D, a Peierls-distorted atomic chain such as polyacetylene has two topologically different ground states and a topological edge state or so-called a topological soliton connecting between them [5,6]. The topological edge states in 1D show many interesting properties such as charge-spin separation, fractional charge, and so on [7,8]. However, they do not exhibit chirality as 2D or 3D topological insulators do. In this talk, we report that the 1D topological edge states, solitons, of the charge-density wave (CDW) system of indium atomic wires self-assembled on a silicon surface have the chiral property [9,10]. Our system can be well described by a coupled double Peierls-distorted atomic chain with zigzag interchain coupling, which induces dynamical sublattice symmetry breaking. This subtle change ensures a dynamically generated topological

structure with four-fold symmetric ground states and has topological edge states with a new degree of freedom, chirality, which is absent in the case of a single Peierls atomic chain. We have performed scanning tunneling microscopy and spectroscopy in order to obtain experimental evidences of the chiral edge states in the 1D CDW. Individual right- and left-chiral edge states are directly identified from non-chiral ones, which are similar to the topological solitons found in a single Peierls atomic chain. Furthermore, we found that chiral edge states can produce quantized charge pumping across the chain that is topologically protected and controllable by their chirality. Thus, these topological chiral edge states or solitons can be utilized for future single-electron-level data storage devices or logic circuits, which are topologically protected.

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4:20pm **SP+2D+AS+NS+SS-WeA7 Electronic Properties of Quasi-one-dimensional Defects in Monolayer h-BN**, *Chuanxu Ma, J. Park,* Oak Ridge National Laboratory, *L. Liu, G. Gu,* The University of Tennessee, *A.P. Baddorf, A.-P. Li,* Oak Ridge National Laboratory
Two-dimensional (2D) hexagonal boron nitride (h-BN) monolayers have wide promising applications in nanoelectronics. The presence of defects could greatly impact its electronic properties. Here, we present experimental results about two types of line defects in h-BN monolayers, prepared on Cu foils by chemical vapor deposition (CVD) method.

Using scanning tunneling microscopy/spectroscopy (STM/STS), the structural and electronic properties of two types of quasi-1D defects are characterized in monolayer h-BN. An energy gap ~4 Ev is observed for h-BN monolayers on Cu foils. The first type of quasi-1D defects is the worm-like defects with length 3~30 nm, and width ~1.5 nm. Nano-ripples with modulation λ ~ 5.2 Å, which is about double the size of h-BN lattice, are observed both from the topographic images and Di/Dv mappings along the worm-like defects. The modulation is in phase at negative bias and out of phase at positive bias between the topographic images and Di/Dv mappings. The defects also show higher tunneling conductance than the h-BN sheet in the Di/Dv mappings. The observed nano-ripples in the defects might indicate interesting electronic properties, such as charge density wave (CDW).

The other type of defcts are the linear boundaries of h-BN. The tilting angle between the two domains at the both sides of the boundary is about 90°, which is well in line with our simulations. From the Di/Dv mapping, the boundary shows lower tunneling conductance than the h-BN sheet, which is different from the first type of quasi-1D defects.

Our experimental results demonstrate that the existence of quasi-1D defects tramendously affect the structure and electronic properties of h-BN, thus could be used to tune the transport properties in h-BN-based nanodevices.

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

4:40pm **SP+2D+AS+NS+SS-WeA8 Real-Space Imaging of the Multiple Scattering in Single Layer Graphene: FT-STM/STS Studies**, *M. Jung, S.-D. Sohn, J. Park, K. Lee, Hyung-Joon Shin*, Ulsan Natioanl Institute of Science and Technology, Republic of Korea
The electrons in graphene exhibit unusual two-dimensional behaviors, which can be described by massless Dirac quasiparticles. In order to understand the fundamental electronic properties of graphene, extensive studies have been focused on graphene both experimentally and theoretically. Undoubtedly, however, not only the electronic property of graphene itself but also that of graphene on metallic substrates is of great importance for the further applications. In this study we investigated the scattering behaviors of electrons in single layer graphene (SLG) on a Cu(111) substrate by means of low-temperature scanning tunneling microscopy (LT-STM) and scanning tunneling spectroscopy (STS). When there is a defect in graphene, we can observe the scattering of electrons in

the form of interference pattern by STM. In previous STM studies, the energy level of Dirac point has been assigned by the position of a dip in dI/dV curve. It is very difficult, however, to determine the exact position of Dirac point from STS for the graphene on metallic substrates, because surface states of the substrate is too close to Dirac point of graphene in energy level. Here, we could successfully deconvolute and identify the electronic dispersion relations in graphene and in Cu(111) by applying Fourier transformation to one-dimensional and two-dimensional STS maps, which enables us to resolve surface states of Cu(111) and Dirac point of graphene respectively. We will also present our first observation of the defect-induced intravalley scattering, which has not been observed experimentally to date for SLG. Our results show that the careful examination of interference pattern can provide valuable information regarding intravalley, intervalley, and interband scatterings of electrons in graphene/Cu(111).

5:00pm SP+2D+AS+NS+SS-WeA9 Tunability of Single-Atom Electron Spin Relaxation Times and Their Characterization by Pump-Probe STM, *William Paul, S. Baumann,* IBM Research - Almaden*, K. Yang,* Chinese Academy of Sciences*, N. Romming,* University of Hamburg, Germany*, T. Choi, C.P. Lutz, A. Heinrich*, IBM Research - Almaden

A single atomic spin constitutes the ultimate limit to the miniaturization of magnetic bits. Can the state of such a spin be made stable against the quantum mechanical tunneling of magnetization? The energy relaxation time, T1, of single spins on surfaces can be measured by spin-polarized pump-probe STM [1]. To date, the relaxation times reported for Fe-Cu dimers on Cu_2N insulating films have been of the order ~100 ns [1]. A three-order-of-magnitude enhancement of lifetime, to ~200 μs, was recently demonstrated for Co on a single-monolayer of MgO [2]. This was accomplished by choosing a less conductive decoupling layer to electronically separate the atom from a metal substrate, along with the careful design of the symmetry of orbital states. Here, we report on the tailoring of the T1 lifetime of single Fe atoms on single- and multi- layer MgO films grown on Ag(001). We focus on the characterization of intrinsic lifetimes for the atom-substrate system which are independent of the STM tip used to probe them, that is, without influence of the nearby STM tip which can be a strong source of electronic de-excitation. We also report on new advances in pump-probe techniques which were necessary to carry out these measurements. These advances extend lifetime detection to the femto-ampere and many-millisecond regimes demanded by the Fe on MgO system.

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5:20pm SP+2D+AS+NS+SS-WeA10 Imaging and Spectroscopy of Graphene Heterostructures*, Brian LeRoy*, University of Arizona
INVITED

The ability to create arbitrary stacking configurations of layered two-dimensional materials opens the way to the creation of designer band structures in these materials. Graphene on hexagonal boron nitride is an example of such a van der Waals heterostructure where the electronic properties of the composite material can be different from either individual material [1]. These van der Waals heterostructures can be formed using a wide variety of layered materials including from transition metal dichalcogenides, graphene and topological insulators. This talk will focus on devices consisting of graphene coupled to other layered materials. The lattice mismatch and twist angle between the layers produces a moiré pattern and affects their electronic properties. In double layer graphene systems, we find a van Hove singularity whose energy depends on the rotation angle [2]. This singularity in the density of states leads to a strong enhancement of the absorption at a particular wavelength. In graphene on transition metal dichalcogenides, the interaction between the materials leads to the possibility of commensurate stackings and the presence of new states in graphene [3].

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6:00pm SP+2D+AS+NS+SS-WeA12 Correlated STM and Electron Transport Study of Individual Nanowires down to Atomic Scale*, Shengyong Qin,* University of Science and Technology of China*, T.H. Kim,* Oak Ridge National Laboratory*, Y. Zhang, R. Wu,* University of California, Irvine*, H.H. Weitering,* The University of Tennessee, Knoxville*, C.K. Shih,* The University of Texas at Austin*, A.-P. Li,* Oak Ridge National Laboratory

The electronic conductance in quantum wires is often dictated by quantum instabilities and strong localization at the atomic scale. We present a novel nano-transport technique which combines local nano-contacts and four-probe STM. The approach allows for correlated study of electron transport

and scanning tunneling spectroscopy in individual nanowires. We first apply it to the $GdSi_2$ quantum wires, which show that isolated nanowires exhibit a metal-insulator transition upon cooling, driven by the defect-induced localizations, while wire bundles maintain a robust metallic state, stabilized by interwire electronic coupling. We then demonstrate applications of this transport technique with cabon nanotubes and copper wires in situ. The method bridges the gap between the transport and the local electronic and structural properties down to the atomic scale.

2D Materials Focus Topic
Room: 212C - Session
2D+EM+MG+NS+SE+SM+SS+TF-ThM

Emergent 2D Materials
Moderator: Paul Sheehan, Naval Research Laboratory

8:00am **2D+EM+MG+NS+SE+SM+SS+TF-ThM1 CVD Growth and Characterization of 2D MoS$_2$, MoSe$_2$, MoTe$_2$, WS$_2$, WSe$_2$, and MoS$_{2(1-x)}$Se$_{2x}$ Alloys**, *David Barroso*, T. Empante, A. Nguyen, V. Klee, I. Lu, E. Preciado, C. Lee, C. Huang, W. Coley, S. Naghibi, G. von Son, A. Brooks, J. Kim, L. Bartels, University of California, Riverside
Transition Metal Dichalcogenides (TMDs) have been of increasing interest over the past years due to their exciting semiconducting properties. In the bulk, TMDs possess a native indirect bandgap and transition to a direct bandgap as they approach the monolayer limit. The bandgaps range from 1.15 eV to 1.95 eV depending on composition. Using organic liquids and/or inorganic powders as precursors, CVD growth techniques have been realized for MX$_2$ TMDs (M = Mo, W; X = S, Se, Te) and their alloys at tunable compositions. We achieved consistent synthesis of these TMDs materials. The films can either be made homogeneous in bandgap or exhibiting a linear bandgap gradient. Characterization of the films include Raman and photoluminescence spectroscopy, as well as AFM. Device fabrication allows for transport measurements. Depending on the composition, the materials show n- or p-doping in a consistent fashion.

8:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM2 Investigation of Manganese Dioxide Nanosheets by STM and AFM**, *Loranne Vernisse*, S. Afsari, S.L. Shumlas, A.C. Thenuwara, D.R. Strongin, E. Borguet, Temple University
Interest in ultrathin two-dimensional nanosheets has grown exponentially thanks to their unique and diverse electronic properties. As they possess atomic or molecular thickness and infinite planar dimension, they are expected to have different properties than the bulk of the material from which they originate. This offers opportunities for the development of devices in various areas, ranging from catalysis to electronics. Using the exfoliation approach, it is possible to investigate 2D nanosheets of different materials in search of new phenomena and applications. Bearing this mind, we focused on manganese dioxide (MnO$_2$), and more specifically δ-MnO$_2$ (Birnessite). This mineral has the advantage to present a low surface enthalpy[1], which results in weak water binding. Moreover, the presence of defects, e.g., oxygen vacancies has a dopant effect on water oxidation. These properties make MnO$_2$ a perfect candidate as a catalytic surface for water splitting and pave the way to the design of clean and renewable energy system. Furthermore, MnO$_2$ can be easily exfoliated into ultrathin nanosheets owing to the layered structure of the manganese oxide precursors.

Our goal is to investigate the catalytic activity of ultrathin MnO$_2$ nanosheets using scanning probe microscopy techniques, especially atomic force microscopy (tapping mode) and scanning tunneling microscopy (ambient and electrochemical conditions). In this perspective, we have first improved the deposition processes and find the imaging conditions to observe MnO$_2$ nanosheets with an average thickness of one or two layers. We have also showed that MnO$_2$ single layer nanosheets exhibit an expected hexagonal atomic pattern and present some defects. We will now resolve and identify the different defects and investigate the evolution of the conductivity as a function of the defect concentration and the number of layers.

This work was supported as part of the Center for the Computational Design of Functional Layered Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award #DE-SC0012575.

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8:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM3 Two-Dimensional Early Transition Metal Carbides and Carbonitrides "MXenes": Synthesis, Properties and Applications**, *Michael Naguib*, Oak Ridge National Laboratory **INVITED**
Ternary layered carbides and nitrides with formula of M$_{n+1}$AX$_n$ (M stands for early transition metal, A for group A element, X is carbon or nitrogen, and n=1, 2, or 3), so called MAX phases, are known for their unique combinations properties of ceramics and metals. It was found recently that etching atomically thin layers of aluminum from the MAX phases results in

forming weakly bonded stacks of two-dimensional (2D) layers of early transition, coined as *MXenes*. The etching was carried out in fluoride contained aqueous systems. Thus MXenes surfaces are terminated with a mixture of groups including OH, O, and F. Sonicating MXenes in water results in delaminating few layers of MXenes from each other. However, to achieve a large-scale delamination, intercalation of a large compound between the layers prior to delamination is needed. MXenes were found to be a very interesting family of 2D materials since they are electrically conductors and hydrophilic. They also showed an excellent performance as electrodes for electrochemical super capacitors and Li-ion batteries. Here the recent progress in MXenes research from the synthesis to properties and applications will be covered, and in more details, large-scale delamination of MXenes will be discussed. Also, light will be shed on the performance of MXenes as electrode materials for electrochemical energy storage systems.

9:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM5 Molecular Beam Epitaxy of Large area HfSe2(ZrSe$_2$)/MoSe$_2$ van der Waals Heterostructures on AlN(0001)/Si substrates**, *Athanasios Dimoulas*, P. Tsipas, E. Xenogiannopoulou, D. Tsoutsou, K.E. Aretouli, J. Marquez-Velasco, S.A. Giamini, N. Kelaidis, NCSR DEMOKRITOS, Greece
Two dimensional (2D) semiconductor van der Waals heterostructures (HS) made of group IVB (Zr, Hf) and group VIB (Mo, W) metal dichalcogenides are predicted [1] to have type II or type III band alignments mainly because of a large difference in their workfunctions and band gaps, which makes them candidates for novel 2D staggered, or broken gap tunneling field effect transistors (TFET). We use molecular beam epitaxy (MBE) to grow high quality large area HfSe$_2$ [2,3], ZrSe$_2$ [4] and MoSe$_2$ [5] films directly on AlN(0001)/Si(111) substrates. We confirm by RHEED and HRTEM that atomically thin layers (1-6 ML) are grown in single crystal form with a well-defined in-plane orientation on AlN. The films are continuous with smooth surface morphology (0.6 nm RMS roughness) and abrupt interfaces with no detectable reaction as verified by in-situ XPS and HRTEM. Micro Raman mapping for all layers confirms their structural integrity down to one monolayer and reveals very good uniformity on a cm-scale wafer and excellent stability of MoSe2 over a period of at least two weeks in air. Strong room temperature PL signal of 1 ML MoSe$_2$ indicate high quality direct gap semiconductor in agreement with valence band structure details imaged by our in-situ ARPES [3, 5]. In a second step, MoSe2/HfSe$_2$ [3] and MoSe$_2$/ZrSe$_2$ [4] HS were grown. Despite the large lattice mismatch, all layers are grown epitaxially as evidenced by RHEED with no detectable defects as confirmed by HRTEM suggesting good quality VdW epitaxy [6]. Using UPS the workfunctions (WF) were estimated to be 5.2, 5.5 and 5.4 eV for MoSe$_2$, HfSe$_2$ and ZrSe$_2$ respectively [3,4]. The last two differ substantially from theoretical values (~ 6 eV). Based on our STM and DFT calculations [3], we conclude that this difference is due to an ordered Se adlayer which lowers the HfSe$_2$ and ZrSe$_2$ WF bridging the WF gap between them and MoSe2. As a result, small valence band offsets of 0.13 and 0.58 eV were found for the HfSe$_2$/MoSe$_2$ and ZrSe$_2$/MoSe$_2$ HS, respectively leading to type II band alignments. The availability of low cost wide-gap-AlN/Si wafers in 300 mm wafer sizes defines a manufacturable route for single crystal 2D semiconductor technology.

We acknowledge financial support from ERC Advanced Grant SMARTGATE-291260. We thank IMEC for providing the AlN/Si substrates.

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[2] R. Yue et al., *ACS Nano* **9**, 474 (2014)

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9:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM6 Surface Investigation of WSe$_2$ Atomically Thin Film and Bulk Crystal Surfaces**, *Rafik Addou*, H. Zhu, University of Texas at Dallas, *Y.-C. Lin, S.M. Eichfeld, J.A. Robinson,* Penn State University, *R.M. Wallace,* University of Texas at Dallas
Heterogeneous fabrication of semiconducting two-dimensional layered◻ materials presents a promising opportunity to develop highly ◻ tunable electronic and optoelectronic materials.(1-2) An example of crystalline monolayer of WSe$_2$ grown by chemical vapor deposition ◻ on epitaxial graphene (EG) grown from silicon carbide had been investigated at nanoscale level. The WSe$_2$ surface was characterized using atomic force microscopy (AFM) scanning tunneling microscopy/spectroscopy (STM/STS) and X-ray photoelectron spectroscopy (XPS).(3,4) AFM and

large STM images show high-quality WSe$_2$ monolayers. The sharpness of the W *4f* and Se *3d* core levels confirms the absence of any measurable reaction at the interface and oxide formation. The photoemission measurements of WSe$_2$-Graphene interface suggest p-type doping due to charge transfer (EG withdraws electrons from WSe$_2$) at the interface and formation of Schottky-type contact,(5) suggesting possible applications of such heterostructures as diodes and photodetectors. High-resolution STM images reveal atomic-size imperfections induced by Se vacancies and impurities. Additionally, the investigation of bulk WSe$_2$(0001) surface shows spatial variation attributed to the presence of two components in W $4f_{7/2}$ core level attributed to the presence of both n- and p-type behavior. STM images exhibit also various types of defect induced by vacancies and dopants. The STS spectra reveal two main characteristics i) expected p-type conductivity where the Fermi level located at the valence band edge, and ii) zero conductivity at negative bias explained by defect-induced band bending as reported on geological MoS$_2$ crystal surfaces.(4) In conclusion, the spatial variation (topography and electronic structure) is more noticeable in bulk WSe$_2$ grown by chemical vapor transport than in CVD thin films.

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(2) Yu-Chuan Lin et al., Nature Comm. arXiv:1503.05592v1.

(3) Robert M. Wallace, *ECS Trans*. **64** (2014) 109-116.

(4) Rafik Addou, Luigi Colombo, and Robert M. Wallace, ACS Appl. Mater. Interfaces (Accepted, 2015).

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11:00am 2D+EM+MG+NS+SE+SM+SS+TF-ThM10 A Kinetic Study on the Adsorption of Polar (Water) and Non-Polar (Benzene) Molecules on CVD Graphene, *Nilushni Sivapragasam*, *U. Burghaus*, North Dakota State University

The adsorption kinetics of water and benzene at ultrahigh vacuum conditions were studied. Two different chemical vapor deposited graphene samples (graphene/SiO$_2$ and graphene/Cu) were utilized. Different surface analytical techniques (Auger electron spectroscopy, X-ray photoelectron spectroscopy, and Raman spectroscopy) were used to characterize the surface. Subsequently, a kinetics study - to understand the adsorption of water and benzene- using thermal desorption spectroscopy (TDS) was conducted. The TDS results revealed the hydrophobicity of water on graphene. However, the adsorption kinetics of water on graphene did not mimic the bare substrate, i.e., graphene is non-transparent for water adsorption. In contrast, graphene was transparent for benzene adsorption. Furthermore, the adsorption kinetics of both, water and benzene were substrate dependent.

11:20am 2D+EM+MG+NS+SE+SM+SS+TF-ThM11 Epitaxial Ultrathin MoSe$_2$ Layers Grown by Molecular Beam Epitaxy, *Ming-Wei Chen*, *M.B. Whitwick, O. Lopez-Sanchez, D. Dumcenco, A. Kis*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

Two-dimensional transition metal dichalcogenides (TMDs) have attracted widespread attention recently, and the focus is specifically on ultrathin layers due to the strong spin-orbit coupling and direct band-gap transition of single-layers. The unique properties of various TMDs also enable the possibilities for future optoelectronic applications. However, the synthesis of TMDs with uniform large-area and high-quality still remains challenging. While chemical vapour deposition has been demonstrated as a promising technique, the complexity of chemical precursors and the lacking of *in-situ* observation technique strongly hinder the progress.

Here, We propose to use ultra-high vacuum molecular beam epitaxy (MBE) to grow MoSe$_2$ ultrathin layers, down to single-layer in a controllable way. Epitaxial MoSe$_2$ layers were successfully grown on different crystalline substrates via van der Waals epitaxy mechanism, benefited from the weak interlayer interaction and the lacking of dangling bonds. Reflection high energy electron diffraction (RHEED) was used to *in-situ* monitor the initial growth stage and revealed a clear transition of the streaks, demonstrating the formation of MoSe$_2$ layer. Sharp streaks were obtained in the growth end, with the streak spacing corresponding to MoSe$_2$ lattice constant, and no significant strain effect was observed. In order to demonstrate the validity of van der Waals epitaxy, different crystalline substrates with lattice mismatch up to 30 % have been tested. The epitaxial layers showed a smooth and uniform surface in atomic force microscopy, and the quality was further confirmed in Raman spectrum and transmission electron

microscopy. Furthermore, photoluminescence of the single-layer MoSe$_2$ showing a sharp peak of ~1.58 eV at room temperature demonstrates the direct band-gap feature and indicates the potentials of photovoltaic applications. In the end, the growth of two-dimensional van der Waals heterostructures has also been addressed and the results pave way for heterostructure studies.

In summary, molecular beam epitaxy has been proved to be a reliable route to grow large-area and high-crystalline transition metal chalcogenides, and is promising to facilitate the integration of other two-dimensional materials in the future.

11:40am 2D+EM+MG+NS+SE+SM+SS+TF-ThM12 A Two-Dimensional Oxide Quasicrystal, *Stefan Förster*, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany, *J.I. Flege*, Institute of Physics, Univerisity of Bremen, Germany, *K. Meinel, R. Hammer, M. Trautmann*, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany, *J. Falta*, Institute of Solid State Physics, University of Bremen, Germany, *T. Greber*, Physik-Institut, University of Zürich, Switzerland, *W. Widdra*, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany **INVITED**

With the recent discovery of the first oxide quasicrystal (QC) aperiodicity is entering the field of two-dimensional materials [1]. Aperiodicity means that the system exhibits long-range order as expressed by sharp diffraction spots but since the ordering follows an aperiodic function the system is lacking translational symmetry. We report here on the complex growth process of the oxide QC involving a high-temperature wetting process and periodic approximant structures.

The QC is derived from BaTiO$_3$ thin films on a hexagonal Pt(111) substrate and exhibits a sharp twelve-fold diffraction pattern [1]. Based on scanning tunneling microscopy the aperiodic atomic structure had been resolved [1]. It is formed by surface atoms arranged in forms of squares, triangles, and rhombi with a next-neighbour distance of 0.69 nm. In addition to this dodecagonal atomic arrangement, building blocks of squares, triangles, and rhombi are also found on $(2+\sqrt{3})$ and $(2+\sqrt{3})^2$ larger scales indicating the characteristic self-similarity of an ordered QC [1]. The high-resolution STM measurements allow furthermore to identify atomic flips in the structure indicating lattice excitations in the quasicrystal called phasons. Using low-energy electron microscopy (LEEM) the preparation and the growth of the QC films on top of the hexagonal Pt(111) is monitored in all details from room temperature up to about 1200 K. LEEM shows that upon high-temperature annealing large 3DBaTiO$_3$ islands are formed with bare Pt(111)-(1x1) in between. At temperatures above 1020 K a wetting layer spreads on the free Pt area. This wetting process can be reversed by annealing in an oxygen atmosphere. In-situ LEEM measurements show that under these conditions the QC decays into small BaTiO$_3$ islands. The observed interface-driven formation of a 2D QC from a perovskite oxide in contact with a hexagonal substrate is expected to be a general phenomenon.

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Helium Ion Microscopy Focus Topic
Room: 211B - Session HI+AS+SS+NS-ThM

Focused Ion Beam Technology (08:00-10:00)/Fundamentals of Helium Ion Microscopy (11:00-12:20)
Moderator: Gregor Hlawacek, Helmholtz-Zentrum Dresden - Rossendorf, Leonidas Ocola, Argonne National Laboratory

8:00am HI+AS+SS+NS-ThM1 Ga+ Ion Beam Nanofabrication Techniques of 3D Micro- and Nano- Fluidic Devices, *Leonidas Ocola*, Argonne National Laboratory

Three-dimensional (3D) fluidic geometries have been fabricated in the past by using several layers of Polydimethylsiloxane (PDMS) molds or double-sided Si etch steps [1], which require highly accurate chip bonding to complete the fluid path and multiple process steps. An alternative to this method is the use of direct write ion beam micromachining as a means to fabricate key components of a microfluidic device that require variations in depth as well as variations in width. 3-D microfabrication currently is mainly constrained to excimer lasers [2-3] and therefore is inherently diffraction limited. Grey scale lithography is also used for 3D structures but has limited capability. On the other hand, ion beam micromachining can scale down below the diffraction limit with no change in the technique and almost unlimited depth bandwidth. The focused ion beam / scanning electron microscope (FIB/SEM) is a powerful tool used for sample analysis

and characterization. When equipped with a sophisticated pattern generator and lithography technology it can expand its use to new applications in nano- and micro-fabrication. Ion beam micromachining is akin to electron beam lithography, where a beam of charged particles are steered to draw structures contained in a computer aid design (CAD) file. Unlike electron beam lithography, one can program arbitrary depths by manipulating the dwell time, or dose, of a particular structure. In this paper the work reported previously [4-5] has been expanded to large and complex geometries to place emphasis on the applicability of ion beam micromachining to practical microfluidic applications, such as straight 3D mixers and serpentine 3D mixers with sections as deep as 70 microns and channel widths as large as 30 microns. We have found that these devices can achieve full mixing of aqueous solutions in about an order of magnitude faster than traditional devices. The challenges encountered and overcome to fabricate these mixers will be described and the scalability of different fabrication techniques to nano-fluidics will be revisited.

References:

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5. E. Palacios et al., J. Vac. Sci. Technol. B 28 (2010) C6I1

8:20am HI+AS+SS+NS-ThM2 Adding 3D to Conventional SEM or FIB Surface Imaging Information - *In situ* Surface Sensing and Nanoprofilometry for Focused Electron and Ion Beam Induced Processes Verification, *Andre Linden*, Raith America, Inc., *A. Rudzinski, M. Levermann, T. Michael*, Raith GmbH, *E. Maynicke*, RWTH Aachen
Nanopatterning processes and corresponding parameters are typically well understood for standard nanofabrication applications using resist based electron beam lithography (EBL) or FIB milling processes (e.g. for TEM lamella preparation).

Recently however, the bandwidth of nanofabrication applications for dedicated nanopatterning tools has significantly broadened and is no more limited to resist based EBL and mere, standard FIB milling tasks. Some latest generation multi-technique electron and ion beam nanolithography tools even facilitate additional *in situ* processes such as resistless focused electron or ion beam induced processes - e.g. material deposition or gas enhanced etching. The number of variable parameters for such complex processes involving e.g. new gas chemistry or ion species is nearly "infinite". Moreover, smart and flexible patterning strategies, e.g. by using loops in conjunction with various multi-directional patterning modes, have significant impact on the final nanostructure´s definition and performance, so that a straight *in situ* characterization of e.g. material deposition, milling or etching rates becomes crucial for most efficient understanding and subsequent optimization of such processes.

In contrast to elaborately using additional analytical equipment outside the vacuum and subsequently re-introducing the sample for further processing and optimization, we have implemented a distance sensitive nanomanipulator with nanoprofilometric capabilities into our professional multi-technique nanofabrication tools, which allows *in situ* characterization of nanostructures in 3D with ~10nm resolution by collecting topographic sample surface information.

First results of direct *in situ* growth rate determination of focused electron beam induced material deposition (FEBID) for process calibration as well as 3D surface topographic information of challenging milling applications will be presented.

8:40am HI+AS+SS+NS-ThM3 Nanofabrication Using Gas-Assisted Focused Ion Beams, *Chad Rue*, FEI Company **INVITED**
A brief introduction to gas-assisted etching for Focused Ion Beams (FIBs) is given, including typical chemical precursors for various applications, and appropriate beam control parameters such as pixel overlap, dwell time, and refresh time. These factors are reasonably well-understood for pattern dimensions that are large compared to the size of the ion beam. However, for applications such as nanofabrication, which require high milling precision over small areas, the limiting size of the ion beam and its associated activated volume begin to influence the milling performance. The remainder of the discussion will focus on the relatively-unexplored regime in which the size of the pattern dimension is comparable to the size of the ion beam itself. The influence of various beam control parameters, particularly refresh time, becomes critically important to the milled profile of the desired structure. Redeposition effects, peripheral erosion, and mill rate trends are discussed. Operating tips and tricks are described, including

the use of drift compensation strategies. The minimum physically achievable via size is examined. For a 10 pA Ga^+ beam at 30 keV, used to mill a via in a SiO_2 substrate with XeF_2-assist, the minimum achievable via size (FWHM) is found to be 50 ± 10 nm, and is relatively independent of depth or aspect ratio. Implications for nanofabrication are discussed and examples are shown.

9:20am HI+AS+SS+NS-ThM5 The Psychology and Applications of a Bipolar Plasma Focused Ion Beam, *Rod Boswell*, ANU, Australia, *N. Smith, P. Tesch, N. Martin*, Oregon Physics
A new high brightness ion source has been developed using bi-polar power supplies that can be used with either positive or negative ions. This has involved a redesign of the plasma source and the acceleration optics to allow high currents to be focused with an energy of up to 30kV. We expect to make significant advances in Ultra High Resolution SIMS with a negative oxygen beam; a second application is the milling of structures in glass with a O- beam, such as a microfluidic set of channels. At the higher voltages mentioned above, it should be possible to cut cross sections of Through Silicon Vias in glass substrates. The challenges encountered in creating and extracting the negative ions will be discussed along with some performance and application data.

9:40am HI+AS+SS+NS-ThM6 Advanced FIB Applications with New Ion Species and Large Area Capabilities, *Sven Bauerdick*, *L. Bruchhaus*, Raith GmbH, Germany, *J. Fridmann*, Raith America, Inc., *P. Mazarov, A. Nadzeyka, R. Jede*, Raith GmbH, Germany
Focused ion beam (FIB) systems are applied to a wide range of applications in R&D nanofabrication, both for creating functional devices as well as for preparing sample imaging and analysis. With different ion species on one hand and very sophisticated patterning approaches on the other hand it is possible to improve results and provide solutions for more advanced applications. Here we show and discuss the capabilities of Ga and new ion species like Au or Si with high resolution, long-term stability and easy handling, which is combined with an instrument design enabling large area or elongated patterns by write field stitching or truly continuous writing, respectively.

The type of ion defines the nature of the interaction mechanism with the sample and has significant consequences on the resulting nanostructures or samples. Therefore, we have extended the FIB technology towards the delivery of multiple ion species selectable into a nanometer-scale focused ion beam by employing a liquid metal alloy ion source (LMAIS). A mass separation filter is incorporated into the column to allow for fast and easy switching between different ions. The respective capabilities of mainly Ga, Au and Si have been investigated (resolution, milling rate, imaging, implantation) and according results and applications will be presented.

Moreover we investigated, optimized and tested milling approaches for pattern (write field) stitching and for truly continuous patterning based on precise stage movement while milling/ cutting with the ion beam. An improved beam pattern needs to mimic the looping strategy of conventional milling, so that grooves with defined depth, steep sidewalls and minimum re-deposition can be achieved. This combination of functionality enables applications like nanofabrication of micro-fluidic mixers, zone plates, large area gratings, or wafer-level nanopore devices as well as sample investigation e.g. imaging, X-sectioning and preparation in an automated way. Examples for new nanofabrication techniques like large area hard masking by implantation, both for reducing and increasing the rate in standard etching processes, or seamless direct milling of nano-fluidic channels over cm's will be discussed.

11:00am HI+AS+SS+NS-ThM10 SIMS on the Helium Ion Microscope : a Powerful Tool for High-resolution High-sensitivity Nano-Analytics, *Tom Wirtz, D. Dowsett,* Luxembourg Institute of Science and Technology (LIST), Luxembourg, *S. Sijbrandij*, Carl Zeiss Microscopy **INVITED**
While the ORION Helium Ion Microscope NanoFab has become an ideal high resolution imaging and nanofabrication tool, its analysis capability is currently limited. By contrast, Secondary Ion Mass Spectrometry (SIMS) is an extremely powerful technique for analysing surfaces owing in particular to its excellent sensitivity, high dynamic range, very high mass resolution and ability to differentiate between isotopes. The combination of He/Ne microscopy and SIMS would not just offer the prospect of obtaining SIMS information limited only by the size of the probe-sample interaction (~10 nm) but also of directly correlating such SIMS images with high resolution (0.5 nm) secondary electron images of the same zone taken at the same time. We have therefore investigated the feasibility of combining SIMS with Helium Ion Microscopy from a fundamental and instrumental point of view.

In order to reach good detection limits when probing very small voxels in imaging applications, the ionization probability of the sputtered atoms and molecules needs to be maximized. When using He^+ and Ne^+ bombardment,

the intrinsic yields are low compared to the ones found in conventional SIMS. However, the yields may be drastically increased by using reactive gas flooding during analysis, namely O_2 flooding for positive secondary ions and Cs flooding for negative secondary ions. Our results show that both negative and positive ion yields obtained with He^+ and Ne^+ bombardment may be increased by up to 4 orders of magnitude when using such reactive gas flooding. This optimization of secondary ion yields leads to detection limits varying from 10^{-3} to 10^{-6} for a lateral resolution between 10 nm and 100 nm.

The prototype instrument we developed during this feasibility study contains extraction optics allowing the emitted secondary ions to be extracted with a maximized efficiency and without negatively impacting the focusing of the incoming He^+ or Ne^+ ion beam (broadening or distortion of the ion beam due to the electric fields). These extraction optics are coupled to a specially designed compact high-performance magnetic sector double focusing mass spectrometer that we developed for the purpose of HIM-SIMS. The specifications of this mass spectrometer include high mass resolution with optimized transmission ($M/\Delta M > 1000$ at 100% transmission or $M/\Delta M > 3000$ at 50% transmission), full mass range (H-U) and parallel detection of several masses.

The results are very encouraging and the prospects of performing SIMS on the Helium Ion Microscope are very interesting. In this paper we will present the main findings of our feasibility study, including fundamental, instrumental and application aspects.

11:40am HI+AS+SS+NS-ThM12 Nanometer TOF-RBS and TOF-SIMS in a Helium/Neon Ion Microscope, *Nico Klingner*, *R. Heller, G. Hlawacek, S. Facsko, J. von Borany*, Helmholtz-Zentrum Dresden - Rossendorf, Germany

Helium ion microscopes (HIM) have become powerful imaging devices within the last decade. Their excellent lateral resolution down to 0.3 nm and their high field of depth make them a unique tool in surface imaging [1]. So far the the analytical capabilities of a HIM are rather limited or need complex detection setups. In addition we will discuss major challenges and physical limitations of ion beam analysis in the HIM.

We will present a new and relatively easy to implement method for ion beam analysis in the HIM by means of time of flight spectrometry to obtain elemental information from the sample. We will demonstrate the flexibility and applicability of the method to image samples with target mass contrast, to analyze the target compositions, and to measure depth profiles of films with few tens of nm thickness.

Pulsing the primary helium or neon ion beam and measuring the time of flight of ejected particles allows to obtain the energy of the backscattered particles as well as the mass of the ionized, sputtered target atoms. This has been achieved by chopping the primary ion beam down to pulse widths of 18 ns by use of the built-in beam blanker and a customized plug-on beam blanking electronics. The secondary particles are detected by means of a multi channel plate mounted on a flange of the HIM.

We will show TOF-RBS and TOF-SIMS measurements for different materials, which can give complementary information. Lateral resolved TOF-SIMS allows to quickly obtain qualitative elemental mapping while the TOF-RBS gives the standard-free quantitative sample composition of regions of interest. We will also show, that with TOF-RBS depth profiling of nm-thick layers is possible.

[1] G. Hlawacek, V. Veligura, R. van Gastel, and B. Poelsema, J. Vac. Sci. Technol. B 32(2), 2014

12:00pm HI+AS+SS+NS-ThM13 Improving Pattern Fidelity in Helium Ion Beam Lithography using Pixel Dose Optimization, *N. Kalhor*, TU Delft, Netherlands, *W. Mulckhuyse*, TNO Technical Sciences, Netherlands, *Paul Alkemade*, TU Delft, Netherlands, *D. Maas*, TNO Technical Sciences, Netherlands

Scanning Helium ion beam lithography (SHIBL) with a sub-nanometer beam probe size at the sample surface is a promising technology for high-resolution lithography with high pattern density.[1] The advantages of SHIBL compared to e-beam lithography are higher sensitivity and a lower proximity effect. Remarkably, there are unique similarities in the activation response of resists to He-ions and extreme-ultraviolet (EUV) photons in EUV lithography (EUVL). Both primary beams produce low energy secondary electrons (SEs) and are not hindered by proximity effect. Recently Maas et al. experimentally demonstrated these similarities and suggested SHIBL as a promising method for pre-screening chemically amplified resists (CARs) prior to their final performance evaluation in an EUV scanner.[2]

However, unlike an EUV photon which only interacts with one resist molecule, an He-ion scatters inelastically in the resist and causes a chain of collisions with resist molecules, producing one or more SEs per collision.

Also, a small dose-to-clear of 0.085 ions/nm^2 for SHIBL in a CAR was measured.[2] Hence, Maas et al. hinted at ion shot noise as a limiting factor in pattern fidelity in SHIBL.[2]

Here, we present a heuristic resist activation model for single-pixel dose SHIBL. The model employs a point-spread function (PSF) to account for all contributing factors in the resist activation. Ion shot noise impact is modeled with Poisson statistics. We show a good agreement between the model and our experimental single-pixel dose SHIBL results for line-and-space (LS) and contact hole patterns. Our model indicates pattern fidelity in sensitive CAR is not only limited by ion shot noise; instability of the He-ion source emission and post-exposure resist processing can also play important roles. Moreover, we introduce optimized-pixel-dose SHIBL to improve critical dimension uniformity (CDU), line width roughness (LWR), exposure latitude and throughput gain. In this approach, we calculate an optimum ion dose map for a given binary pattern such that the pattern's edges are exposed at the steepest part of the PSF to improve resist-pattern contrast and to minimize ion shot noise effect. Pixel dose optimization is advantageous to single-pixel exposure when the feature size is larger than the FWHM of the PSF. We discuss this by comparing our modeling results for single-pixel and optimized-pixel-dose SHIBL exposure modes for a desired LS pattern. We show that pixel-dose optimization could reduce LWR by ~45% (~1.3 nm) with a concurrent 20% dose reduction.

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Nanometer-scale Science and Technology
Room: 212B - Session NS+MN-ThM

Nanopatterning and Nanolithography/Nanoscale Mechanics
Moderator: Stephane Evoy, University of Alberta, Jeremy Robinson, Naval Research Laboratory

8:00am NS+MN-ThM1 Electron Stimulated Desorption and Raman Investigations of HafSOx Inorganic Resists, *Ryan Frederick*, *G. Herman*, Oregon State University

Hafnium oxide hydroxide sulfate (HafSOx) materials are under investigation as inorganic photoresists due to their high patterning fidelity, which is important for next-generation nano-lithography. In order to develop materials with better patterning sensitivity and higher resolution it is critical to understand the underlying mechanisms that result in the soluble/insoluble transition after exposure to radiation. Prior studies have shown that the incorporation of hydrogen peroxide into HafSOx is necessary to provide radiation sensitivity. In this presentation we will demonstrate that electron stimulated desorption (ESD) is a very useful technique for the characterization of radiation-induced mechanisms in HafSOx, and potentially other inorganic photoresists. These ESD studies are being performed with low energy electrons, E_{kin} = 50 - 500eV, which includes the range of photoemitted and secondary electron energies expected during extreme ultraviolet (EUV) lithography. In the case of HafSOx films we found significant O_2 desorption during ESD for films containing hydrogen peroxide, and found no O_2 desorption during ESD for films not containing hydrogen peroxide. These studies suggest that O_2 is the primary ESD species, and this desorption product can be correlated with the radiation sensitive hydrogen peroxide that is incorporated in the HafSOx films. We have used the Menzel-Gomer-Redhead desorption model to determine the O_2 ESD cross-sections over a range of electron energies and doses, and determined that the cross-sections range from 2×10^{-15} to 8×10^{-15} cm^2. To confirm that these low energy electrons can drive the soluble/insoluble transition in HafSOx we have measured contrast curves using ellipsometry to measure film thickness after exposing HafSOx to 100eV electrons for various electron doses and after development. The soluble/insoluble transition was found to occur in the electron dose range between 100 to 250 $\mu C/cm^2$. We have also used Raman spectroscopy to better understand the radiation-induced processes in HafSOx by monitoring the metal coordinated peroxide species after various electron doses. There were very similar reaction kinetics when comparing the increase in O_2 desorption signal during ESD and the decrease in the peroxide Raman signal for increasing electron dose. Finally, we will discuss the radiation-induced mechanisms in HafSOx and relate these to other inorganic photoresists being developed for EUV lithography.

8:20am NS+MN-ThM2 Fundamental Limits of Material Toughening with Molecularly Confined Polymers, *Scott Isaacson,* Stanford University, *K. Lionti, W. Volksen, T.P. Magbitang,* IBM Almaden Research Center, *R.H. Dauskardt,* Stanford University, *G. Dubois*, IBM Almaden Research Center

Low-density hybrid molecular materials with organic and inorganic components engineered at molecular length scales can be made to exhibit diverse mechanical, thermal, and optical properties. We present a novel class of hybrid nanocomposites created through a unique backfilling approach in which selected polymers are homogeneously infiltrated into the pores of a sol-gel nanoporous glass scaffold, leading to uniform mixing at unprecedentedly small length-scales (~1 nm) and confinement of polymer chains to dimensions far smaller than their bulk radius of gyration [1-3]. The second-phase material may be chosen from an extensive library of polymers, allowing for the development of composites with novel electrical, optical, and mechanical properties. This synthesis technique is versatile and can produce uniform, high-quality films over large areas.

We show that it is possible to dramatically improve the mechanical and fracture properties of a nanoporous organosilicate matrix by filling the porosity with a polymeric second phase. The degree of toughening is shown to increase with the polymer molecular weight, and is also found to depend on synthesis conditions. These studies of confined polymers enable us to explore the fundamental limits of nanocomposite toughening in terms of molecular strength, molecular size, and degree of confinement. We describe a novel toughening mechanism based on the molecular bridging and pullout of individual confined polymer chains from the porous matrix, distinct from the more common entanglement-based crazing mechanisms exhibited by bulk polymers. This mechanism is supported and quantified with a model that describes the nanomechanical processes occurring on the length scale of individual polymer chains. The toughening model is further leveraged to calculate the tensile strength of individual polymer chains and find it in agreement with our own independent estimates of molecular strength. This study provides new insight into the mechanical behavior of polymer chains under nanoscale confinement and suggests potential routes for increasing the cohesive strength of multifunctional nanocomposites, where the traditional bulk toughening mechanisms may be absent.

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8:40am NS+MN-ThM3 Nanomanufacturing from Silicon to DNA, *James Liddle*, Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD 20899-6203
INVITED

The production of integrated circuits using silicon fabrication technology is the dominant nanofabrication technology in the world today. However, the industry is maturing, and the technology used for integrated circuit manufacturing, although extraordinarily impressive, is suited, economically, only for that function. At the same time, the nanotechnology revolution has delivered an array of novel structures and materials with fascinating and useful properties, but has presented us with several challenges. These include scaling up production and reducing costs to levels that are commercially interesting, and finding ways of integrating heterogeneous nanostructures into fully functional systems. I will illuminate these issues with a brief description of the strengths and weaknesses of the semiconductor manufacturing paradigm, a comparison with the possibilities offered by DNA-mediated assembly, and an illustration of how a deep understanding of nanoscale physics can turn optical metamaterials from a laboratory curiosity into a manufacturable product.

9:20am NS+MN-ThM5 Pattern Formation by Ion Beam Sputtering on Thermally Treated Ge Surfaces Implanted with Si Ions, *AngélicaGuadalupe Hernández, Y. Kudriavtsev*, CINVESTAV-IPN, Mexico

We have investigated formation of patterned surfaces after low energy oxygen (O_2) ion sputtering on germanium (Ge) crystals implanted with silicon (Si) ions and subsequent thermal annealing by using Atomic Force Microscopy (AFM).

A commercially available Ge crystal wafer was implanted with Si^+ ions. The energy of implantation was 25 keV. This low energy and the high dose regime (2×10^{16} cm^{-2}) results a relatively high Si concentration obtaining at the implanted maximum of 5.3×10^{21} atoms/cm^3. Distribution and depth near-surface of implanted ions were calculated by Montecarlo simulations using TRIM software as 15 nm and confirmed by the Secondary Ion Mass Spectrometry (SIMS).

After ion sputtering a study of the surface morphology was performed by AFM for comparison of the obtained results with the Ge surface without implantation. In other hand, Raman spectra of the as implanted samples shows the vibration modes of α-Ge, c-Ge, Ge-Si, α-Si and Si-Si, which is an indicator of Si clusters formation in to the Ge bulk due to the ion implantation.

In order to recover the crystallinity of the Ge lattice, the thermal annealing at 700 ºc during 5min under nitrogen (N_2) atmosphere was performed. The corresponding Raman spectra shows the transition from amorphous to crystalline Ge.

After the thermal process, ion beam sputtering was performed by using O_2 ions and energy beam of 0.5, 1 and 2 keV at different ion doses under ultra-high vacuum conditions (base pressure ~10^{-9} mbar). Due to the differences in the sputtering yield between Ge and Si, the preferential sputtering of Ge results in an enrichment of Si on the surface. The Si nano-crystals produces an effect of "shadow" leading to a formation of nano-structured surfaces. This results were compared with our previous work, where Ge surfaces (not implanted) were bombarded under the same sputtering conditions (ion specie, energy and ion dose).

Morphology of the surface was investigated by AFM of the original surface, as implanted samples, thermally treated and after ion bombardment. Finally, we compared the experimental morphology with ones obtained previously by the oxygen sputter Ge crystal.

9:40am NS+MN-ThM6 Poor Q-factor? - No Problem: Nano-Optomechanical Mass Sensing in Ambient Conditions, *Swapan Roy, V.T.K. Sauer, A. Venkatasubramanian, W.K. Hiebert*, University of Alberta and The National Institute for Nanotechnology, Canada

It has been demonstrated that optimum dynamic range (DR) and high quality factor (Q) of NEMS resonators provides unprecedented mass sensitivity [1]. The mass sensitivity and frequency stability of these devices are limited by their thermomechanical (TM) noise. TM noise goes down with Q as pressure increases, at the same time enhanced critical amplitude leads to a higher DR value with better sensitivity. However, detecting TM noise signal at ambient condition is always challenging. Optomechanical transduction successfully resolved this challenge with high displacement sensitivity and high bandwidth of NEMS devices [2]. Previously we have demonstrated robustness of our optical racetrack resonator transduction scheme in detecting TM noise signal [3]. Taking advantage of this measurement protocol we have found zeptogram level mass sensitivity at atmospheric pressure for a double clamped beam. This is similar to the sensitivity in high vacuum, even though Q-factor drops 300 fold from vacuum to ambient pressure. These intriguing experimental results challenge assumptions about fundamental limits of mass sensitivity of NOMS sensors and open the door for ultrasensitivity in ambient conditions.

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11:00am NS+MN-ThM10 Frequency Division Using a Micromechanical Resonance Cascade, *K. Qalandar, M. Sharma, B. Gibson, Kimberly Turner*, University of California, Santa Barbara
INVITED

A coupled micromechanical resonator array demonstrates the first successful realization of multi-stage frequency division. Frequency converters, dividers and multipliers, are necessary over a wide range of frequencies for a variety of applications, including vibration energy harvesters, RF transceivers, phase-locked loops, and quantum cascade lasers. In the VHF and UHF frequency range, solid-state and electromagnetic devices have traditionally dominated on-chip signal processing activities due to their wide bandwidth operation, programmability, and ease of implementation. However, design becomes more complicated and noise increases when cascading electronic dividers, due to buffers, amplifiers, and complex impedance matching circuits. Increasing constraints in size, power, and phase noise have led microelectromechanical systems (MEMS) to be considered in place of many traditional electronic elements. In particular, MEMS resonators are of interest since these high Q narrow bandwidth devices can provide better phase noise characteristics than similar devices that utilize amplifier technology. Coupled vibratory modes in micro-resonators have been shown to provide phase noise improvements in frequency sources, and have been considered in other contexts. This frequency divider combines the benefits

of cascading, internal resonance, and mechanical coupling in a single microdevice. The operation is based on nonlinear dynamics and exploits the robustness of parametric resonance. This narrow-band approach uses a subharmonic resonance cascade in a chain of internally resonant subsystems with specific coupling that allows energy exchange between successive divide-by-two stages. The mechanical structure consists of a set of N sequentially perpendicular microbeams that are connected by relatively weak elastic elements such that the system vibration modes are localized to individual microbeams and have natural frequencies with ratios close to 1 : 2 : _ _ _ : 2N. Conservative (passive) nonlinear inter-modal coupling provides the required energy transfer between modes and is achieved by finite deformation kinematics. When the highest frequency beam is excited, this arrangement promotes a cascade of subharmonic resonances that achieve frequency division of 2j at microbeam j for j = 1; : : : ;N. Results are shown for a capacitively driven three-stage divider in which an input signal of 824 kHz is passively divided through three modal stages, producing signals at 412 kHz, 206 kHz and 103 kHz. The system modes are characterized and used to delineate the range of AC input voltages and frequencies over which the cascade occurs. This narrow band frequency divider has simple design rules that are scalable to higher frequencies, and can be extended to a larger number of modal stages.

11:40am NS+MN-ThM12 Single-Molecule Analysis with Nanomechanical Systems, *Michael Roukes*, California Institute of Technology **INVITED**
Mechanical resonators based on NEMS (nanoelectromechanical systems) now enable measurement of the inertial mass of individual atoms and molecules [1]. We have employed NEMS to realize a new form of mass spectrometry (MS) with single molecule sensitivity, and have demonstrated the analysis of individual large-mass biomolecular complexes, one-by-one, in real-time [2]. In this talk I will survey progress and prospects in this emerging field. In particular, NEMS-MS offers transformational capabilities for the field of native MS, which focuses upon the topological investigation of intact protein complexes with high sensitivity and a theoretically unrestricted mass range. Recently, we have developed an approach that greatly enhances the capabilities of NEMS-MS by enabling imaging the spatial mass distribution of individual analytes – in real time, and with molecular-scale resolution – when they adsorb onto a NEMS resonator [3]. This new approach, which we term inertial imaging, employs the discrete, time-correlated perturbations induced by each single-molecule adsorption event to the ensemble of modal frequencies of a NEMS resonator. The spatial moments of each adsorbing analyte's mass distribution are deduced from the discrete, time-correlated shifts it induces to a multiplicity of vibrational modes. The lowest moment of the measured mass distribution function yields the total analyte mass; higher moments reveal the center-of-mass position of adsorption, the analyte's average diameter, and its spatial skew and kurtosis, etc. Together, these higher moments completely characterize the analyte's molecular shape. Once acquired, these moments can subsequently be inverted to yield an "inertial image" of each analyte. Unlike conventional imaging, the minimum analyte size detectable through nanomechanical inertial imaging is not limited by wavelength-dependent diffraction phenomena; instead frequency fluctuation processes determine the ultimate attainable resolution. Advanced NEMS devices are capable of resolving molecular-scale analytes.

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Scanning Probe Microscopy Focus Topic
Room: 212A - Session SP+AS+NS+SS-ThM

Probing Chemical Reactions at the Nanoscale
Moderator: Stephen Nonnenmann, University of Massachusetts - Amherst, Shengyong Qin, University of Science and Technology of China

8:40am SP+AS+NS+SS-ThM3 Adsorption of Trimethyl Acetic Acid on (1x2) Reconstructed TiO$_2$(110), *Kenneth Park*, K. Zhu, Y. Xia, Z. Zhang, Baylor University
The adsorption of trimethyl acetic acid on (1x2) reconstructed TiO$_2$(110) is investigated using scanning tunneling microscopy (STM) with the same area analysis. After de-protonation, trimethyl acetate (TMA) molecules preferentially adsorb in the troughs between two adjacent 1x2 strands. The nearest neighbor distance between TMA molecules is about 5.9 Å, twice the lattice constant along [001], corresponding to the bridging bidentate configuration over two 5-coordinated Ti^{4+} sites. With increasing coverage, they form linear chains, separated by (1x2) strands leading up to the nominal saturation coverage of 0.25 ML. Upon further adsorption, the second-layer of TMA molecules start clustering on top of 1x2 strands. The coverage-dependent TMA adsorption structures on (1x2) reconstructed TiO$_2$(110) will be compared and discussed with the reported TMA adsorption on (1x1) TiO$_2$(110), and relative reactivity of TMA with other defect sites including cross-links will be presented.

9:00am SP+AS+NS+SS-ThM4 Anticorrelation between Surface and Subsurface Point-Defects and Influence on Redox Chemistry at TiO$_2$(110), *Igor Lyubinetsky*, Y. Yoon, Y. Du, Pacific Northwest National Laboratory, *J.C. Garcia*, Worcester Polytechnic Institute, *Z. Zhu, Z.-T. Wang, N.G. Petrik, G.A. Kimmel, Z. Dohnalek, M.A. Henderson, R. Rousseau*, Pacific Northwest National Laboratory, *N.A. Deskins*, Worcester Polytechnic Institute
The atoms at the surface that constitute reactive sites clearly govern surface chemistry. But subsurface atoms, particularly substitutional and/or interstitial defects, can also influence surface chemistry, though a detailed understanding is still emerging. Here we report the interplay and relative impact of surface vs. subsurface defects on the surface chemistry of rutile TiO$_2$, a prototypical metal oxide. Importantly, it contains both surface and subsurface intrinsic point-defects in the reduced state (along with residual extrinsic defects). Our scanning tunneling microscopy results show that O vacancies (V_O's), the dominant surface defects, are virtually absent in the vicinity of positively-charged subsurface point-defects. Such anticorrelation of defects is consistent with density functional theory (DFT) calculations of the impact of subsurface defect proximity on V_O formation energy, which narrows down the possible candidates to certain interstitial defects, of both intrinsic and extrinsic nature. To monitor the influence of such (electron-donor type) defects on surface redox chemistry, a test reaction of the electron-mediated dissociative adsorption of O$_2$ is employed, which is observed to be suppressed around these defects. DFT results attribute this to a perceived absence of the intrinsic (Ti) (and likely extrinsic) interstitials in the nearest subsurface layer beneath "inhibited" areas, while the underlying energetic driver is largely repulsive electrostatics. Finally, we postulate that the entire subsurface region up to several atomic layers deep could be voided of any charged point-defects, whereas such defects are proposed to exist beyond the subsurface region. Subsequently, prevalent V_O's are largely responsible for both the surface/subsurface reduction and mediation of the redox chemistry at reduced TiO$_2$(110) surface. Overall, this work provides new fundamental insights into the relation between surface and subsurface defects. In a broader perspective, the uncovered effects may prove to be general for other reducible oxides, and thus have potential implications in such diverse research fields as environmental remediation or microelectronics.

9:20am SP+AS+NS+SS-ThM5 Dissociation of Water on Oxygen Pre-Covered Cu(110) Observed with Scanning Tunneling Microscopy, *Zongqiang Pang*, Lawrence Berkeley National Laboratory (LBNL)
The dissociation of water on the oxygen pre-covered Cu(110) surface has been studied with Scanning Tunneling Microscopy (STM). At low temperature (77K), water reacts with pre-covered oxygen to produce hydrogen atoms and hydroxyl groups. Non-dissociated water molecules and hydroxyl groups combine to form a hexagonal network on the top of Cu(110) where water donates one hydrogen to the hydroxyl, while uncoordinated hydroxyls bind to the second layer intact water molecules. Following excitation by tunneling electron or by heat, the water molecules in the hexagonal network gradually dissociate. The oxygen atoms involved in the reaction of water dissociation return to its original position, leaving

ordered Cu-O and hydroxyl dimer chains on the Cu(110) surface which both align along <001> direction. Our results demonstrate that the oxygen atoms pre-adsorbed on the Cu(110) surface lower the energy barrier for water dissociation on the Cu(110) surface.

9:40am SP+AS+NS+SS-ThM6 Probing Local Electrochemical Activity within Yttria-Stabilized-Zirconia *via In Situ* High-Temperature Atomic Force Microscopy, *Jiaxin Zhu*, University of Massachusetts - Amherst, *C. Perez, T. Oh, R. Kungas, J. Vohs, D. Bonnell*, University of Pennsylvania, *S.S. Nonnenmann*, University of Massachusetts - Amherst

Considerable interest in understanding interfacial phenomena occurring across nanostructured solid oxide fuel cell (SOFC) membrane electrode assemblies has increased demand for *in situ* characterization techniques with higher resolution. We briefly outline recent advancements in atomic force microscopy (AFM) instrumentation and sub-systems in realizing real time imaging at high temperatures and ambient pressures, and the use of these *in situ*, multi-stimuli probes in collecting local information related to physical and fundamental processes. Here we demonstrate direct probing of local surface potential gradients related to the ionic conductivity of yttria-stabilized zirconia (YSZ) within symmetric SOFCs under intermediate operating temperatures (500 °C – 600 °C) via variable temperature scanning surface potential microscopy (VT-SSPM). The conductivity values obtained at different temperatures are then used to estimate the activation energy. These locally collected conductivity and activation energy values are subsequently compared to macroscopic electrochemical impedance results and bulk literature values, thus supporting the validity of the approach.

Thin Film
Room: 111 - Session TF+AS+NS+SA-ThM

Thin Film: Growth and Characterization, Optical and Synchrotron Characterization I
Moderator: Divine Kumah, North Carolina State University

8:00am TF+AS+NS+SA-ThM1 Oxynitride Thin Films by Reactive Radiofrequence Magnetron Sputtering - Versatile Materials for Optical Applications, *Angelique Bousquet*, *A. Farhaoui, F. Zoubian, C. Taviot-Gueho, J. Cellier, E. Tomasella*, Institut de Chimie de Clermont-Ferrand, France **INVITED**

Transition metal oxynitrides are increasingly studied because of their high versatility. Indeed, by tailoring the material composition, their optical, mechanical or electrical properties are tuned. Among thin film deposition processes, reactive sputtering is particularly attractive for this purpose because of its robustness, its wide using in industry and its high versatility. For several years, our research group at ICCF is specialized in control of reactive sputtering process, especially by plasma analysis using Optical Emission Spectroscopy, to deposit thin films for optical applications.

In this presentation, we will show how by tuning the $Ar/O_2/N_2$ atmosphere during sputtering of elemental target, it is possible to control the film composition in a ternary diagram in metal-rich, oxide, nitride or oxynitride region. The potentiality of this technique will be illustrated by tantalum and silicon oxynitride deposition.

In order to investigate the nature of oxynitride films (Random Bond Model or Random Mixture Model), thin films were characterized by various techniques, such as IR spectroscopy, XPS, XRD/Pair Distribution Function technique and Rutherford Backscattering Spectroscopy. Hence, we obtained an accurate picture of the diversity and the complexity of our material, following the Random Mixture Model, where segregated oxide and nitride phases are randomly distributed at very short scale.

Moreover, the modification of material composition allows controlling their optical properties, characterized by UV-visible spectroscopy and spectroscopic ellipsometry. This latter technique appears as a powerful technique to discriminate metallic, semiconductor and/or insulator contributions into such complex films by using model combining Tauc-Lorentz law and additional Lorentz oscillator. Hence, in a one hand, optical band gap of TaO_xN_y can be changed from 0-4.3 eV. This Eg fine-tuning more particularly in the range of 1.7-2.7 eV is interesting for application in photocalytic water splitting using visible light. In the other hand, the refractive index variation in the 1.56-3.7 range (at 1.96 eV) of $Si_xO_yN_z$ films is used to realized antireflective multilayer system from only one target. Finally, oxynitride films present promising properties for applications in material for Energy.

8:40am TF+AS+NS+SA-ThM3 Surface Science in The Wild: Using Synchrotron Radiation and Lab Grown Thin Films to Understand The Behavior Of SiC in Accident Tolerant Nuclear Fuels, *Jeffery Terry*, Illinois Institute of Technology **INVITED**

Out in the "real world," systems are typically much less clean and much more complex than what is seen in the laboratory. This is often the case in the extreme environment of the core of a nuclear reactors. However, complexity often makes it very difficult to understand the dynamics that are occurring in the "real world" systems. Often our understanding can be greatly improved by using measurements on the "real world" system in combination with fundamental surface science measurements on likely components. We have applied these combinations to study the behavior of irradiated accident tolerant nuclear fuels. Development of new accident tolerant nuclear fuels is important because the explosions at Fukushima were the direct result of interactions between water and the Zr cladding on the fuel. The high temperature chemistry of those interactions led to the production of hydrogen gas which eventually ignited. Our research group has looked at potential claddings such as ZrC, ZrN, and SiC. Specifically, we are using synchrotron radiation techniques to collect data on reactor irradiated materials. We compare the results of those measurements with well controlled laboratory grown systems. The data is then provided to modelers to evaluate the performance of reactor components in extreme environments (temperature, neutron flux, chemistry). This talk will focus on the carbides and nitrides that may be used in accident tolerant, TRISO fuel pellets for application in both conventional and advanced nuclear reactors.

9:20am TF+AS+NS+SA-ThM5 iTF Modulus Solution with xProbe Applications for Ultra-thin Film Systems (<=10nm), *Anqi Qiu*, *A. Romano*, Hysitron, Inc.

Reliable measurements of the Elastic Modulus of thin films is particularly challenging due to substrate effect. The prevalent rule of limiting indentation depth to 10% of the coating thickness to avoid the substrate's influence on the mechanical properties is challenging to assure, especially when the film thickness goes below 200nm. The tip radius can be one of the many factors limiting the application of Oliver-Pharr model on the elastic modulus calculation, just as the surface roughness. With the newly developed ultra-low noise **xProbe** transducer combined with the **Intrinsic Thin Film Property Solution from Hysitron**, quantitative mechanical properties from nanoindentation tests on 10nm thin film systems become possible. Here a MEMS based transducer with a noise floor similar to that of a contact mode Atomic Force Microscope (AFM). The linear actuation allows for direct and fully quantitative measurements without the need of modeling, which leads to more precise mechanical properties estimation and higher analysis throughput. By combining the ultra-low noise xProbe transducer and analytical intrinsic thin film solution (Itf), we quantitatively estimate elastic properties of the ultra-thin film systems of 10nm or below.

9:40am TF+AS+NS+SA-ThM6 Real-time Study of Plasma Enhanced Atomic Layer Epitaxy of InN Films by Synchrotron X-ray Methods, *Neeraj Nepal*, *V. Anderson, S.D. Johnson, B. Downey, D. Meyer*, U.S. Naval Research Laboratory, *A. DeMasi, K.F. Ludwig*, Boston University, *C. Eddy*, U.S. Naval Research Laboratory

Atomic layer epitaxy (ALE) is a layer-by-layer materials growth method. Recently, plasma enhanced ALE (PA-ALE) has been used to grow epitaxial III-nitride films at temperatures ≤500°C [1-2]. At these growth temperatures, the ad-atom mobility is low and the growth process is significantly influenced by the nature of the substrate surface. Thus, the mechanisms of nucleation and growth kinetics is very important to understand to improve material quality for technological applications. Synchrotron x-ray characterization is one of the best methods for this study.

The temporal evolution of high quality InN growth on a-plane sapphire at 200-250°C were probed by synchrotron x-rays. The growth was carried out in a thin film growth facility installed at beamline X21 of the National Synchrotron Light Source at Brookhaven National Laboratory and at Cornell High Energy Synchrotron Source, Cornell University. Real-time grazing incidence small angle x-ray scattering (GISAXS) measurements at the x-ray incidence angle of 0.8 degrees show that H_2 plasma cleaning roughens the sapphire substrate surface, but this same surface is recovered completely during subsequent N_2 plasma pretreatment. GISAXS also reveals InN growth steps for each PA-ALE cycle at the optimal growth conditions. During the initial cycles the specular peak broadens and the Yoneda Wing (YW) scattering has a correlated length scale (CLS) of 17.4 nm indicating roughening of the surface during homogenous nucleation. At about 1.3 nm of growth the intensity of YW is increased at the CLS of 10.1 nm indicating a decrease in the surface roughening CLS. Despite this scattering, *ex situ* atomic force microscopy-measured roughness is below instrument sensitivity limits, demonstrating the effectiveness of GISAXS compared to more conventional approaches. *In situ* x-ray reflectivity measurements suggest that the InN growth was self-limited with a growth rate of 0.35 nm/cycle between 200-250°C. Hall measurements show

electron sheet carrier density and resistance of 3.5×10^{13} cm^{-2} and 3.59 kW/sq, respectively. An electron mobility of 50 cm^2/V-s is measured for a 5.6 nm thick InN film on a-plane sapphire, which is higher than the reported value of 30 cm^2/V-s for a 1300 nm thick InN grown by MBE directly on sapphire [3]. *In situ* synchrotron x-ray study of the epitaxial growth kinetics of InN films is one of the most powerful methods to understand nucleation and growth mechanisms to improve material quality and broaden material applications.

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11:00am TF+AS+NS+SA-ThM10 Nucleation and Growth of Few-Layer ALD Films on Various Substrates Studied by Low Energy Ion Scattering (LEIS), *Malcolm Hathaway*, Harvard University, *T. Grehl, P. Bruener,* ION-TOF GmbH, Germany, *M. Fartmann,* Tascon GmbH, Germany, *H. Brongersma*, ION-TOF GmbH, Germany

Atomic Layer Deposition has found applications in many semiconductor processes due to its several unique characteristics, including high purity, conformality, pin-hole-free character, and atomic level thickness controllability. It is these last two characteristics which are of particular interest in this present work. The thickness control of ALD films is precise down to the angstrom level, even when depositing layers as thin as a few atomic layers. Ideally, in layers only a few angstroms thick, the ALD process produces material which is completely continuous and free of pin-holes. One of the challenges of characterizing ALD processes is the difficulty of directly measuring such thin films and confirming their continuous nature.

Low Energy Ion Scattering (LEIS) spectroscopy is uniquely suited to exploring these questions, due to its extreme surface sensitivity, easy quantification and its ability to yield additional information about the sub-surface composition. Using LEIS, analytical questions like layer closure, surface composition, diffusion processes, or growth modes can be addressed. In this work, we explore the limits of this technique to characterize few-layer ALD films on a variety of substrates, to confirm the capabilities of LEIS in this arena, and to shed new light on the nature of few-layer ALD films.

In the LEIS process, a noble gas ion beam of (1 -10 keV) is directed at the sample, and the fraction of backscattered ions is measured as a function of kinetic energy. Two main mechanisms determine the spectral response: Firstly, scattering in the first monolayer of atoms creates elemental peaks, allowing quantitative determination of the elemental composition of the outermost atomic layer. The intensity of these peaks is directly proportional to the surface coverage. Secondly, scattering processes below the surface (with the ion penetrating the surface, scattering at deeper layers and returning to the surface before leaving it) provide information about sub-surface layers, sometimes as deep as 10 nm, in a non-destructive way. As the additional energy loss is proportional to penetration depth, these data can be evaluated to determine the layer sequence, layer composition and layer thickness in a single measurement and in addition to the top layer composition.

In this study a number of oxide films (e. g. HfO_2, AL_2O_3) on Si and other substrates like glassy carbon are evaluated. We apply LEIS among other techniques to characterize the films, especially in the early phases of film growth. Using the unique information from LEIS, conclusions on the nucleation behavior and growth are drawn.

11:20am TF+AS+NS+SA-ThM11 $Ni_{1-x}Pt_xSi$ Film Characterization for sub-32 nm CMOS Fabrication, *Suraj Patil*, R. Rai, S. Beasor, L. Zhou, GLOBALFOUNDRIES, NY, USA

Aggressive scaling of CMOS devices demands silicide engineering for high performance in the sub-32nm technology node and beyond. Ni-silicide can satisfy many of the integration challenges but it is limited by morphological stability at elevated temperatures. On the other hand, incorporating Pt into Ni-silicide forms a more robust nickel platinum silicide ($Ni_{1-x}Pt_xSi$) and improves morphological stability. Advantages of Pt incorporation include extension of the temperature range over which the NiSi exists, delay in the agglomeration of NiSi phase, suppression of the high resistive $NiSi_2$ phase formation and retardation of the Ni diffusion at the interface and grain boundaries which could lead to encroachment or piping. This work discusses three important aspects of $Ni_{1-x}Pt_xSi$ formation: (1) understanding NiPt diffusion with two step RTA anneals – formation (RTA1) and transition (RTA2), which is very important for thickness uniformity across structures with varying CDs, encroachment control, device performance and yield; (2) understanding NiSi phase formation for thermal stability, and (3) understanding Pt distribution in the final film with low RTA1 temperatures. For this study $Ni_{1-x}Pt_xSi$ samples were fabricated from a simple n-

Si/$Ni_{0.85}Pt_{0.15}$/TiN stacks, annealed at range of RTA1 temperatures from RTA-20°C to RTA+30°C for 20s followed by a standard RTA2 anneal for 30s. Characterization of final $Ni_{1-x}Pt_xSi$ films obtained at different RTAs based on XRD phase identification and XPS analysis will be presented. Pt distribution in the final silicide films will be discussed.

11:40am TF+AS+NS+SA-ThM12 Growth of β-Tungsten Films Towards a Giant Spin Hall Effect Logic Device, *Avyaya Narasimham*, University at Albany-SUNY, *R.J. Matyi,* State University of New York, *A. Green,* University at Albany-SUNY, *A.C. Diebold, V. LaBella,* State University of New York

Spin-orbit coupling in metastable β-W generates spin transfer torques strong enough to flip magnetic moment of an adjacent magnetic layer. In a MTJ stack these torques can be used to switch between high and low resistive states. This technique can be used in designing efficient magnetic memory and non-volatile spin logic devices. Deposition conditions selective to β- W need to be understood for the large scale fabrication of such devices. The transition from β to α phase of Tungsten is strongly governed by thickness of W layer, base pressure and oxygen availability for example, above 5 nm β film relaxes and forms an α phase. Resistivity measurements as well as x-ray photoelectron spectroscopy and x-ray diffraction and reflectivity analysis are performed to determine the phase and thickness of tungsten films. We show that β phase is influenced by ultrathin thermal oxide of Si layer and the amount of oxygen flow during the growth. These results demonstrate a reliable technique to fabricate β W films up to 20 nm on bare Si and silicon dioxide, while providing insight to growing it anywhere in the device stack.

12:00pm TF+AS+NS+SA-ThM13 Aluminum Nitride Grown by Atomic Layer Epitaxy Characterized with Real-Time Grazing Incidence Small Angle X-ray Scattering, *Virginia Anderson*, N. Nepal, S.D. Johnson, US Naval Research Laboratory, *A. DeMasi,* Boston University, *J.K. Hite,* US Naval Research Laboratory, *K.F. Ludwig,* Boston University, *C.R. Eddy, Jr,* US Naval Research Laboratory

Aluminum nitride, gallium nitride, and indium nitride have desirable qualities for many semiconductor applications, and have recently been studied intensely.[1] Because of their direct, tunable band gaps and capacity for high current density they are attractive for photovoltaics and high power transistors. The current methods of depositing high-quality III-nitride films, are metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). The temperatures for the depositions make ternaries challenging. Indium nitride, for example, is difficult to mix with aluminum nitride, as typical MOCVD temperatures for AlN and for InN are 1000°C and 450°C respectively. Aluminum nitride deposition with atomic layer epitaxy (ALE) is currently being explored by some groups as a fabrication friendly technique for thin films at lower temperatures.[2]

Crystalline AlN deposited with plasma assisted ALE (PA-ALE) in a Fiji reactor from Ultratech/Cambridge Nanotech at 500°C currently has lower material purity than the AlN deposited by MBE and MOCVD, and understanding the film deposition mechanism in order to improve quality is the subject of ongoing research.[3] There is a need for a better understanding about the film evolution during nucleation. Grazing incidence small angle x-ray scattering (GISAXS) is sensitive to changing surface features and can be conducted at a wide range of pressures, making it useful for real time monitoring of deposition.[4]

AlN deposited by PA-ALE was grown using trimethylaluminum and hydrogen/nitrogen plasma pulses in a custom reactor at the Brookhaven National Synchrotron Light Source and the Cornell High Energy Synchrotron Source. In both instances, GISAXS was used to examine surface changes during the deposition.

GISAXS information collected during AlN growth at nominally 400°C, 450°C, and 500°C suggested that temperature influenced nucleation, with changes in roughening behavior observed. Post-growth examination of the AlN films with x-ray photoelectron spectroscopy and atomic force microscopy gave important information on the final film elemental composition and morphology. The GISAXS data also show that the surface continued to evolve during the cooling after growth completion while still in the reactor. This information only adds to the necessity of *in situ* growth monitoring to fully understand the mechanisms involved in the ALE growth process.

References:

[1] M. Mori et al., *Appl. Phys. Express* **5** 082301 (2012)

[2] M. Bosund et al., *Appl. Surf. Sci.* **17** 7827 (2011)

[3] N. Nepal et al., *Appl. Phys. Lett.* **103** 0 82110 (2013)

[4] K. Devloo-Casier et al., *Appl Phys. Lett.* **98** 231905 (2011)

Thin Film
Room: 114 - Session TF+EM+NS+PS+SM-ThM

Plasma ALD and Nano-applications

Moderator: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, Richard Vanfleet, Brigham Young University

8:00am TF+EM+NS+PS+SM-ThM1 Atomic Layer Deposition of Silicon Dielectrics: Precursors, Processes, and Plasmas, *Dennis Hausmann*, Lam Research Corporation **INVITED**
As the dimensions of modern semiconductor devices continue to shrink below the current 14 nm technology node, novel processes for the deposition of highly conformal, low temperature, silicon based dielectrics will be needed for applications that include sidewall spacers, barriers, and patterning layers. Atomic layer deposition (ALD) is an ideal method for achieving the high conformality and has been used in high volume manufacturing (HVM) to deposit high-k dielectric materials (HfO_2, ZrO_2, etc.) for several technology generations. Plasma assisted ALD is the best known method to meet low temperature ($<500^0C$) requirements and is now being used for depositing conformal silicon dielectrics such as silicon oxide (SiO_2) and silicon nitride (Si_3N_4).

In this presentation, we discuss the current state of the art of precursors, plasmas, and process conditions required to deposit conformal silicon dielectrics by plasma ALD. Theoretical and experimental data will be presented in order to explain the observed reaction characteristics for the plasma ALD of silicon oxide (SiO_2), silicon nitride (Si_3N_4), and the lack (so far) of silicon carbide (SiC). Generic to all ALD processes is the high cost of the precursors relative to traditional chemical vapor deposition (CVD); in the case of silicon dielectric ALD, this is exacerbated by the relative low "reactivity to cost ratio" of available silicon precursors. Although plasmas enable low temperature deposition, they pose challenges for achieving isotropic film properties over the complex topography on today's semiconductor devices.

8:40am TF+EM+NS+PS+SM-ThM3 ALD Dielectrics for Power Electronics, *Veena Misra*, NCSU **INVITED**
Owing to a high critical electric field and high electron mobility, wide band gap materials such as GaN and SiC are being sought for high voltage power electronics applications. In the case of GaN devices, the reliability continues to be a challenge to must be addressed before successful commercialization. In our work, different dielectrics deposited by Atomic Layer Deposition (ALD) have been investigated for improving the threshold voltage stability and dynamic reliability of AlGaN/GaN based MOSHFETs. A novel pulsed-IV-based methodology was developed and demonstrated to be applicable for detecting both shallow and deep traps and implemented on evaluating different high-k and low-k ALD dielectrics. Using physics-based simulation models and experimental data, it was demonstrated that the leakage at the surface of the AlGaN, whether through the passivation dielectric bulk or the dielectric/AlGaN interface, must be minimized to restrict the formation of a "virtual gate" and minimize current collapse. It was also found that an optimal passivation dielectric must create a high density of shallow interface donor traps to quicken the de-trapping of electrons from the "virtual gate" and the recovery of the channel underneath. Combining simulation and experimental results, an optimal set of ALD dielectrics for a reliable gate stack and access-region passivation regions, respectively, was determined and will be discussed. In the area of SiC devices, low inversion channel mobility, caused high density of interface states (Dit) at SiO2/SiC interface, limits the wide adoption of SiC MOS devices. Atomic Layer Deposition offers key advantages in the area of gate dielectrics such as good film quality, low substrate damage, superior uniformity, precise thickness control, and low process temperature. Additionally, deposited SiO2 enables interface engineering to independently control the interface properties. To enhance the channel mobility and maintain good overall gate dielectric properties, a thin layer of a different dielectric material can be inserted to improve interface properties and high quality deposited SiO2 can be used as the bulk gate dielectric. We have demonstrated a novel interface engineering technique utilizing ultra thin lanthanum silicate (LaSiOx) at the SiC/dielectric interface and ALD SiO2 as the bulk gate dielectric. The lanthanum silicate interface engineering dramatically improves the mobility of 4H-SiC metal oxide semiconductor field effect transistors (MOSFETs) and is attributed to the large driving force of La_2O_3 to react with SiO_2.

9:20am TF+EM+NS+PS+SM-ThM5 Pb(Zr$_x$Ti$_{1-x}$)O$_3$ Magnetoelectric Tunnel Junctions for Magnetoelectric RAM (MeRAM) Memory Applications, *D. Chien, X. Li, K. Wong, P. Khalili, K. Wang, Jane P. Chang*, University of California at Los Angeles
As existing memory systems approach fundamental limitations, ultra-thin uniform conformal PZT films are needed for next-generation ultralow-power voltage-controlled non-volatile magnetoelectric RAM (MeRAM) memory devices. By utilizing the magnetoelectric effect, where an electric field or voltage can be used to control the magnetization switching (instead of current), the writing energy can be reduced, resulting in increased memory density (Amiri, P.K. et al., Journal of Applied Physics, 2013). Previous research has shown that the voltage-controlled magnetic anisotropy (VCMA) effect increases with the capacitance of the stack (Kita, K. et al., Journal of Applied Physics, 2012). Therefore, integrating an ultra-thin PZT film (having a dielectric constant 1-2 orders of magnitudes higher than currently used MgO) into the tunneling oxide layer will enhance the VCMA coefficient, allowing for a lower voltage to switch the magnetization of the free magnetic layer and thus decreasing the write energy.

Using atomic layer deposition (ALD), a surface-reaction controlled process based on alternating self-limiting surface reactions, an ultra-thin film of PZT can be synthesized with precise control of the film thickness and elemental composition (Zr/Ti = 52/48). ALD PZT thin films were synthesized by depositing alternating layers of PbO, ZrO2, and TiO2 layers using Pb(TMHD)$_2$, Zr(TMHD)$_4$, and Ti(O i-Pr)$_2$(TMHD)$_2$ as metal precursors and H2O as the oxidant. The number of local cycles and global cycles were regulated to achieve the desired stoichiometry and thickness, respectively. The bottom layers of Ta/CoFeB (free magnetic layer)/MgO were sputtered, the PZT film with thickness of 1.7 nm was deposited by ALD, the top layers of MgO/CoFeB (fixed magnetic layer)/Ta/Pt were sputtered, and the entire stack was annealed at 200°C for 30 minutes in order to fabricate PZT magnetoelectric tunnel junctions (MEJs).

The perpendicular magnetic anisotropy (PMA) of the bottom free magnetic CoFeB layer was verified via superconducting quantum interference device (SQUID) magnetometer, confirming that the ALD PZT deposition process is a viable method for synthesizing PZT MEJs. The tunnel magnetoresistance (TMR) was measured to be 50%, demonstrating a promising read-out process. Due to the integrated ALD PZT layer in the tunneling barrier, the VCMA coefficient of PZT MEJ devices is expected to be double that measured for CoFeB/MgO/CoFeB devices (ξ = 37 fJ/V·m) (Zhu, J. et al., Physical Review Letters, 2012).

9:40am TF+EM+NS+PS+SM-ThM6 Plasma-Assisted ALD of High-Quality Molybdenum Oxide Films, *Martijn Vos, B. Macco, N.F.W. Thissen, A.A. Bol, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands
In this contribution we present a novel plasma-assisted atomic layer deposition (ALD) process to deposit high-quality molybdenum oxide films, with a high growth per cycle (GPC) over a wide temperature range of 50 °C to 350 °C. This process complements existing (thermal) ALD MoO$_x$ processes, which are less suited for deposition at low temperature, due to low GPC and contamination. A decent deposition process is of importance as MoO$_x$ films have received great interest due to their remarkable optoelectronic and catalytic properties and find their use in many applications, including solid state lithium batteries, gas sensors, and more recently solar cells.

A variety of deposition techniques exists for the deposition of MoO$_x$, such as evaporation, sputtering, chemical vapor deposition and ALD. While many of the applications of MoO$_x$ films can benefit from the merits of ALD, i.e. conformality and digital thickness control, only few ALD processes are known from literature [1, 2]. Recently bis(tert-butylimido) bis(dimethyamido) molybdenum ((NtBu)$_2$(NMe$_2$)$_2$Mo) appeared as a promising precursor for ALD of MoO$_x$ films, using O$_3$ as oxidant [2].

The plasma-assisted ALD process we report on uses (NtBu)$_2$(NMe$_2$)$_2$Mo and O$_2$ plasma and shows a relatively high GPC between 0.70 Å and 0.93 Å for amorphous films deposited at temperatures up to 250 °C. In comparison, the analogous O$_3$ process is featured by a low GPC of 0.17 Å at 150 °C. For deposition temperatures above 250 °C polycrystalline growth was observed, accompanied by an increase in GPC to 1.88 Å for 350 °C. From Rutherford backscattering measurements it was determined that the C and N content in the films is below the detection limit (3 at.% and 2 at.% respectively) for all deposition temperatures, which demonstrates the high-quality of the films (while the aforementioned O$_3$ process resulted in 9.2 at.% N). Furthermore the O/Mo ratio was found to be just below 3, indicative of oxygen vacancies, which are common for MoO$_x$ films and can lead to an increased conductivity, which is beneficial for many applications. Additional material properties such as band gap, work function and surface morphology will also be discussed and finally an outlook to the application of this ALD process in silicon solar cells will be given.

[1] M. Diskus *et al.*, J. Mater. Chem. **21** (2011) 705

[2] A. Bertuch *et al.*, J. Vac. Sci. Technol. **32** (2014) 01A119

11:00am TF+EM+NS+PS+SM-ThM10 Status and Prospects of Plasma-Assisted Atomic Layer Deposition, *Harm Knoops*, Oxford Instruments Plasma Technology, UK, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands **INVITED**
Plasma-assisted atomic layer deposition (ALD) or plasma ALD has established itself as a prominent branch in ALD processing and a wide range of plasma ALD processes are currently available. Due to the complexity of plasmas, plasma ALD is different from thermal ALD in various aspects. Even though the main relevant species in plasmas have been identified,[1] the effects of plasma chemistry and plasma-surface interaction need further study. In this contribution an overview on the status of plasma ALD is given and the key prospects for plasma ALD are highlighted.

Regarding the current understanding of plasma ALD, three subjects will be treated. First the basic plasma species (i.e., radicals, electrons, ions, and photons) and their role in plasma ALD will be discussed. For instance, potential damage to the surface from photons, but also cases where plasma species can repair defects (e.g., N_2 plasmas on GaN surfaces).[2] Second plasma chemistry and potential poisoning or inhibition processes will be treated, which can play a big role in the ALD of nitrides and conductive films. Third, dissociation in the plasma of reaction products can lead to redeposition effects which can have a large influence on for instance SiN_x and TaN_x ALD.

Several topics will be discussed regarding the prospects for plasma ALD. Even though plasma ALD provides additional possibilities, many cases exist where material properties or cycle times are still unsatisfactory and advances in reactor design such as the capability to provide additional energy in the form of a controlled ion bombardment are needed. In addition, advanced processing schemes such as 3-step ABC ALD cycles can be beneficial as shown by ALD of noble metals at low deposition temperatures (e.g., Pt ALD).[3] Whether metal films initially grow as continuous films or as nanoparticles (as well as the particle size), will depend on the chemistry, the surface energy, and the growth temperature. Recently, plasma ALD has shown to allow ALD of Ag by spatial ALD at high pressure.[4] This case shows that more understanding of the plasma is needed because of an unexpected decreased growth at long plasma exposures (presumably caused by NH_3 poisoning). In general, increasing control of the plasma and understanding of the relevant processes at the surface and in the plasma will be key to further develop plasma ALD.

[1] Profijt et al., *JVST A* **29**, 050801 (2011)

[2] Chen et al., *Phys. Status Solidi A* (2014) / DOI 10.1002/pssa.201431712

[3] Mackus et al., *Chem. Mater.* **25**, 1769 (2013)

[4] Van den Bruele et al., *JVSTA* **33**, 01A131 (2015)

11:40am TF+EM+NS+PS+SM-ThM12 A Novel Plasma-Enhanced ALD Process for HfO_2 using $HfCp(NMe_2)_3$ and O_2 Plasma, *Akhil Sharma*, V. Longo, A.A. Bol, W.M.M. Kessels, Eindhoven University of Technology, The Netherlands
In atomic layer deposition (ALD) the associated precursor chemistry has a large effect on the quality and properties of the deposited thin films. The most commonly used hafnium precursor for ALD of HfO_2 is $HfCl_4$. This precursor is not ideal for all applications due to possible chlorine contamination and the generation of corrosive by-products during the ALD process. Organometallic precursors such as $Hf(NtMe)_4$ promise to be a better choice but they typically suffer from a limited thermal stability. In this context, $HfCp(NMe_2)_3$ might offer a better alternative because of its higher thermal stability. However, while using H_2O as oxygen source in a thermal ALD process it yields a low growth rate[1]. This creates an opportunity for studying this precursor in combination with other oxygen sources. In this work, we report on the development of a novel plasma-enhanced ALD (PE-ALD) process using $HfCp(NMe_2)_3$ in combination with an O_2 plasma to deposit HfO_2 thin films. To our knowledge, to date, the PE-ALD for this precursor has not been reported in the literature.

Our results show that the PE-ALD process offers significant advantages over the reported thermal ALD process such as a high growth rate, reduced deposition temperature, shorter cycle time and good control over composition of the deposited films. In contrast to the thermal ALD process using $HfCp(NMe_2)_3$ and water[1], the PE-ALD process has resulted into a wide ALD temperature range (150-400°C) with significantly higher growth per cycle values (1.1Å/cycle) and shorter cycle times which ultimately improves the wafer throughput. The level of impurities were found to decrease with increasing the deposition temperature as concluded from XPS and ERD analyses. The concentrations of residual carbon and hydrogen reduced from 1.0 at% to 0.2 at% and 3.4 at% to 0.8 at%, respectively, by increasing the deposition temperature from 200°C to 400°C. Moreover,

RBS studies showed an improvement in stoichiometry of HfO_2 thin films with increase in deposition temperature resulting in a Hf/O ratio of ~0.5 at 400°C. Furthermore, GI-XRD measurements detected a strong transition from amorphous (300°C) to fully crystallized films (400°C), consisting of a mixture of monoclinic, tetragonal and cubic phases. These results therefore have demonstrated that PE-ALD using $HfCp(NMe_2)_3$ and O_2 plasma is a promising and viable alternative to the thermal ALD process producing high quality HfO_2 thin films over a wider temperature range and with faster cycle times.

1. Consiglio et al, J. Vac. Sci. Technol. A 30(1), 2012

12:00pm TF+EM+NS+PS+SM-ThM13 Conductive Hafnium Nitride Layers By Plasma-Assisted Atomic Layer Deposition, *Saurabh Karwal*, B.L. Williams, W.M.M. Kessels, M. Creatore, Eindhoven University of Technology, The Netherlands
Transition metal nitrides (TMNs) have gained much attention in the semiconductor industry due to their characteristics such as copper and lithium diffusion barriers, metal-like behaviour (i.e. low resistivity) and high hardness, mechanical strength and chemical inertness. Among TMNs, hafnium nitride exhibits a low bulk resistivity of 33 μΩcm and highest negative Gibbs free energy of formation (HfN: -88.2, TiN: -80.4, TaN: -60.3 kcal/mol) and hence could serve as novel material for several applications, such as diffusion barrier and gate electrode in microelectronics, and reflective back contact for CIGS solar cells.

Conductive hafnium nitride thin films were deposited by inductively coupled plasma (ICP)- assisted atomic layer deposition using a heteroleptic metalorganic hafnium precursor, tris(dimethylamino)cyclopentadienylhafnium $CpHf(NMe_2)_3$ [TDMACpH] and H_2-or N_2- fed plasmas serving as co-reactants. The effects of the substrate temperature, plasma chemistry and plasma exposure time have been investigated in terms of growth-per-cycle (GPC), chemical, electrical and morphological properties of the deposited layer. It has been observed that highly resistive (0.75 Ωcm) Hf_3N_4 thin films are obtained via an A-B type ALD cycle (TDMACpH/N_2 –fed plasma) with a GPC of 0.035 nm/cycle. Furthermore, a limited abstraction of the ligands leads to a residual carbon content in the layer of 7%.

Instead, conductive films (1.8×10^{-3} Ωcm) are achieved upon the application of an A-B-C ALD cycle where an intermediate H_2- fed plasma exposure step is included between the TDMACpH exposure and the N_2-fed plasma step, with a GPC of 0.045 nm/cycle. This intermediate step is found to be responsible for a more efficient removal of the precursor ligands and for the reduction of Hf^{4+} state to Hf^{3+} state, essential for guaranteeing electron conductivity. This transition of chemical and electrical properties of the deposited thin films is also accompanied by a change in crystallographic properties from amorphous (A-B ALD cycle) to conductive cubic HfN (A-B-C ALD cycle), as revealed by grazing incidence X-ray diffraction.

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2D Materials Focus Topic
Room: 212C - Session 2D+EM+MG+NS+SS+TF-ThA

Heterostructures of 2D Materials
Moderator: Stefan Förster, Martin-Luther-Universität Halle-Wittenberg, Michael Naguib, Oak Ridge National Laboratory

2:20pm 2D+EM+MG+NS+SS+TF-ThA1 Dielectrics Layer Deposition on 2D Materials by Functionalization with Polar Titanyl Phthalocyanine, *JunHong Park*, UC San Diego, *S. Fathipour,* University of Notre Dame, *I.J. Kwak,* UC San Diego, *H.C.P. Movva,* UT-Austin, *S. Vishwanath, H. Xing,* Cornell University, *S.K. Banerjee,* UT-Austin, *A.C. Seabaugh,* University of Notre Dame, *A.C. Kummel,* University of California at San Diego

Several novel designs for beyond CMOS devices have emerged using two-dimensional semiconductors. These devices require deposition of thin insulators on 2D semiconductors or between two sheets of 2D semiconductors. However, 2D semiconductors are nearly inert surfaces thereby making uniform nucleation of oxide growth challenging preventing scaling of the insulator thickness. A new technique has been developed to employ a monolayer of ordered metal phthalocyanines (MPc) on 2D semiconductors directly as a nucleation layer for growth of ALD dielectric. TiOPc monolayers were deposited on HOPG surfaces and WSe_2 by organic molecular beam epitaxy. TiOPc forms a monolayer with only few defects, and the crystal structure of monolayer has four-fold symmetry in a 1.6 x 1.6 nm grid on both HOPG and WSe_2. Observation of bright protrusions on each O-TiPc indicates that each O-TiPc in the monolayer is directed outward to vacuum. After exposure O-TiPc monolayer to 5 cycles ALD pulse (tri-methyl-aluminum (TMA)+H_2O), insulating aluminum oxide was deposited uniformly on TiOPc/HOPG. After formation of AlO_x on TiOPc/HOPG, the band gap of surface increases from 1.7 eV to 3.4 eV, while the conductance decreased. A metal-oxide-TiOPc-graphene capacitor has the lower thickness and the higher capacitance value than any reported graphene MOSCAPs. In the dual gated graphene FET with 40 cycles of AlO_x, TiOPc assisted AlO_x shows very low leakage current. Employing the TiOPc seeding layer also can be expanded to other TMD materials. The bottom gated WSe_2 FET was fabricated. On the bottom gated WSe2 FET, the TiOPc monolayer was deposited, then 50 cycle of AlO_x was deposited via ALD. In this dual gated WSe_2 FET, the leakage current of the AlO_x is measured as ~0.05 pA/μm^2 at 0.5 VTG. As a control, 20 cycles of Al_2O_3, and 140 cycles of HfO_2 were deposited on bare WSe_2. The leakage current of the TiOPc assisted 50 cycle Al_2O_3 oxide is 3 orders of magnitude lower than $HfO_2/Al_2O_3/WSe_2$, consistent with a high nucleation.

2:40pm 2D+EM+MG+NS+SS+TF-ThA2 Direct Probing of the Electronic Structure of Bilayer Homo- and Hetero-Structures and Tracking their Evolution with Interlayer Twist-Angle, *Nader Zaki, P. Yeh, W. Jin, R.M. Osgood, Jr.*, Columbia University

2D atomic layer materials such as graphene and transition-metal dichalcogenides such as MoS_2 have garnered much interest over the last few years due to their surprising electronic properties. For example, graphene possesses an exceptionally high mobility while monolayer MoS_2 possesses a direct bandgap with an exceptionally high light-matter interaction. One of the directions the 2D materials community is now pursuing is one in which these materials are combined together by way of vertical stacking in order to fabricate custom layered structures with potentially rich physics and unique device properties. Naturally, determining the electronic structure of these custom assembled structures is a necessary task to understanding their electronic behavior. While the electronic structure of the constituent materials have already been studied for monolayer form, the electronic structure of the stacked structures has only recently started to be deciphered. This talk will report on the direct determination of the electronic structure of two bilayer systems: twisted bilayer MoS_2 and twisted graphene/MoS_2. Using LEEM, µLEED, and µARPES, the stack quality, stack orientation, and stack electronic structure are directly probed and resolved with few *µm* and higher spatial resolution. To be discussed will be the evolution of the electronic structure with twist angle and its implications on the electronic properties of the respective homo- and hetero-structures.

3:00pm 2D+EM+MG+NS+SS+TF-ThA3 *In Situ* Microscopy on 2D Materials: Heterostructures, Nanostructures, Novel Materials Systems, *Peter Sutter*, University of Nebraska - Lincoln **INVITED**
Two-dimensional (2D) materials, such as graphene, hexagonal boron nitride, and a family of metal dichalcogenides have fascinating properties

and show promise for applications. The broad exploration and use of these materials depends on the development of scalable synthesis methods, and of a fundamental understanding of their properties. I will discuss recent advances in understanding the synthesis, processing, and properties of 2D materials derived primarily from in-situ surface imaging.

In-situ microscopy provides the basis for creating complex heterostructures of different 2D materials, such as graphene and hexagonal boron nitride, and for studying atomically precise graphene nanostructures. Real-time imaging yields quantitative information on the growth and processing of new classes of 2D materials, such as metal dichalcogenide semiconductors. Finally, the combination of in-situ microscopy with synchrotron-based spectroscopy represents a unique approach for exploring the electronic band structure of 2D materials.

Our results illustrate that in-situ microscopy can be a powerful tool for realizing and probing the unique characteristics of two-dimensional materials.

4:00pm 2D+EM+MG+NS+SS+TF-ThA6 Direct Growth of Graphene/h-BN(0001) Multilayer Heterostructures for Novel Device Applications, *S. Driver, D. Beatty, B. Olanipekun, S. Reid, Jeffry Kelber*, University of North Texas
We report the direct layer-by-layer growth of h-BN(0001) multilayers on Co(0001) by atomic layer epitaxy (ALE), and the direct growth of graphene multilayers on h-BN(0001) by molecular beam epitaxy (MBE). For the first time, this allows the growth of graphene/BN heterostructures with graphene and BN thicknesses controlled with atomic precision, and with all graphene and BN layers in azimuthal registry. Such control is a prerequisite for many proposed spintronic and electronic applications that emphasize charge or spin transport perpendicularly through the heterojunction. Further, the growth by direct, scalable methods without physical transfer, is essential for industrial development of such devices. h-BN(0001) multilayers have been deposited on Co(0001)/Al_2O_3(0001), using a BCl_3/NH_3 ALE process at 600 K. X-ray photoelectron spectroscopy (XPS) indicates B:N atomic ratios of 1:1 with negligible Cl contamination or reaction with the metallic substrate. Low energy electron diffraction (LEED) data indicate BN domain sizes of ~ 300 A or greater, with the lattice in registry with that of the Co(0001) substrate. LEED data also indicate BN domains larger than those of the Co substrate, suggesting BN overgrowth of Co domain boundaries. The XPS-derived average BN film thickness scales linearly with the number of BCl_3/NH_3 cycles, and the lack of Co oxidation after ambient exposure of a BN bilayer indicates that these films are macroscopically continuous over the 1 cm x 1 cm sample size. Graphene formation on h-BN(0001) was achieved using MBE with a graphite rod source, with deposition carried out at 800 K. LEED data show the expected 6-fold LEED pattern in exact registry with that of the h-BN(0001)/Co(0001) substrate. XPS C 1s spectra indicate a C 1s binding energy near 284.5 eV and with the expected pi-to-pi* transition. A heterojunction consisting of ~ 3 monolayers (ML) graphene/3 ML h-BN on Co(0001) proved stable in vacuum to at least 1000 K, indicating the adaptability of this growth process to a variety of industrial applications. Other recent results indicate the adaptability of this process to other substrates, such as Ru(0001) or $CoSi_2$(111). These developments make possible a variety of spin filters, spin valves, and tunneling transistors proposed on the basis of close BN/graphene lattice matching, but not readily achievable with physically transferred films.

4:20pm 2D+EM+MG+NS+SS+TF-ThA7 Al_2O_3 on Black Phosphorus by Atomic Layer Deposition: An *in situ* Interface S tudy, *Hui Zhu, S. McDonnell, X. Qin, A. Azcatl, L. Cheng, R. Addou, J. Kim*, UT-Dallas, *P.D. Ye,* Purdue University, *R.M. Wallace*, UT-Dallas
Black phosphorus ("black-P") is considered to be an appealing 2D material because of its novel properties and potential application in few-layer transistor structures.[1,2,3] However, a clear challenge in the implementation of black-P is the strong hydrophilic[4] and oxidation[5] reactions during device processing and thereafter. Thus, efficient isolation layers are necessary for black-P to preserve its electronic properties. Al_2O_3[2] or HfO_2[6] dielectric layers deposited by atomic layer deposition (ALD) have been used as isolation layers in recent black-P transistors. In this work, three different samples oxidized by ambient air were investigated to understand the interfacial chemistry, and nucleation of atomic layer deposited Al_2O_3 on black-P using *in situ* X-ray photoelectron spectroscopy (XPS). This work suggests that exposing a sample that is initially free of phosphorus oxide to the ALD precursors does not result in detectable oxidation. However, when

the phosphorus oxide is formed on the surface prior to deposition, the black-P can react with both the surface adventitious oxygen contamination and the H_2O precursor at the deposition temperature of 200 °C. As a result, the concentration of the phosphorus oxide increases after both annealing and the atomic layer deposition process. The nucleation rate of Al_2O_3 on black-P is correlated with the amount of oxygen on samples prior to the deposition. The growth of Al_2O_3 follows a "substrate inhibited growth" behavior where an incubation period is required. *Ex situ* atomic force microscopy is also used to investigate the deposited Al_2O_3 morphologies on black-P where the Al_2O_3 tends to form islands on the exfoliated black-P simples.

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4:40pm 2D+EM+MG+NS+SS+TF-ThA8 Topological Winding Number Change and Broken Inversion Symmetry in a Hofstadter's Butterfly, *Marc Bockrath*, UC Riverside
Recently several research groups have demonstrated accurate placement of graphene on hexagonal BN (hBN) with crystallographic alignment. Due to the resulting superlattice formed in the graphene/hBN heterostructures, an energy gap, secondary Dirac Points, and Hofstadter quantization in a magnetic field have been observed. Using aligned layer transfer we are able to produce graphene/hBN heterostructures with ~1 degree alignment accuracy, and measure the transport properties of the resulting systems. We observe an additional π Berry's phase shift in the magneto-oscillations when tuning the Fermi level past the secondary Dirac points, originating from a change in topological winding number from odd to even when the Fermi-surface electron orbit begins to enclose the secondary Dirac points. At large hole doping inversion symmetry breaking generates a distinct hexagonal pattern in the longitudinal resistivity versus magnetic field and charge density. This results from a systematic pattern of replica Dirac points and gaps, reflecting the fractal spectrum of the Hofstadter butterfly.

5:00pm 2D+EM+MG+NS+SS+TF-ThA9 Compliant Substrate Epitaxy: Au on MoS_2, *Yuzhi Zhou*, C. Daryl, UC Berkeley
The heteroepitaxial growth of Au on MoS_2, a layered van der Waals bonded dichalcongenide, is analyzed. It is argued that the weak coupling between the layers in the dichalcogenides enables the first substrate layer to deform elastically almost independently from the substrate layers below, and hence enables epitaxial growth for a larger mismatch than might otherwise be expected. Linear, continuum elasticity theory and density functional theory are used to show that a {111} oriented Au film is the preferred over an {001} oriented Au film, despite the fact that the {111} orientation leads to a much higher elastic strain. During the initial stages of growth, the {111} orientation is favored over the {001} orientation due to its lower surface and interfacial energies. As the Au film grows thicker, the elastic relaxation of the first layer of the substrate leads to a reduction in the elastic energy of the growing film. This reduces the elastic energy difference between the {001} and {111} orientations enabling the {111} orientation to remain stable for all film thicknesses. This work is supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

5:20pm 2D+EM+MG+NS+SS+TF-ThA10 Direct Synthesis of 2D van der Waals Heterostructures, *Judy Cha*, Yale University **INVITED**
Two-dimensional (2D) chalcogenides have gained renewed interest due to their interesting electrical properties such as topological insulator surface states in Bi_2Se_3 and hydrogen evolution catalytic activities in MoS_2. Our ability to thin them down to a single layer and their anisotropic bonding nature opens up possibilities for novel heterostructures where we can tailor their electronic properties. I will present one-step, scalable heterostructure synthesis method to synthesize these chalcogenide nanostructures and examine their electronic transport properties. Intercalation into 2D materials will be considered as a novel way to design 2D heterostructures, in which the optical and electrical properties of the host 2D materials can drastically change. I will also discuss ways to control the alignment of molecular layers in these 2D chalcogenides, which exploits stress and strain built in the film during the growth. Electron tomography will be used to reconstruct the 3D structure of vertically oriented molecular layers in MoS_2 thin films. In the second part of the talk, I will present synthesis and electronic properties of SnTe topological crystalline insulator nanoplates. Although SnTe is cubic and not a layered material, large SnTe nanoplates expanding hundreds of microns in lateral dimension with ~ 100 nm in thickness are possible. I will discuss effects of substrates and growth conditions to promote thin film growth of non-layered materials.

Helium Ion Microscopy Focus Topic
Room: 211B - Session HI+AS+NS-ThA

Imaging and Milling with He and Ne Ion Beams
Moderator: Richard Livengood, Intel Corporation, John A. Notte, Carl Zeiss Microscopy

2:20pm HI+AS+NS-ThA1 Focused Ion Beam Circuit Edit in the Nano-Device Age: A Search for the Ultimate Nano-Ion Beam, *Shida Tan*, Intel Corporation **INVITED**
Evolution of the IC process technology continues to increase the challenge of circuit edit with smaller critical device dimensions, thinner process layers, densely packed structures, and complex device routing and design architecture. In this paper, the general approach employed, challenges encountered, and results acquired in neon application development using Zeiss NanoFAB (noble GFIS) platform for circuit edit will be presented. The merits and limitations of applying a Ne^+ beam in high precision circuit edit applications will be shared with the audience.

3:00pm HI+AS+NS-ThA3 Electrical Nano-Patterning of Graphene Film by Helium Ion Beam Irradiation, *Shinichi Ogawa*, T. Iijima, Y. Naitou, AIST, Japan
The helium ion microscopy is a unique technology for observation of soft materials such as low-k materials and photo resist patterns for LSI fabrication [1] and for nm order etch patterning. Graphene, a two-dimensional sheet of carbon atoms [2], is a promising channel material for next-generation transistors, and we have shown an on-off gating of current through a graphene nano-ribbon which was etched down by the helium ion beam using the helium ion microscope [3] and by controlling electrical properties of the graphene films themselves by the nano-scale helium ion irradiations generating defects [4]. This study precisely shows a nano-scale direct electrical patterning of the graphene film from a point of view of irradiation conditions.

Helium ion beams of 0.3 nm diameter were 500 X 500 nm^2 regions scanned on single-layer graphene films on Si/SiO_2 substrates at doses of 0.62 - 10 10^{16} cm^{-2} at 30 kV. A spatial resolution of the helium ion microscope patterning on the single-layer graphene was investigated by fabricating nano-ribbons of lines of 100 - 5 nm width. Dynamic force microscopy and scanning capacitance microscopy measurements revealed that helium ionirradiated regions appeared as depressed about 1 nm in topography image at above conditions, while a darker image was acquired at 2.0 10^{16} cm^{-2} than those at less dose conditions which means transition to dielectric from metal occurred at the higher dose. A spatial resolution of the helium ion microscope patterning non-monotonically depended on the dosage of the helium ions. Increasing the dose to 5.0 10^{16} cm^{-2} improved the spatial resolution to several tens of nanometers. However, doses of more than 1.0 10^{17} cm^{-2} degraded the patterning characteristics.

Those results are discussed precisely changing irradiated beam conditions followed by structural analyses by such as CS-TEM.

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3:20pm HI+AS+NS-ThA4 Nanopores in Silicon Nitride Membranes, Graphene and CNM: Milling and Imaging Techniques at the Helium Ion Microscope, *Daniel Emmrich*, *E. Marschewski*, Bielefeld University, Germany, *A. Nadzeyka*, *F. Nouvertné*, Raith GmbH, Germany, *A. Gölzhäuser*, *A. Beyer*, Bielefeld University, Germany

The Helium Ion Microscope (HIM) is a focussed ion beam system which can be used for both imaging and milling. In the low dose regime, the HIM operates as a microscope; high doses enable material modification and sputtering. Compared to conventional focussed ion beams (FIB), the HIM offers a very small focal spot size down to 0.35 nm and a strongly localized sputter interaction with the material. We employ the HIM for milling nanopores in free standing membranes, such as 30 nm thick Silicon Nitride, Graphene and 1 nm thick carbon nanomembranes (CNM) made from aromatic self-assembled monolayers by electron-induced cross-linking. HIM is also used for the inspection of pores. The smallest He^+-milled nanopores have a diameter of about 3 nm in all investigated membranes. The He^+ beam thus overcomes the resolution limit of conventional FIB tools as we show in a comparison with a high resolution Ga-FIB. Different strategies for the characterization of pores with the HIM will be discussed. In particular, we compare the feasibility of the ion generated secondary electron signal to the He^+ transmission signal.

4:00pm HI+AS+NS-ThA6 Application of Focused Helium Ion Beams for Direct-write Lithography of Superconducting Electronics, *Shane Cybart*, University of California San Diego **INVITED**

The 1986 discovery of high transition temperature (high-T_C) superconductivity in copper-oxide materials set in motion an intense research effort to develop superconducting electronics functioning in the range of liquid nitrogen temperatures (77 K). Scientists and engineers soon after discovered that these materials were much more complicated than initially imagined. Anisotropic electrical properties and a very short superconducting coherence length seriously narrowed or eliminated the possibility of using classical superconducting electronic structures. These new materials demanded novel device architectures that proved very difficult to realize. Nearly three decades have passed and progress in high-T_C superconducting devices has been very slow because process control at the sub ten nanometer scale is required to make high quality, reproducible Josephson junctions: the basic building block of superconducting electronics. Recent advances in gas field focused helium ion beams provide a new and promising approach for direct-write lithography of high-T_C materials for the realization of predictable and scalable high-T_C electronics. In this work, we demonstrate fabrication of *a-b* plane superconducting Josephson tunnel junctions for $YBa_2Cu_3O_{7-\delta}$ (YBCO) by utilizing a focused helium ion beam to create a narrow (~nm) in-plane tunnel barrier between two superconducting electrodes. The key to this method is that YBCO is sensitive to point defects in the crystal lattice caused by ion irradiation. Increasing irradiation levels has the effects of increasing resistivity and reducing the superconducting transition temperature. At very high irradiation levels YBCO becomes insulating and no longer superconducts. Test samples were written with ion fluence ranging between 10^{14} and 10^{18} He^+/cm^2. In between these two extremes we were able to determine doses that could create very high-quality Josephson junctions with both metallic and insulating barriers. .The current-voltage (I-V) characteristics for lower doses show nearly ideal Josephson junction behavior with a zero voltage supercurrent that oscillated in magnetic field as expected for the Josephson effect. At much higher doses (I-V) exhibited insulator behavior. Using ac techniques we measured the differential conductance (dI/dV) in this regime which revealed the YBCO superconducting energy gap near 33 mV. This feature is a result of quasi particle tunneling which provides strong evidence that we have created an insulating barrier less than 2 nm wide. These results demonstrate the unique ability of focused helium ion beams for maskless direct write lithography of oxide tunnel barriers for electronic devices.

4:40pm HI+AS+NS-ThA8 A Novel Efficient Approach for Investigating the Ion Implantation Effect on Small Volume Copper, *Zhang-Jie Wang*, Xi'an Jiaotong University, China, *F.I. Allen*, University of California, Berkeley, *Z.W. Shan*, Xi'an Jiaotong University, China, *P. Hosemann*, University of California, Berkeley

Ion implantation has been used for decades to investigate the response of materials to radiation damage. Understanding the effect of He in materials is a key aspect in the optimization of fusion, fast reactor and spallation sources suffering from high He/dpa (displacements per atom) ratios. The traditional large-area He implantation techniques are rather materials-constrained and time consuming, thus limiting systematic studies. The work presented here utilizes the Zeiss ORION NanoFab instrument which deploys He and Ne ion beams in combination with a Ga ion source to quickly and efficiently manufacture nanostructures and then perform direct He implantation in selected areas of interest. Demonstrated in single crystal and copper nanotwinned structures, the systematical study of He bubble lattice distribution and twin structure evolution under different implanting

doses and dose rates is achieved in a fast and efficient manner. We also utilize the combined Ga-He beam system to increase sample throughput to manufacture nanopillars and implant with He in the same chamber. Each pillar was subsequently tested using a JEOL 3010 TEM equipped with a Hysitron PI95 nanomechanical testing system. The results show that the resistance of deformation twinning in single crystal Cu and twin boundary migration in nanotwinned Cu are both significantly improved for increasing He doses up to $1x10^{18}He^+$/cm^2. The novel technique presented here makes it feasible and efficient to evaluate He ion damage and its effect on small volume materials.

5:00pm HI+AS+NS-ThA9 Helium Ion Microscopy Analysis of Itokawa Asteroid Particles Obtained from Hayabusa Mission, *Vaithiyalingam Shutthanandan*, Pacific Northwest National Laboratory, *R.C. Ogliore*, *K. Nagashima*, University of Hawai`i at Manoa

Particles returned from the S-type asteroid Itokawa by JAXA's Hayabusa mission show evidence of space weathering Features. These features can be very small (<1 μm in size) and very shallow (within a 100 nm of the surface). The smallest space-weathering surface features and textures are difficult to resolve by field-emission SEM (FEG-SEM). In order to see these effects, we have used Helium ion microscopy (HIM). Two Hayabusa particles: RB-QD04-0062 ("#62": 40 μm, olivine and plagioclase) and RB-QD04-0091 ("#91": 43 μm, olivine and plagioclase) were imaged using HIM. The particles were removed from their glass slides with a Sutter micromanipulator and tungsten needle and then stuck on a SEM stub with a thin layer of Post-It note glue. The stub was coated with ~6 nm of carbon for electrical conductivity. Helium ion microscopy images of the surfaces of two Hayabusa grains revealed diverse space-weathering features on scales from several nm to several μm. Both Hayabusa particles show variable surface textures, a variety of splash melt features, adhering grains, and small holes. Two porous particles, with structures reminiscent of chondritic-porous interplanetary dust particles, were found adhering to the surface of the Hayabusa grains (a 1.2 μm object on #91, a 350 nm object on #62). Much of the surface of #62 was covered with small bumps 25–100 nm in size, whereas other regions were free of small bumps. A large, 6 μm quenched melt splash feature was found on the surface of #62. On the other hand, faces of #91 showed multiple concoidal fractures and splash melt droplets and pancakes, but fewer and smaller surface bumps compared to #62. For comparison purposes a 30 μm grain of lunar soil, which had a much higher density of sub-μm splash melt features than the Hayabusa grains, was also imaged. No obvious impact craters (holes with raised rims) were found on this surface. The variations in surface textures indicate that the grains of Itokawa asteroid experienced a complex history of fracturing and exposure to space-weathering processes on the surface of asteroid Itokawa.

5:20pm HI+AS+NS-ThA10 Multi-Beam Ion Microscopy and Nanofabrication at UC Berkeley, *Frances Allen*, UC Berkeley, Lawrence Berkeley National Laboratory (LBNL), Biomolecular Nanotechnology Center/QB3, *P. Lum*, Biomolecular Nanotechnology Center/QB3, *T.C. Pekin*, UC Berkeley and LBNL, *Z.J. Wang*, UC Berkeley and Xi'an Jiaotong University, Republic of China, *R. Thayer*, UC Berkeley, *J. Hong*, UC Berkeley and LBNL, *A.A. Omrani*, UC Berkeley, *M.F. Crommie*, *J. Bokor*, UC Berkeley and LBNL, *N.H. Patel*, UC Berkeley, *A.M. Minor*, UC Berkeley and LBNL, *P. Hosemann*, UC Berkeley

A Zeiss Orion NanoFab Helium Ion Microscope (HIM) has recently been installed at UC Berkeley in the Biomolecular Nanotechnology Center. The specialized gas-field ion source is operated using He or Ne gas and a separate column with a liquid-metal ion source is used to generate a Ga^+ beam. Thus, the advanced imaging and nanofabrication capabilities of the HIM using He^+ and Ne^+ can be combined with the bulk milling capability of Ga^+ enabling a range of imaging and nanofabrication modalities all in one tool.

We will present a selection of initial results from the microscope, highlighting the versatility of this multi-beam instrument and a close collaboration with Transmission Electron Microscopy (TEM) facilities at the National Center for Electron Microscopy in the Molecular Foundry of Lawrence Berkeley National Laboratory for the characterization of NanoFab-fabricated electron-transparent specimens. For example, using Ne^+ and Ga^+ beams and subsequent TEM analysis we explore the effect of Ne^+ milling versus conventional Ga^+ milling of TEM specimens focusing on aluminum alloys and their nanomechanical properties. We use the He^+ beam to selectively implant Ga^+-milled nanopillars for TEM investigation of He-bubble superlattices and *in situ* TEM nanomechanical testing for a range of implantation doses. Further applications combining fine milling with high-resolution HIM imaging include the fabrication of magnetic multilayer tunnel junction island structures down to a diameter of <10nm, fabrication of MoS_2 nanoribbons, and site-specific cross-sectioning of scales from the wing of the *Junonia coenia* butterfly species for investigations of the development of nanostructures responsible for structural color. In many

applications the use of the electron flood-gun for charge compensation when imaging insulating specimens is a crucial component.

Scanning Probe Microscopy Focus Topic
Room: 212A - Session SP+BI+NS+SS+TF-ThA

Probing Material Growth on the Surface
Moderator: Chuanxu Ma, Oak Ridge National Laboratory

2:20pm SP+BI+NS+SS+TF-ThA1 Tailoring the Growth of Organic Thin Films via Chemical Reactions at the Molecular Scale, *Pengpeng Zhang*, Michigan State University **INVITED**
Control of highly ordered organic molecular thin films with extended π systems is currently of intense interest for integrating molecules into modern electronics due to their tunable nature. Selection of molecules and substrates can lead to desired transport properties such as charge transfer, charge injection, exciton diffusion, etc., at the heterointerface, which is crucial to the development of organic and molecular electronics. However, achieving large-scale molecular ordering remains a significant challenge that requires a thorough understanding of the growth mechanism. I will discuss our recent discovery of the anisotropic crystalline step-flow growth of the prototypical metal phthalocyanine molecules on the deactivated Si(111)-B surface. I will then address the growth mechanism and show that the molecular ordering and molecular orientation can be effectively controlled through selective orbital coupling between the molecule and substrate. Finally, I will illustrate an abnormal temperature dependent growth evolution and discuss the associated mechanism.

This research is funded by the U.S. Department of Energy (DOE) Office of Science Early Career Research Program (DE-SC0006400) through the Office of Basic Energy Sciences.

3:00pm SP+BI+NS+SS+TF-ThA3 Investigation of Initial Stages of Oxidation of Ni-Cr and Ni-Cr-Mo alloys by Scanning Tunneling Microscopy and Spectroscopy, *Gopalakrishnan Ramalingam**, *P. Reinke*, University of Virginia
Ni-Cr alloys are excellent candidates for use in highly corrosive environments due to the formation of a protective Cr_2O_3 layer. Molybdenum is a common alloying addition as it improves the resistance to localized corrosion and prevents the breakdown of the oxide layer. While the effect of Mo addition on corrosion resistance is well known, the underlying mechanisms at the atomic scale and the role of electronic structure changes due to Mo addition are poorly understood. In the current work, we have used STM/STS to investigate the initial stages of oxidation of Ni, Cr and Ni-Cr (10-25wt.% Cr) alloy thin films and subsequently, the effect of Mo addition (2-10 wt.%) on the oxidation behavior. The alloy thin films are grown on MgO(001) substrates using two recipes that yielded smooth films: (a) deposition at 100 °C and subsequent anneal at 300 °C for 2 hours, and (b) deposition at 400 °C with no post-growth annealing. While recipe (a) yielded smooth Ni films, co-deposition of Ni and Cr resulted in the formation of secondary Ni_2Cr phases. Alloy films grown using recipe (b) did not result in secondary phases and are optimal for oxidation studies of alloy films. STM/STS data of the oxidation (30 L of O_2) of a pure Ni thin film at 200 °C reveal preferential oxidation of some terraces compared to others and indicates a dependence of oxidation rate on the crystallographic orientation of the terrace. dI/dV maps of a Cr surface after 10 L oxidation at 200 °C shows the presence of a bandgap (1.32 eV) throughout the surface and indicates the growth of a uniform oxide layer. In the case of Ni-13wt.%Cr binary alloy, a 25 L exposure (at $1x10^{-8}$ mbar) at 300 °C results in a complete loss of step structure with a fully formed oxide layer as shown by STS spectra. A bandgap of 1.42 eV is observed throughout the surface and this value is less than the bulk bandgap of all possible oxide species (NiO, Cr_2O_3 or mixed). We will present the results of the initial stages of oxidation (<3 L) of the pure Ni thin films and discuss the differences in the oxidation processes due to the addition of 8-25 wt.% Cr. The progression from chemisorption regime (at low temperatures) to the oxide nucleation regime will be shown for different alloys by performing room temperature O_2 exposures and post-exposure annealing cycles and the effect of alloying additions on this transition will be discussed. Preliminary data on the changes in the atomic and electronic structure of the thin film and oxidation behavior due to the addition of Mo will be presented.

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* Morton S. Traum Award Finalist

4:00pm SP+BI+NS+SS+TF-ThA6 Growth and Properties of Skyrmionic Nanowires and Thin Film, *Zheng Gai*, Oak Ridge National Laboratory, *J. Yi, S. Tang*, University of Tennessee, Oak Ridge National Laboratory, *D. Mandrus*, University of Tennessee **INVITED**
Magnetic skyrmion lattice, a vortex-like spin texture recently observed in chiral magnets, is of great interest to future spin-electronic data storage and other information technology applications. The combined effect of a large ferromagnetic exchange and a weak DM interaction is to twist the magnetization into a long-period spiral that can be tens to hundreds of nanometers in length. As these spirals are only weakly bound to the underlying lattice in cubic systems, they can be readily manipulated with modest applied fields. The skyrmion lattice in MnSi appears in a small region (known as the A phase) of the H-T phase diagram in bulk samples, but in 2D samples like thin films the skyrmion phase is much more robust. If skyrmion ordering can persist in one-dimensional MnSi nanowires and 2D films, then these systems are very promising for spintronics applications as the magnetic domains and individual skymions could be manipulated with small currents. We have systematically explored the synthesis of single crystal MnSi nanowires via controlled oxide-assisted chemical vapor deposition and observed a characteristic signature of skyrmion magnetic ordering in MnSi nanowires. The SiO_2 layer plays a key role for the high yield, correct stoichiometric and crystalline growth of the B20 MnSi nanowires. A growth phase diagram was constructed. For the thin films, an unique growth receipt was developed for the growth of high quality of thin films. The structure and magnetic properties of the films at different thickness were studied.

4:40pm SP+BI+NS+SS+TF-ThA8 Sulfur-induced Structural Motifs on Cu(111) and Au(111) Surfaces, *Holly Walen***, Iowa State University, *D.-J. Liu*, Ames Laboratory, *J. Oh, H. Lim*, RIKEN, Japan, *J.W. Evans*, Iowa State University, *C.M. Aikens*, Kansas State University, *Y. Kim*, RIKEN, Japan, *P.A. Thiel*, Iowa State University
The interaction of sulfur with copper and gold surfaces plays a fundamental role in important phenomena that include coarsening of surface nanostructures, and self-assembly of alkanethiols. Here, we identify and analyze unique sulfur-induced structural motifs observed on the (111) surfaces of these two metals. We choose very specific conditions: very low temperature (5 K), and very low sulfur coverage (≤ 0.05 monolayers, ML). In this region of temperature-coverage space, which has not been examined previously for these adsorbate-metal systems, the effects of individual interactions between metals and sulfur are most apparent and can be assessed extensively with the aid of theory and modeling. Furthermore, at this temperature diffusion is minimal and relatively-mobile species can be isolated. The primary technique is scanning tunneling microscopy (STM).

On Cu(111), at 0.004 ML S, we find unexpected heart-shaped Cu_2S_3 complexes on the terraces, made up of intersecting linear S-Cu-S units. With supporting density functional theory (DFT) and reaction-diffusion equation analysis, we propose that these hearts are a viable candidate for S-enhanced mass transport of Cu on Cu(111) at higher temperature. As S coverage increases (up to 0.05 ML), a diverse group of Cu-S structures develops which includes concatenated hearts, and eventually the known ($\sqrt{43}$ x $\sqrt{43}$)R±7.5° reconstruction[1-2]. Analysis of the step edges of Cu(111) indicates that S decorates the step edges preferentially (relative to the terraces) and that the complexes observed on terraces originate at the step edges.

In contrast, no metal-sulfur complexes are observed on Au(111) under similar conditions (0.03 ML). Instead, we observe striking $\sqrt{3}$R30° rows made up of S adatoms. Using DFT and *ab-initio* Monte Carlo analysis, we construct and test a lattice gas model. This analysis shows that these short rows of S adatoms form because of a complex set of through-metal interactions: a linear three-body attraction, as well as long-range pairwise interactions (up to 5a) between S atoms.

These experimental observations for Cu(111) and Au(111) surfaces—made under essentially-identical conditions—together with extensive DFT analyses, allow comparisons and insights into factors that favor the existence of metal-sulfur complexes, vs. chemisorbed atomic sulfur, on metal terraces.

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5:00pm SP+BI+NS+SS+TF-ThA9 Surface Strain-Modulated Binding of Adsorbates on TiO₂(110), *D.V. Potapenko, Richard Osgood, Jr.*, Columbia University
Mechanical elastic strain is commonly present in nanostructured materials and it has been found to change chemical and electronic properties in a broad range of solids. Systematic study of reactivity-strain relationship on

surfaces is difficult because of the fact that only very low values of strain (~0.1%) are achievable through mechanical deformation of macroscopic samples. We have developed a method of preparation of nano-scale strain fields on TiO_2 rutile(110) surface by low energy (1keV) Ar ion bombardments combined with specific thermal treatment. Titanium oxide is a brittle material regarded as a prototypical photocatalyst with numerous applications in the areas of solar energy utilization. Subsurface Ar clusters, which are formed through our preparation procedure, cause 5 – 25 nm wide surface deformations with the tensile strain values as high as 4 %. Surface distributions of various molecular and atomic adsorbates on TiO_2(110) have been studied with atomically resolved STM imaging. Our results indicate significant strain-related variations in the surface binding properties. In this presentation we will concentrate on surface hydroxyl groups (OH) as a mobile adsorbate. We derive the O-H binding energy from the statistical analysis of the adsorbate distribution. Then we demonstrate a roughly linear relationship between the values of surface strain and the O-H binding energy.

5:20pm SP+BI+NS+SS+TF-ThA10 STM/STS Investigation of Organic Charge Transfer Complex TTF-TCNQ on Noble Metal Surfaces at 4.3K, *Seokmin Jeon*, *P. Doak, P. Ganesh, B. Sumpter,* Oak Ridge National Laboratory, *J.I. Cerda,* Instituto de Ciencia de Materiales de Madrid, Spain, *P. Maksymovych*, Oak Ridge National Laboratory

TTF-TCNQ (TTF = tetrathiafulvalene; TCNQ = 7,7,8,8-tetracyanoquinodimethane) is a prototypical organic charge-transfer complex providing with a metallic conductivity (up to 900 ohm-1cm-1 at 300K). It also represents a broad class of organic electronic compounds that exhibit strong electron correlations and a rich gamut of phase transitions involving charge ordering, Mott and Peierls metal-insulator transitions and superconductivity, etc. Despite decades of research in this area, quantitative understanding of this compound is still elusive and their low-dimensional form is barely explored. We investigated ultrathin films of TTF-TCNQ on silver surfaces using scanning tunneling microscopy/spectroscopy (STM/STS) at 4.3 K. TTF-TCNQ forms self-assembled molecular lattices on noble metal surfaces with a few different TTF-to-TCNQ ratios depending on evaporation condition. Among them the islands with 1 to 1 stoichiometric ratio are found ubiquitously in less dependent on the evaporation condition. Structures of the monolayer islands are elucidated from sub-molecular resolution STM topography images. Single-point conductivity spectroscopy and conductivity mapping elucidate new electronic states which do not stem from their molecular orbital states are spatially located in the void areas of the TTF-TCNQ molecular lattices. We propose the *sp*-derived metal surface states are confined in the molecular lattices. Due to small periodicity of the lattice, the band minimum of the *sp*-derived metal surface states is shifted by as much as 1eV. This shift is much more significant than the ones normally observed in organic self-assemblies. As a result, we can also infer the height of the potential barrier within a 1D potential well model, which in turn is directly related to strong molecular dipole associated with large charge transfer and bent molecular geometry due to metal-molecule interactions.

Acknowledgement: A portion of this research (SJ, PD, PG, BS, PM) was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Thin Film
Room: 111 - Session TF+AS+NS+SA-ThA

Thin Film: Growth and Characterization, Optical and Synchrotron Characterization II
Moderator: Jay Hendricks, National Institute of Standards and Technology

2:20pm TF+AS+NS+SA-ThA1 Dynamic and Structural Stability of Cubic Vanadium Nitride, *Antonio Mei**, University of Illinois at Urbana-Champaign, *O. Hellman,* California Institute of Technology, *N. Wireklint,* Chalmers University of Technology, Sweden, *C.M. Schlepütz,* Argonne National Laboratory, *D.G. Sangiovanni, B. Alling,* Linköping University, Sweden, *A. Rockett,* University of Illinois at Urbana-Champaign, *L. Hultman,* Linköping University, Sweden, *I. Petrov, J.E. Greene,* University of Illinois at Urbana-Champaign

Structural phase transitions in epitaxial stoichiometric VN/MgO(011) thin films are investigated using temperature-dependent synchrotron x-ray diffraction (XRD), selected-area electron diffraction (SAED), and resistivity measurements combined with high-resolution cross-sectional transmission electron microscopy (HR-XTEM) and *ab-initio* molecular dynamics (AIMD). At room temperature, VN has the B1 NaCl structure. However, at temperatures below $T_c = 250$ K, XRD and SAED results reveal forbidden (00*l*) reflections of mixed parity associated with a non-centrosymmetric tetragonal structure. At $T \leq T_c$, forbidden reflections intensify continuously following the scaling behavior I α $(T_c - T)^{1/2}$. This suggests a transition of second-order character, but the incompatible symmetries of the parent cubic VN (space group) and product tetragonal VN () phases ultimately requires that the structural transition be first order. Resistivity $\rho(T)$ plots between 300 and 4 K consist of two linear regimes resulting from different electron/phonon coupling strengths in cubic and tetragonal VN.

The VN transport Eliashberg spectral function $\alpha^2_{tr}F(\hbar\omega)$, the product of the phonon density-of-states $F(\hbar\omega)$ and the transport electron/phonon coupling strength $\alpha^2_{tr}(\hbar\omega)$, is determined and used in combination with room-temperature inelastic neutron scattering results to establish that while entropy favors the higher-temperature cubic phase, as T is lowered below T_c, tetragonal VN becomes the thermodynamic ground state due to its lower enthalpy. AIMD renormalized phonon dispersion relations are in agreement, showing that the energy of (00*l*) X-point phonons in NaCl-structure VN decreases and eventually becomes imaginary at $T \leq 250$ K. We demonstrate that free energy contributions due to vibrational entropy, often-neglected in theoretical modeling, are essential in understanding the room-temperature stability of NaCl-structure VN, and of strongly anharmonic systems in general.

2:40pm TF+AS+NS+SA-ThA2 Comparison of Solution Based Aluminum Oxide Phosphate Thin Films Deposited via Spin Coating vs. a Novel Mist Deposition System, *Nishit Murari*, *R.H. Mansergh, Y. Huang, G. Westerfield, D. Keszler, J.F. Conley*, Oregon State University

Solution based spin coating techniques are well known for producing high quality organic as well as inorganic metal oxide thin films. However, spin coating is primarily suitable for planar substrates and lacks the ability to form uniform ultrathin films over large surface areas. In recent years, several alternative mist based deposition techniques have been introduced to enable solution based deposition over large areas and non-planar substrates. Mist deposition involves the creation of a precursor mist and its subsequent condensation on the substrate. Mist deposition techniques to date have been limited by disadvantages such as the requirement for highly volatile precursors and the non-homogeneous distribution of the mist, both of which lead to inferior film thickness uniformity. To address these limitations, we employ a new mist deposition system with a novel mist creation technique consisting of an atomizer with two opposing precursor jets. The unique opposing configuration of the atomizer enables the formation of a highly uniform mist even from low volatility precursors. In this work, we address the question of whether this new mist deposition technique can produce film quality comparable to spin coating technique.

Amorphous aluminum phosphate (AlPO) thin films were deposited via mist deposition using a BENEQ ACS 200-101 as well as standard spin coating. All films were deposited at room temperature and pressure using precursors based on aqueous suspensions of aluminum phosphate inorganic clusters. The inorganic ligands decompose at low temperature with minimal volume change presenting a route to high density films at low temperature. Both mist and spin coating achieve thickness uniformity of 5% across a 150 mm Si substrate. Both techniques result in ultra-smooth films with average surface roughness of less than 1 nm RMS. Variation in film density and roughness as a function of annealing temperature was identical for both techniques. Finally, similar charge transport behavior and dielectric constant were exhibited as a function of anneal temperature.

An aqueous precursor was used in a side by side comparison of spin coating and a novel mist deposition technique. High quality AlPO thin films of similar uniformity, density, roughness, and electrical properties were obtained using both techniques. Based on these results, this novel mist based deposition technique appears to be a promising candidate for the next generation of thin film deposition techniques for large area electronics.

3:00pm TF+AS+NS+SA-ThA3 Electro-Optic Studies of $Pb_{0.95}La_{0.05}Zr_{0.54}Ti_{0.46}O_3$ Thin Films Deposited by Chemical Solution Deposition Method, *Vaishali Batra*, *S. Kotru, V.N. Harshan*, The University of Alabama, *M. Varagas, C.V. Ramana*, University of Texas at El Paso

Lanthanum doped lead zirconate titanate (PLZT) of perovskite type crystalline structure is an interesting transparent ferroelectric material due to its large remnant polarization and electro-optic effects, near the morphotropic phase boundary. The excellent optical and electrical properties make it material of choice for applications in MEMS, optical modulators/transducers and smart sensors. Recent studies reveal that this material possesses great potential for use in future photovoltaic (PV) devices which involves combination of optical transparency and

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* TFD James Harper Award Finalist

ferroelectric properties. The advantage of using this material for PV applications is that the effect can be realized without a need of p-n junction as in semiconductor devices. Additionally the material exhibits bulk PV effect due to internal electric field originating from electric polarization. However, the optimization of processing conditions of deposited films is important to design efficient devices, which require understanding of the structure, its behavior with light, and response to electric field.

Lanthanum-modified lead zirconate titanate (PLZT) thin films with a composition of $(Pb_{0.95}La_{0.05})(Zr_{0.54}Ti_{0.46})O_3$ were deposited on $Pt/TiO_2/SiO_2/Si$ substrates. The films were rapidly annealed in the temperature range of 550 to 750 °C in oxygen ambient to study the effect of crystallization on the electric and optical properties. X-ray diffraction revealed that the post deposition temperature changes the preferential orientation of the films. Optical band gap values determined from UV-visible spectroscopy and spectroscopic ellipsometry for PLZT films were found to be in the range of 3.42-4.00 eV. The optical constants and their dispersion profiles for PLZT films were also determined from SE analyses. PLZT films exhibit an index of refraction ~2.5 (λ=630 nm). The electrical properties were studied using the model for metal-ferroelectric-metal (MFM) heterostructures with Schottky contacts using Au electrodes. High remnant polarization (41.85 $\mu C/cm^2$), low coercive voltage (1.19 V) and high free carrier concentration (~1.1×10^{18} cm^{-3}) were obtained from films annealed at 750 °C. Thus post deposition annealing temperature plays a major role in deciding the electrical and optical properties.

3:20pm TF+AS+NS+SA-ThA4 Electron Scattering at Surfaces of Expitaxial Metal Layers, *Pengyuan Zheng, D. Gall*, Rensselaer Polytechnic Institute

Epitaxial Cu(001) is grown on MgO(001) with different overlayers to demonstrate that electron surface/interface scattering can be engineered by surface doping, causing a decrease in the resistivity. For instance, the resistivity of 9.3-nm-thick epitaxial and polycrystalline Cu layers is reduced by 11-13% when coated with 0.75 nm Ni. This is due to partially specular surface scattering with specularity parameters $p = 0.3$ and 0.15 for the Ni-coated Cu in vacuum and air, respectively, while scattering is completely diffuse ($p = 0$) for a pure Cu surface in air. This is attributed to the suppression of Cu_2O formation, leading to a lower localized density of states (LDOS) at the surface, and therefore less diffuse electron scattering. The change of surface scattering by controlling the LDOS is further confirmed: the sheet resistance of 9.5-nm-thick epitaxial Cu(001) increases by 4-43% if a 0.1-4 monolayer thick Ti coating is added, but subsequent exposure to 37 Pa of O_2 causes a resistivity reduction of 3-24%. This reduction is due to a recovery of specular interface scattering associated with a reduction of the LDOS during Ti oxidation from 15-27.4 to 2.4-6.5 eV^{-1}nm^{-2}, as quantified by ab initio calculations. Furthermore the surface scattering effect is found to be orientation dependent. For example, the resistivity of 5-nm-thick epitaxial tungsten layers is two times higher for 001 vs 110 orientated layers. This is due to the anisotropy in the Fermi surface, as indicated by transport simulations based on first-principles band structure calculations, which suggest a 1.5 times smaller size effect for the 110 orientation. These epitaxial films were sputter deposited onto Al2O3(11-20) and MgO(001) at 1050 °C and 900 °C, respectively, followed by in situ annealing at 1050 °C for 2 hrs. X-ray diffraction θ-2θ, ω, and φ-scans confirm epitaxy and X-ray reflectivity indicates atomically smooth film-substrate interfaces and smooth film surfaces with a root-mean-square roughness that increases from 0.32±0.05 to 0.81±0.05 nm for W(110) with t = 5.7-39.2 nm, and from 0.21±0.05 to 0.40±0.05 nm for W(001) with t = 4.8-50 nm. In summary, we have systematically shown that (1) surface scattering can be altered by carefully controlling the surface LDOS at the Cu surface or interface with the barrier and (2) the crystalline orientation of interconnect wireswith non-spherical Fermi surfaces is a major factor when considering alterative metals to replace Cu interconnects.

4:00pm TF+AS+NS+SA-ThA6 Lattice Relaxation in Multilayered Si₁₋ₓGeₓ/Si (001) Metamorphic Heterostructures, *Tedi Kujofsa, J.E. Ayers*, University of Connecticut

The inclusion of compositionally-graded metamorphic buffer layers in multilayered heterostructures allows tremendous flexibility designing novel SiGe/Si microelectronic and optical semiconductor devices. For example, advanced CMOS transistors can be fabricated on strain relaxed buffers to obtain enhanced mobility in n-channel and p-channel devices using tensile and compressive strain, respectively. While it is necessary to control the strain in the device layers, it is also desirable to fabricate these structures with low threading dislocation densities and minimum buffer thickness. Thus, understanding lattice relaxation in multilayered and compositionally-graded heterostructures is desirable to provide guidance in designing SiGe/Si devices. This work focuses on the design of the multilayered heterostructures comprising a uniform layer of $Si_{1-x}Ge_x$ (device layer) deposited on a Si (001) substrate with an intermediate compositionally-graded buffer layer of $Si_{1-x}Ge_x$. The objective of this work is to study the

relaxation dynamics and misfit dislocations in the device and buffer layer. We present minimum energy calculations and show that for a given device layer with fixed germanium composition and layer thickness, there exists a combination of the buffer layer thickness and compositional grading to provide tight control of the strain in the device layer. Furthermore, we give a simple model describing the strain in the device layer.

4:40pm TF+AS+NS+SA-ThA8 Growth Stress Evolution in Low Adatom Mobility Fe(Cr) Thin Films, *Xuyang Zhou*, The University of Alabama, *T. Kaub, R.L. Martens*, The Univeristy of Alabama, *G.B. Thompson*, The University of Alabama

During the post coalescence portion of thin film deposition, thin film stress is related to the grain size and adatom mobility of the depositing material. This stress state can be regulated by the mobility of atoms into or out of these grain boundaries. Using Fe(Cr) alloy thin films as a case study, the stress evolution during growth was investigated as a function of Cr content up to 8 at.%. During the deposition of the elemental films, each film grew with a tensile stress state on a Si wafer because of their low adatom mobility. Upon alloying 4 at.% Cr to the Fe film, the as-deposited grains grew from ~40 nm (pure Fe) to ~65 nm (Fe-04Cr), resulting in a stress relaxation from ~200 GPa*nm to 50 GPa*nm at a thickness of 300 nm. As the Cr content increased further, the grains refined back towards ~ 50 nm in size resulting in a recovery of the higher tensile stress condition. The reduction of the grain size is contributed to Cr solute segregation to the grain boundaries, clustering, and ultimately precipitation at the boundaries. The real-time stress evolution during growth will be discussed in terms of the inferred microstructural evolution of the film using post-mortem atom probe tomography and transmission electron microscopy characterization. The results of which address how segregating behavior can be used as a means of thin film stress engineering.

5:00pm TF+AS+NS+SA-ThA9 Development of an Analytical Model for Langmuir-Blodgett Silica Microsphere Assembly and Investigation of Ge Back Filling of the Opal Template by Polymer-Assisted Deposition, *Sarun Atiganyanun, M. Zhou, S.E. Han, S.M. Han*, University of New Mexico

Self-assembled photonic crystals find a wide variety of applications, including low-loss waveguides, high-efficiency solar cells, and thermal emission control. Here, we investigate a low-cost scalable fabrication of an opal structure via self-assembly of colloidal silica microspheres and propose a model describing a relationship between assembly parameters. To fabricate an opal structure, silica microspheres with a diameter of ~900 nm are first functionalized with allyltrimethoxysilane. Langmuir-Blodgett (LB) method is then used to self-assemble silica microspheres onto Si(100) substrates. By optimally adjusting the pulling speed of the substrate and surface pressure within the trough, a hexagonally closed-packed structure is achieved. By repeating LB coating processes for *n* number of times, an *n*-multilayer assembly is formed, creating an opal template structure. Scanning electron microscopy and light diffraction experiment are used to identify assembly parameters that give the largest domain size. An analytical model is also derived from material flux balance and a 2D van der Waals equation of state of silica spheres on water surface to describe the relationship between pulling speed, surface pressure, barrier speed, number of layers, and sphere's diameter for optimal assembly. In this presentation, we will also discuss a facile approach to back-fill opal templates via polymer-assisted deposition of Ge. After forming the template structure, a solution of polyethylenimine, ethylenediaminetetraacetic acid and germanium dioxide is used to back-fill the voids between microspheres. The sample is then annealed in a forming gas environment, forming Ge films around the microspheres. After the microspheres are removed, the Ge structure is characterized with SEM, XRD, and light transmission.

5:20pm TF+AS+NS+SA-ThA10 The Determination of Porosity and Pore Size Distribution of The Al₂O₃ Antireflection Coating Deposited By Atomic Layer Deposition, *Chao Li, M. Goorsky*, University of California at Los Angeles

The porosity and pore size distribution of coatings prepared by atomic layer deposition and by other deposition techniques is important to understand their optical and mechanical properties. Specular X-ray reflectivity (SXRR) is capable of extracting layer thickness with angstrom resolution as well as determining the layer density. This makes it a good candidate for the porosity characterization of the antireflection coatings. On the other hand, advances in the development of X-ray generators and optics have made in-house glancing incidence small angle X-ray scattering (GISAXS) experimentation suitable for thedetermination of the size and shape of pores (in the scale of sub-nanometer to 100 nm) existing in thin films. It can be realized through the simulation of pore scattering based on distorted wave Born approximation (DWBA). Unfortunately, previous GISAXS studies failed to exclude the scattering from the rough surface and interfaces of thin films from the total scattering that was used for the simulation. In this study,

we propose a refined GISAXS method characterizing the pore size distribution with the scattering from the rough surface and interfaces excluded. The scattering from the surface and interfaces was determined by the simulation of X-ray reflectivity (XRR) longitudinal scan with the parameters of the surface roughness σ, the lateral correlation length ξ and the Hurst parameter h extracted from the atomic force microscopy measurement, and layer thicknesses, densities and compositional grading determined by the specular XRR simulation. This refined GISAXS method, together the SXRR technique, was applied to utilized to reveal the effect of deposition techniques on the nanostructures of single-layer Al_2O_3 -based antireflection coatings. They were deposited using atomic layer deposition (ALD) which is a good candidate for multilayer antireflection coatings, due to the self-limiting nature of chemical reactions resulting in the precise control of film thickness and large-area uniformity. Each of them has two amorphous structures on a Si substrate grown with different deposition parameters. It is indicated by the refined GISAXS method that the first Al_2O_3 single layer is porous with a mean pore (spherical shape) radius of 7.2 nm while there are no pores in the second Al_2O_3 single layer. This agrees well with the SXRR showing a lower density of the first Al_2O_3 single layer (2.93 g/cm^3) than that of the second Al_2O_3 single layer (3.04 g/cm^3).

5:40pm TF+AS+NS+SA-ThA11 Tuning Static and Dynamic Magnetic Properties of FeGa/NiFe Multilayer Composites, *Colin Rementer, Q. Xu, K. Fitzell, Z. Yao, P. Nordeen, G. Carman, Y. Wang, J.P. Chang*, University of California at Los Angeles
Traditionally, the use of magnetic materials in high frequency applications has been limited to oxides. This is because the materials' high resistivity, which reduces the formation of eddy currents by the incident electromagnetic waves. However, these oxides have limited applications in multiferroics, which are materials that possess more than one ferroic ordering in a single phase or strain-coupled composite systems, due to their low magnetomechanical coupling. Metallic materials are more desirable to this end, but their magnetic hardness and conductive losses have limited their use.

Rare-earth-free iron-gallium (FeGa) is one of the most promising magnetostrictive materials for use in composite multiferroics, due to its high piezomagnetic coefficient (3 ppm/Oe) and high stiffness (70 GPa). It has been integrated into several multiferroic systems, but generally in the MHz range or below[1]. This is due to the fact that the material has a large ferromagnetic resonance (FMR) linewidth (>300 Oe) at *X* band (9.6 GHz), which will result in incident energy being converted to heat. Metalloid dopants have been used to soften magnetic materials and to tune frequency dependent properties, such as permeability and piezomagnetic behavior, but at the cost of saturation magnetization as well as magnetostriction[2]. In this work, multilayer laminates containing alternating hard and soft ferromagnetic layers were fabricated to reduce loss at high frequencies.

FeGa (hard) and NiFe (soft) were sputtered via alloy targets into multilayers on Si [100] and piezoelectric substrates with total thicknesses ranging from 40-500 nm. The compositions of the films were verified via X-ray photoelectron spectroscopy (XPS) and were found to be Fe_yGa_{1-y} (78≤y≤85 at%) and Ni_xFe_{1-x} (79≤x≤83 at%). Static magnetic properties were evaluated via superconducting quantum interference device (SQUID) magnetometry, and it was found that the incorporation of NiFe layers was found to reduce the coercivity by up to 80%, while only reducing the saturation magnetization by 20%. FMR measurements revealed a narrowing of the linewidth by up to 90% at *X* band. Permeability extracted from the reflection coefficient (S11) obtained via stripline measurement was found to be affected by layer thickness and number of layers. FeGa showed strong magnetoelastic behavior and the multilayers are expected to exhibit an enhanced piezomagnetic effect due their reduced coercivity.

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Tribology Focus Topic
Room: 230B - Session TR+AS+NS+SS-ThA

Molecular Origins of Friction
Moderator: Nicolas Argibay, Sandia National Laboratories

2:20pm TR+AS+NS+SS-ThA1 Atomic-Scale Mechanisms of Single Asperity Sliding, *Ashlie Martini, X. Hu,* University of California Merced, *M.V.P. Altoe*, Lawrence Berkeley National Laboratory   **INVITED**
Isolating a single asperity to characterize its response to sliding is a heuristic approach to understanding the fundamental mechanisms that underlie friction and wear. A single asperity can be realized experimentally as the tip of an atomic force microscope cantilever. When the tip slides across a surface, friction is measured with atomic lattice-scale resolution and wear can be quantified in terms of nano- or even atom-scale volumes of material removed. However, challenges remain in interpreting these measurements because the observed friction and wear are due to processes that take place in the interface buried between the tip and the substrate on which it slides. Further, the nanometer scale of the contact implies that discrete atomic events in the interface may determine sliding behavior. Together, these observations suggest that the experiments could be complemented by atomistic models of the apex of the tip, near-contact substrate material and, of course, the interface itself. Although the simulations are limited to relatively small size and time scales, they have the potential to provide detailed information about mechanisms underlying phenomena that occur over short periods of time and small sliding distances. Specifically, in this research, we focus on the initial stages of friction and wear, and the processes that occur during the first tens of nanometers of sliding. The simulations are carefully designed such that they faithfully capture the corresponding experiments, including matching the materials, crystallography and geometry of the contacting bodies as observed through transmission electron microscope images of the tip and atomic force microscope images of the substrate taken at 10 nm intervals during the sliding process. The experiments offer an unprecedented view of wear occurring single atomic layers at a time, and the simulations provide detailed complementary information about the atomic-scale mechanisms underlying this process.

3:00pm TR+AS+NS+SS-ThA3 Investigation of Epitaxy and Friction in Model Boundary Films, *Hongyu Gao,* University of California Merced, *W.T. Tysoe,* University of Wisconsin-Milwaukee, *A. Martini*, University of California Merced
Sliding friction of boundary films is investigated using ultrahigh vacuum (UHV) tribometer measurements of model alkali halide films on metals with complementary molecular dynamics (MD) simulations. We focus on a model system consisting of thin potassium chloride (KCl) films on an iron (Fe) substrate. The interaction potential between KCl and Fe is tuned using activation energy obtained from temperature programmed desorption (TPD) data and structures inferred from low-energy electron diffraction (LEED) measurements. The simulation is then used to explore the effect of film thickness and pressure on the formation of an epitaxial KCl film. The nature of this film and its near surface structure is then correlated with sliding friction behavior.

3:20pm TR+AS+NS+SS-ThA4 Temperature Dependence of Atomic-scale Friction on Two-dimensional Materials, *Zhijiang Ye,* University of California Merced, *X.Z. Liu, K. Hasz, R.W. Carpick,* University of Pennsylvania, *A. Martini*, University of California Merced
Temperature plays an essential, yet complex role in determining atomic-scale friction. Recent studies of the temperature dependence of atomic-scale friction have reported different trends that suggest distinct and possibly contradictory underlying mechanisms. Specifically, friction is usually found to decrease with increasing temperature (due to thermolubricity), but this behavior is not always observed (attributed to adsorbates or meniscus effects). To understand the origins of these trends, we use molecular dynamics (MD) simulations and parallel replica dynamics (PRD) to study the temperature dependence of atomic friction on two-dimensional (2-D) materials, such as molybdenum disulfide. The MD simulations are designed to be closely-matched with corresponding atomic force microscope (AFM) measurements [1, 2]. Using the simulations and experiments, we explore how friction varies with temperature and how that variation is affected by other parameters, including sliding velocity, material, and environment. These studies provide new insights into how temperature affects friction on 2-D materials, and into the origins of atomic-scale friction generally.

References:

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4:20pm TR+AS+NS+SS-ThA7 Single Molecule Experiments to Explore Friction and Adhesion, *Rémy Pawlak, S. Kawai, A. Baratoff, T. Meier,* University of Basel, Switzerland*, W. Ouyang,* Tsinghua University, China*, T. Glatzel,* University of Basel, Switzerland*, E. Gnecco,* IMDEA-Nanociencia - Universidad Autónoma de Madrid, Spain*, A. Filippov,* Donetsk Institute of Physics and Engineering, Ukraine*, M. Urbakh,* Tel Aviv University, Israel*, E. Meyer,* University of Basel, Switzerland **INVITED**

Controlled manipulation processes of single-molecules with an atomic force microscope (AFM) provide valuable information about their interactions with surfaces, leading to fundamental insights into adhesion and friction properties. To understand such phenomena at such scale, tuning-fork based AFM operated at low temperature is an appropriate tool since complex manipulations of single-molecules can be readily performed and detected via advanced force spectroscopic techniques [1] . With such approach however, the measured frequency shifts are related to normal force gradients, and thus the interpretation of friction phenomena is not fully straightforward. To overcome this issue, we developed analytical models to simulate the experimental AFM data which allow us to determine adhesive energy and nanoscale friction. In this presentation, a first example will be given by the vertical pulling of long polymeric chains on Au(111), where their detachment leads to oscillations of the normal and lateral forces [2] . As in Frenkel-Kontorova (FK) models of friction, the polymer is represented by a chain of units connected by springs of stiffness k , each one interacting with a 2D periodic substrate potential. Force and gradient variations are dominated by the sequential detachment of each molecular units if k i s large enough to cause superlubric sliding. A second example will show vertical and lateral manipulations over a Cu(111) surface of a single porphyrin molecule attached to the AFM tip apex. In the frequency shift traces, atomic sawtooth modulations are systematically observed while sliding over the surface and are related to the internal degree of freedom of the molecular structure [3] .

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5:00pm TR+AS+NS+SS-ThA9 Effects of Humidity on the Adhesion and Friction of Carbon-Based Materials, *Judith Harrison, M. Fallet, K.E. Ryan,* United States Naval Academy*, T. Knippenberg,* High Point University*, S.H. Kim, A. Al-Azizi*, Pennsylvania State University

Atomic-scale wear in nanoscale contacts is of particular importance for tip-based nanomanufacturing applications. As a result, wear resistant materials, such as diamond-like carbon (DLC), have been used to coat AFM tips to improve the lifespan and reliability of AFM probes and surfaces. Unfortunately, the tribological performance of these materials is known to depend on environmental conditions, such as humidity levels. We have performed macroscopic and atomic force microscopy friction experiments and molecular dynamics (MD) simulations aimed at examining adhesion and wear of DLC in humid environments.

Macro-scale friction tests showed friction and transfer film dependence on humid conditions. Low humidity suppresses transfer film formation while keeping the friction low. Intermediate humidity, however, does not reduce transfer film formation and increases the friction. The effect of humidity on friction was found to agree with the adhesion dependence on relative humidity as measured with atomic force microscopy.

Because it is difficult to elucidate atomic-scale mechanisms via experimental methods, molecular dynamics simulations have been employed to examine this behavior. Adhesion and sliding simulations of non-hydrogenated, ultrananocrystalline diamond (UNCD) and DLC surfaces with various levels of hydrogen in the presence of water using the qAIREBO and the ReaxFF potentials have been performed. Because both of these potentials are able to model chemical reactions, the atomic-scale mechanisms responsible for adhesion and wear can be identified. Results obtained with both potentials will be compared to the experimental results.

5:20pm TR+AS+NS+SS-ThA10 Single Asperity Tribochemical Wear of Silicon AFM Tips Sliding on Aluminum Oxide, *Erin Flater, S. Sorenson,* Luther College*, N. Ansari, A. Poda, W.R. Ashurst,* Auburn University*, B.P. Borovsky*, St. Olaf College

Understanding of tribological mechanisms at the submillimeter scale continues to be relevant since friction and wear limit the commercial viability of small-scale mechanical devices such as microelectromechanical systems (MEMS). For example, tribochemical processes play a significant role in many materials systems, including silicon oxide and aluminum oxide, which are relevant materials for MEMS devices. Our work focuses on understanding tribological processes at the interface of silicon AFM tips and amorphous aluminum oxide surfaces. We observe wear of silicon tips after repetitive sliding on the aluminum oxide surface, which occurs even at low contact pressures, implying that the wear process is chemical in nature. We quantify tip wear by intermittently interrupting the wear experiment to perform indirect *in-situ* tip imaging on a sharp-spiked sample. We use these tip images to quantify volume of material lost during scanning. Wear as a function of sliding distance is modeled using reaction rate theory and is compared to the Archard wear model. While some of our results appear to agree with an Archard model, these results may be more appropriately interpreted in light of the more fundamental reaction rate theory.

5:40pm TR+AS+NS+SS-ThA11 Molecular Simulation of Indentation as a Probe of Scanning Probe Tip Mechanical Properties, *J. David Schall, K. Vummaneni,* Oakland University*, J.A. Harrison,* United States Naval Academy

Scanning probe tips should be robust, have low adhesion, and low wear to ensure repeatability and long tip life. As new tip materials are developed these properties must be quantified and compared to existing tip materials. In this study, molecular simulation is used to measure the elastic modulus and work of adhesion of a variety of tips against a common substrate material, in this case H-terminated diamond (111). The tip materials investigated include Si, SiC, amorphous SiC, diamond, diamond like carbon and ultra-nanocrystalline diamond (UNCD). SiC was recently proposed as a new high hardness, low wear tip material. In simulation the tip geometry can be controlled to enable direct comparisons between each tip material. Both dynamic simulations at 300K and quasi-static indentions using stepwise energy minimization with and with out adhesion between tip and substrate were used. Simulations of sliding friction and wear have also been conducted to investigate the correlation between tip materials properties and friction and wear.

Friday Morning, October 23, 2015

2D Materials Focus Topic
Room: 212C - Session 2D+EM+IS+NS+PS+SP+SS-FrM

Surface Chemistry of 2D Materials: Functionalization, Membranes, Sensors

Moderator: Peter Sutter, University of Nebraska - Lincoln, Judy Cha, Yale University

8:20am 2D+EM+IS+NS+PS+SP+SS-FrM1 Chemically Modifying Graphene for Surface Functionality, *Paul Sheehan, S. Tsoi, S.C. Hernández, S.G. Walton, T.L. Reinecke, K.E. Whitener, J.T. Robinson*, Naval Research Laboratory, *R. Stine*, Nova Research
Graphene has many superlative properties that may be tailored for specific applications, or even enhanced, through chemical functionalization. Chemical functionalization dramatically changes almost every critical property of graphene, changing it from opaque to transparent, from diamagnetic to ferromagnetic, from electron rich or electron poor, from electrically conducting to insulating (and back again!). This extensive control suggests that chemically modified graphene may aid applications from flexible sensors to surface engineering. I will discuss how stacks of 2D materials can control the dominant surface forces—van der Waals,[1] acid-base interactions, electrostatic interactions, etc.—and so surpass conventional methods of preparing surfaces with, for example, self-assembled monolayers. I will also briefly address goals as diverse as biosensing[2] or sloughing off chemical warfare agents.[3]

[1] ACS Nano, **2014**, *8* (12), pp 12410–12417

[2] BioTechniques, Vol. 57, No. 1, July 2014, pp. 21–30

[3] ACS Nano. 2013 Jun 25;7(6):4746-55.

8:40am 2D+EM+IS+NS+PS+SP+SS-FrM2 Structural Phase Stability Control of Monolayer MoTe$_2$ with Adsorbed Atoms and Molecules, *Yao Zhou, E.J. Reed*, Stanford University
Of the Mo- and W- dichalcogenide monolayers, MoTe$_2$ is particularly interesting because it exhibits a small energy difference (approximately 31 meV per MoTe$_2$) between its semiconducting 2H phase and metallic 1T' crystal structures. This feature makes it particularly interesting for potential phase change applications.

We study the adsorption of some common atoms and molecules onto monolayer MoTe$_2$ and the potential for adsorption to induce a phase change between the semiconducting 2H and metallic 1T' crystal structures of the monolayer. Using density functional theory with spin orbit and van der Waals energy contributions, we determined the most energetically favorable adsorption positions and orientations on the two phases of monolayer MoTe$_2$. We then obtained the formation energies for these adsorption reactions and found that atomic adsorption generally favors 1T' metallic phases while molecular adsorption favors semiconducting 2H phases. A possible application of this work may be the chemical stabilization of a preferred phase during the growth process.

Further, we consider the Mo$_x$W$_{1-x}$Te$_2$ alloy monolayers that exhibit even smaller energy difference between phases. Our calculations indicate that it may be possible to engineer an alloy (0<x<0.5) such that specific molecules will induce a phase change to 1T' while other molecules studied stabilize the 2H phase, which suggests that alloying may provide some molecular selectivity. This potentially provides the basis for molecular sensing applications due to the large electronic contrast between 2H and 1T' phases.

9:00am 2D+EM+IS+NS+PS+SP+SS-FrM3 Selective Nanochemistry on Graphene/Silicon Carbide: Substrate Functionalization and Polycyclic Aromatic Hydrocarbons Formation, *Patrick Soukiassian*, CEA, France **INVITED**
Graphene & silicon carbide (SiC) are advanced semiconductors having figures of merit scaling well above those of well-established ones [1,2]. Understanding/mediating SiC and graphene surfaces & interfaces properties are of central importance toward functionalization and applications. As a 2D material, graphene is a single atomic layer of carbon atoms in a *sp2* bonding configuration. Therefore, functionalization remains challenging since interacting too strongly with the graphene atomic layer may change its bonding configuration and properties. Instead, interacting with the SiC substrate offers an alternative approach. The 1st case of hydrogen-induced metallization of a semiconductor surface has been shown for a 3C-SiC(001) surface [3]. Here, combining investigations using advanced experimental techniques such as STM/STS, vibrational & 3rd generation synchrotron radiation-based photoelectron spectroscopies together with state-of-art

calculations will be presented and discussed. It includes: i) the 1st evidence of H/D-induced nanotunnel opening at a semiconductor sub-surface shown here for SiC [4]. Depending on H coverage, these nanotunnels could either be metallic or semiconducting. Dangling bonds generated inside the nanotunnels offer a promising template to capture atoms or molecules. These features open nano-tailoring capabilities towards advanced applications in electronics, chemistry, storage, sensors or biotechnology. Understanding & controlling such a mechanism open routes towards selective surface/interface functionalization of epitaxial graphene [4]. ii) The role of H interaction with graphene on SiC dust grains in polycyclic aromatic hydrocarbons (PAH) formation in the interstellar space with a possible route toward prebiotic roots of life in the universe [5].

1–W. Lu, P. Soukiassian, J. Boeckl "*Graphene: fundamentals and functionalities*" **MRS Bull. 37**, 1119 (2012)

2–P. Soukiassian "*Will graphene be the material of the 21th century?*" **MRS Bull. 37**, 1321 (2012)

3-V. Derycke, P. Soukiassian, F. Amy, Y.J Chabal, M. D'angelo, H. Enriquez, M. Silly, "*Nanochemistry at the atomic scale revealed in hydrogen-induced semiconductor surface metallization*", **Nature Mat.2**, 253 (2003)

4–P. Soukiassian, E. Wimmer, E. Celasco, Cl. Giallombardo, S. Bonanni, L. Vattuone, L. Savio, A. Tejeda, M. Silly, M. D'angelo, F. Sirotti, M. Rocca "*Hydrogen-induced nanotunnel opening within semiconductor subsurface*" **Nature Com. 4**, 2800 (2013)

5–P. Merino, M. Švec, J.I. Martinez, P. Jelinek, P. Lacovig, M. Dalmiglio, S. Lizzit, P. Soukiassian, J. Cernicharo, J.A. Martin-Gago "*Graphene etching on SiC grains as a path to interstellar PAHs' formation*" **Nature Com. 5**, 3054 (2014)

9:40am 2D+EM+IS+NS+PS+SP+SS-FrM5 Intrinsic Wettability of Graphene, *Haitao Liu*, Department of Chemistry, University of Pittsburgh
Graphene and graphite are long believed to be hydrophobic. Here we show that a clean graphitic surface is in fact mildly hydrophilic [1]. We find that an as-prepared graphene sample is hydrophilic with a water contact angle of ca. 40°. Upon exposure to ambient air, the water contact angle gradually increased to ca. 60° within 20 min and plateaued at ca. 80° after 1 day. Infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) showed that airborne hydrocarbon adsorbed onto the graphene surface during this process. Both thermal annealing and controlled UV/O$_3$ treatment removed the hydrocarbon contaminants, which was accompanied by a concurrent decrease in the water contact angle. Our findings show that graphene is more hydrophilic than previously believed and suggest that the reported hydrophobic nature of graphene is due to unintentional hydrocarbon contamination from ambient air.

Reference

[1] Zhiting Li; et al.; Nature Materials, 12, 925-931, (2013)

10:00am 2D+EM+IS+NS+PS+SP+SS-FrM6 Au-doped Graphene As a Promising Electrocatalyst for the Oxygen Reduction Reaction in Hydrogen Fuel Cells: Prediction from First Principles, *Sergey Stolbov*, University of Central Florida, *M. Alcantara Ortigoza*, Tuskegee University
One of the main obstacles hindering large scale practical application of hydrogen fuel cells is a prohibited cost of the Pt (or Pt-based) catalysts for the oxygen reduction reaction (ORR) on the fuel cell cathode. In this work, we consider Au-doped graphene as an alternative to Pt for facilitating ORR. Our first-principles calculations show that Au atoms incorporated into graphene di-vacancies form a thermodynamically and electrochemically stable structure. Furthermore, calculation of the binding energies of the ORR intermediates reveals that Au-C bonding makes the C atoms neighboring to Au optimally reactive for ORR. The calculated ORR free energy diagrams suggest that the Au-graphene structures have an ORR onset potential as high as that of Pt. We also demonstrate that the linear relation among the binding energy of the reaction intermediates assumed in a number of works on computational high-throughput material screening does not hold, at least for this none purely transition-metal material.

10:20am 2D+EM+IS+NS+PS+SP+SS-FrM7 Spontaneous Deposition of Palladium Nanoparticles on Graphene through Redox Reaction, *Xiaorui Zhang, W. Ooki, Y.R. Kosaka, T. Kondo, J. Nakamura*, University of Tsukuba, Japan
Due to its unique properties such as huge surface area and excellent conductivity, graphene becomes great interesting for supporting noble metal catalysts. Some noble metals such as palladium, platinum, gold nanoparticles was reported to be able to spontaneous deposition on as-synthesized reduced graphene oxide with external reducing agent-free

recently. Yet the mechanism of spontaneous deposition of metals on graphene has not been clarified until now. In the present research, we spontaneously deposited palladium nanoparticles on as-synthesized reduced graphene oxide in H_2O medium without external reducing agent. It was found that the deposited amount of palladium varied with pH, meanwhile, the bivalent Pd^{2+} precursor was reduced to metallic palladium, and graphene was oxidized simultaneously with an increasing of its oxygen functional groups. The atomic ratio of the deposited Pd and the increased O in rGO located in a range from 1 to 2. As reducing agent-free, the mechanism on spontaneous redox deposition of metal nanoparticles on graphene was proposed, firstly, an efficient adsorption of metal precursor on graphene is a prerequisite which is determined by their electrical charges and adjusted by pH. Secondly, a positive galvanic potential between metal precursor and graphene is necessary for metal spontaneous deposition.

10:40am **2D+EM+IS+NS+PS+SP+SS-FrM8 Gradient Electrochemical Response of Template Synthesized Thickness Sorted MoS₂ Nanosheets for Cellular Level Free Radical Detection**, *Ankur Gupta*, *T. Selvan*, *S. Das*, *S. Seal*, University of Central Florida

The human body is a complex system capable of defending in adverse conditions. A classic example of such complex process is balanced equilibrium production between pro-oxidant and antioxidant in cells. However, when this equilibrium is disturbed, production of free radicals such as superoxide and nitric oxide strengthen, and causes serious cellular damages. Furthermore, myeloperoxidase (MPO) is released during the oxidative burst. This MPO combines with hydrogen peroxide (H_2O_2) and Cl^- and generate hypochlorous acid (HOCl). This is a short-lived and powerful diffusible oxidant strong oxidizer and could react with O^{2-} to produce OH^-. Therefore, in physiological condition HOCl has a major role as a potent microbicidal agent in the immune defense; however, during the oxidative burst HOCl not only damage healthy tissue and generate radicals that are extremely reactive. Therefore, monitoring of the production of free radicals at the cellular level is important for diagnostic purpose. Over past years, several material have been used to develop sensors for free radical detection such as cerium oxide nanoparticles, MoS₂ nanosheets and nanoparticles. However, detection of free radicals at cellular level is still a challenge.

In this attempt, layered molybdenum disulfide (MoS₂) were synthesized via hydrothermal method. SBA-15 polymer template were utilized during hydrothermal process to grow MoS₂ around it to develop porosity. After the hydrothermal synthesis and washing, polymer template was removed by dissolving it in isopropanol which leaves high surface area layered MoS₂ crystal. Wet chemical exfoliation of MoS₂ were carried out in aqueous solution of Pluronic° F-127 having hydrophobic and hydrophilic chains. Pluronic° F-127 was used to bring down the buoyant density of MoS₂. Non-templated nanosheets were synthesized as control. The exfoliated solution were centrifuged at 3000 rpm to remove large particle and supernatant was collected for density gradient ultracentrifugation (DGU). Separation of different thickness layers is carried out by DGU. Thickness sort MoS2 nanosheets were characterized using AFM, XPS, HRTEM, Raman and UV-Vis spectroscopy for structural and chemical analysis. XPS, HETEM and EFTEM analysis of nanosheets have illustrate the sulfur deficiency at the edges of the nanosheets. MoS2 nanosheets were deposited on glassy carbon electrode for cyclic-voltammetry and chronoamperometry measurements. Higher sensitivity and repeatability were demonstrated by nanosheets prepared via template method as compared to control for reactive oxygen and nitrogen species, and HOCl.

11:00am **2D+EM+IS+NS+PS+SP+SS-FrM9 Methanol Synthesis on Defect-Laden Single-Layer MoS₂ Supported on Cu(111): Results of a First Principles Study**, *D. Le*, *Takat B. Rawal*, *T.S. Rahman*, University of Central Florida

Despite being found to be the preferred structure in single layer MoS₂, the sulfur vacancy row does not facilitate alcohol synthesis from syngas [1] because its narrow size limits adsorption, diffusion, and formation of possible intermediates. On the Cu(111) surface, strong interactions between MoS₂ and Cu are expected to reduce the corrugations caused by sulfur vacancy rows, resulting in a larger exposure of vacancies to adsorbates which could enhance the catalytic activity of the row towards alcohol synthesis from syngas. Based on the results of our density functional theory (DFT) simulations utilizing the DFT-D3 correction for accounting the van der Waals interactions, we show that: (1) there is a significant charge transfer from the Cu(111) surface to MoS₂, enhancing its catalytic properties, (2) the binding energies of CO and dissociated H_2 increase by 0.3 eV in comparison to that on unsupported MoS₂, indicating stronger interactions, and (3) the barriers for forming intermediate species in alcohol synthesis process reduce significantly in comparison to that on unsupported MoS₂. On the basis of these energetics, we conclude the Cu(111) substrate promotes methanol synthesis from syn gas on single-layer MoS₂ with a vacancy row. We will also present the energetic pathways for the

formations of other reaction products such as methane, formaldehyde, and water, as well as that of (the reverse) water gas-shift reaction.

[1] D. Le, T. B. Rawal, and T. S. Rahman, *J. Phys. Chem. C* **118**, 5346 (2014).

11:20am **2D+EM+IS+NS+PS+SP+SS-FrM10 The Happy Marriage of Graphene and Germanium: Graphene Achieves Exceptional Conductivity and Protects Germanium from Oxidizing**, *Richard Rojas Delgado*, University of Wisconsin-Madison, *F. Cavallo*, University of New Mexico, *R.M. Jacobberger*, *J.R. Sanchez Perez*, *D. Schroeder*, *M.A. Eriksson*, *M.S. Arnold*, *M.G. Lagally*, University of Wisconsin-Madison

The properties of graphene (G) make it an outstanding candidate for electronic-device applications, especially those that require no band gap but a high conductance. The conductance, involving both carrier mobility and carrier concentration, will depend critically on the substrate to which G is transferred. We demonstrate an exceptionally high conductance for G transferred to Ge(001) and provide an understanding of the mechanism.[1] Essential in this understanding is an interfacial chemistry consisting of Ge oxide and suboxide layers that provide the necessary charges to dope the graphene sheet, and whose chemical behavior is such that one can obtain long-term stability in the conductance. In contrast, when high-quality G is grown directly on Ge (100), (111), or (110), the conductance is unexceptional, but oxidation of the surface is significantly delayed and slowed, relative to both clean Ge and Ge with G transferred to its surface . [2,3] We fabricate Hall bars in G transferred to Ge and G grown using atmospheric-pressure CVD with methane precursors . X-ray photoelectron spectroscopy (XPS) is used to investigate the oxide in all stages of the measurements. The sheet resistance and Hall effect are measured from 300K to 10K for transferred and grown samples. Values of mobility and carrier concentration are extracted. It appears we have reached the highest combination of mobility and carrier concentration in graphene (suspended or supported) for temperatures from 10 to 300K. The implication is that the primary mechanisms for scattering charge in the G, roughness and a non-uniform electrostatic potential due to fixed charges, have limited effect when the substrate is oxidized Ge. Finally the subsequent oxidation kinetics of Ge (001) are compared for graphene directly grown on Ge and for graphene transferred to Ge. XPS shows that for graphene grown on Ge(001) the interface is oxide-free and remains so over long periods of time. For graphene transferred to Ge(001) the interface contains stoichiometric and substoichiometric oxides. The thickness of these oxides increases with time, but quite slowly. Using spatially resolved XPS, we propose a model of diffusion limited oxidation initiated at edges of the graphene.

[1]Cavallo, Francesca, et al. "Exceptional Charge Transport Properties of Graphene on Germanium." *ACS nano* 8.10 (2014): 10237-10245.

[2] R. M. Jacobberger, et al. "*Oriented Bottom-Up Growth of Armchair Graphene Nanoribbons on Germanium.*" *Nature Comm.*, under review.

[3] R. Rojas, et. al "Passivation of Ge by Graphene.", in process.

Electronic Materials and Processing
Room: 211C - Session EM+AS+EN+NS-FrM

Nanoparticles for Electronics and Photonics
Moderator: Jessica Hilton, Mantis Deposition, Joseph G. Tischler, U.S. Naval Research Laboratory

8:20am **EM+AS+EN+NS-FrM1 Elimination of Bias-stress Effect in Ligand-free Quantum Dot Field-effect Transistors**, *Matt Law*, UC Irvine **INVITED**

Colloidal quantum dot (QD) solids are the subject of active research with applications emerging in light-emitting diodes, field-effect transistors, and solar cells. In this talk, I describe the use of atomic layer deposition (ALD) infilling to engineer the surfaces and interfaces of PbSe QD films in order to produce high-performance QD field-effect transistors (FETs) that completely lack bias-stress effect (i.e., drain current transients caused by charge trapping near the dielectric/channel interface). This ALD "matrix engineering" approach includes steps designed to manage ligand concentrations, passivate surface states, and arrest ionic motion within the films, resulting in the first high-mobility (~14 cm V^{-1} s^{-1}), environmentally stable, and transient-free PbX QD transistors. Two bias-stress mechanisms in QD FETs are identified and discussed. The implications of these mechanisms for the operation of QD solar cells is highlighted.

9:00am EM+AS+EN+NS-FrM3 Ultra High Sensitive CO Sensors with Less Overhead: Influence of Doping Methods and Dopants on the CO Sensitivity of Cu, Pt and Pd Doped SnO$_2$ Pellets, *Karthik Tangirala, M.A. Olvera*, CINVESTAV-IPN, Mexico

In this work, we report the synthesis, characterization and manufacturing of Cu, Pt and Pd doped SnO$_2$ pellets with ultra high sensitivities for CO atmospheres. To the best of our knowledge, we have accounted for the first time the ultra high CO sensitivities for Cu doped than Pt and Pd doped SnO$_2$ pellets. In order to obtain high sensitivities, we have employed novel methods, which are the mixture of chemical and physical synthesis methods. Non-spherical SnO$_2$ structures were prepared via two chemical synthesis routes using Urea (R1) and ammonia (R2) as precipitation agents. The resultant SnO$_2$ powders were doped with transition metal, Cu, and noble metals like Pt and Pd via two doping methods D1 and D2. In D1, the powders were bulk doped and then ball milled, whereas in D2, the powders were ball milled and then surface doped. All the powders obtained were later pressed using manual pressing machine to manufacture the SnO$_2$ pellets. The effect of synthesis routes, doping methods and dopants, on the structural, morphological and also on CO sensing were studied by different characterization techniques and reported with their detailed explanations. Interestingly, the Cu-SnO$_2$ pellets manufactured from the powders obtained by method D1R1, showed highest sensitivity around 1783 due to various reasons like uniform and small particle size, necks formation, inter-particle conductance and high oxygen adsorption due to stacking faults. All the reasons mentioned above were demonstrated by comparing the established sensor theory with our different experimental results obtained using XRD, Raman, SEM, HRTEM and sensitivity analysis.

9:20am EM+AS+EN+NS-FrM4 Selective Nucleation of Quantum Dots on Spontaneously Nanopatterned Surfaces, *Davide Del Gaudio, S. Huang, L. Aagesen, K. Thornton, R.S. Goldman*, University of Michigan, Ann Arbor

Controlled lateral ordering of self-assembled semiconductor quantum dots (QDs) is desirable for a wide range of solid-state applications, including solar cells, lasers, and telecom devices. To date, lateral alignment of QDs has been demonstrated for multilayers of QDs.[1]

In these cases, the first layer of QDs is isotropically distributed; subsequently, during the growth of QD stacks, the accumulation of anisotropic strain often results in lateral QD alignment. However, a significant remaining question concerns the *direct* influence of spontaneous surface patterning on the selective nucleation of QDs.

In this work, we use a combined experimental-computational approach to directly examine correlations between buffer surface morphology and QD nucleation. For this purpose, we exploit a surface instability induced by the anisotropy of the surface diffusion constant of ad-atoms (the Ehrlich-Schwöbel effect[2]) which leads to the formation of elongated ripples, often termed "mounds". For epitaxial growth of InAs QDs on GaAs, Ye et al. reported a preference for in-plane QD alignment along the mound lengths[1]. Here, our one-dimensional phase-field model reveals a preference for QD nucleation in regions of positive curvature,[3] such as on the sides of the mounds and/or in the "valleys" between the mounds. In our experiments, we explore the formation of InAs QDs on AlGaAs mounds using various substrate temperatures and indium exposure times.

We explore the use of fixed geometry indium evaporation as an approach to restrict QD nucleation to one side of the AlGaAs mounds, resulting in the formation of 1D QD chains.[4] Specifically, for substrate temperature of 580°C, a high density of AlGaAs mounds is observed along [0-11]. For 3 monolayer (ML) of InAs deposition, we achieved selective positioning of QDs, with an average diameter of 16nm, on one side of the mounds.

We will discuss the influence of the As species (As2 vs As4) and growth interrupts on the size, density, and spatial arrangement of QDs. We will also present a detailed analysis of the surface instabilities that induce ripple formation, and the As adsorption kinetics, which lead to the anisotropic nucleation.

References

[1] W. Ye, S. Hanson, M. Reason, X. Weng, and R. S. Goldman. (2005). *J. Vac. Sci. Technol.* B **23**, 1736-1740.

[2] Schwöbel, R. L., & Shipsey, E. J. (1966). *J. App. Phys.*, **37**(10), 3682–3686.

[3] Seol, D. J., Hu, S. Y., Liu, Z. K., Chen, L. Q., Kim, S. G., & Oh, K. H. (2005) *J. Appl. Phys.*, **98**(4), 044910.

[4] Arciprete, F., Placidi, E., Magri, R., Del Gaudio, D., Patella, F. (2013) *J. Mat. Res.* **28**(23), 3201–3209

9:40am EM+AS+EN+NS-FrM5 Tailor-made Gas Phase based Nanoparticles with Functional Properties, *Gert ten Brink, B. Kooi, G. Palasantzas*, University of Groningen, The Netherlands **INVITED**

Using a home modified Mantis dedicated nanocluster© source we have the possibility to produce nanoparticles (NPs) of a great variety of materials with relatively small size dispersion and with properties that can be novel and different from their bulk counterpart. The system works on the principle of inert gas condensation and magnetron sputtering. We have produced a whole range of different NPs with size and motif control.

Covalent bonded NPs, in particular carbon;

Metallic NPs: Cu[1], Fe, Mg, Mo, Co, Al, Ag, Nb, Ti, Pd;

Semiconductor NPs, in particular Ge;

Bimetallic NPs: MgNi, MoCu, MgTi with several compositions;

Ternary alloy NPs, e.g. GeSbTe with several compositions and with amorphous and crystallinity control.

The particles can be deposited on most surfaces provided they have good vacuum compatibility.

The applications range from novel:

Wetting phenomena; Cu NPs covered surfaces giving rose petal effect[2];

Bimetallic Mo-Cu NPs which are bulk immiscible but in NPs fully miscible[3];

Bimetallic NPs for hydrogen storage[4]: MgNi, MgTi, MgCu;

Magnetic NPs: Fe-Fe$_3$O$_4$ core-shell particles for medical applications.

1. Brink, G. H. ten, Krishnan, G., Kooi, B. J. & Palasantzas, G. Copper nanoparticle formation in a reducing gas environment. *J. Appl. Phys.* **116**, 104302 (2014).

2. Ten Brink, G. H., Foley, N., Zwaan, D., Kooi, B. J. & Palasantzas, G. Roughness controlled superhydrophobicity on single nanometer length scale with metal nanoparticles. *RSC Adv.* **5**, 28696–28702 (2015).

3. G. Krishnan, M.A. Verheijen, G.H. ten Brink, G. Palasantzas, B.J. Kooi, Tuning structural motifs and alloying of bulk immiscible Mo-Cu bimetallic nanoparticles by gas-phase synthesis, *Nanoscale* **5**, 5375-5383 (2013).

4. Krishnan, G. *et al.* Synthesis and exceptional thermal stability of Mg-based bimetallic nanoparticles during hydrogenation. *Nanoscale* **6**, 11963-11970 (2014).

10:20am EM+AS+EN+NS-FrM7 A New Surfactant for Directed Deposition of Carbon Nanomaterials, *Hanna Nilsson*, University of Maryland, *L. de Knoop*, Chalmers University, *J. Ticey, B. Meany, Y. Wang*, University of Maryland, *E. Olsson*, Chalmers University, *J. Cumings*, University of Maryland

We show the results of using a new surfactant, ammonium laurate (AL), to suspend and deposit carbon nanostructures. In a recent publication[1], we show that multi-walled carbon nanotubes (MWCNTs) can be suspended in AL with much better shelf stability as compared with the common surfactant sodium dodecyl sulfate (SDS). AL differs from SDS only by the choice of ionic species, but the deposition process with AL is more reliable and cleaner than with SDS. We use a process of producing a charged self-assembled monolayer on the substrate and then exposing the substrates to the aqueous surfactant solution of MWCNTs to achieve directed deposition of clean individual MWCNTs, which can then be used for fabrication of individual nanotube devices. In addition to these results, we show results for single-walled carbon nanotubes (SWCNTs) in AL, which show that nanotubes deposited from AL have lower electrical contact resistance as compared to those deposited from SDS. Photoluminescence results also show that SWCNTs with specific chirality are preferentially suspended in AL, which may present a separation and purification pathway. We will also present extensions of the work to single and few layer graphene sheets, where AL can be used to make clean depositions from aqueous solution onto sensitive substrates.

(1) Nilsson, H. M.; Meany, B.; Ticey, J.; Sun, C.-F.; Wang, Y.; Cumings, J. Ammonium Laurate Surfactant for Cleaner Deposition of Carbon Nanotubes. *Langmuir* **2015**, *31*, 6948-6955.

10:40am EM+AS+EN+NS-FrM8 Compositional Control and Doping Uniformity in Spray Pyrolyzed CZTS Nanoparticles and Films, *Stephen Exarhos, A. Alvarez, J. Hernandez, L. Mangolini*, University of California - Riverside

An innovative and scalable synthesis approach to the formation of stoichiometric Cu$_2$ZnSnS$_4$ (CZTS) nanocrystals has been developed using aerosol spray pyrolysis. This quaternary phase material is a potential replacement for currently commercialized semiconductors such as CdTe and CIGS that are used in photovoltaic devices. However, sustainability and environmental issues threaten long-term viability of these materials. Based upon earth abundant constituents and low chemical toxicity, CZTS, with a

reported bandgap of ~1.5 eV[1], appears to be a superior alternative to these other materials. Additional research and development is necessary to increase the efficiency of CZTS-based cells from the current record (12.6% by Wang *et al.*[2]) to the >18% necessary to be considered commercially viable. Our work demonstrates the controllable, cost-effective, and reproducible synthesis of high-quality CZTS nanoparticles and films. A modified spray pyrolysis method involving decomposition of copper, zinc, and tin diethyldithiocarbamate precursors allows uniform incorporation of dopants (such as sodium) that are known to increase crystal grain growth during nanoparticle sintering[3]. Once formed, the nanoparticles are deposited onto a substrate from a methanol dispersion using an "ink-spray" process with an argon-driven airbrush. To form an efficient absorber layer in a photovoltaic device, the coating is then annealed in a sulfur-vapor atmosphere resulting in a thin film with uniformly large crystal grain morphology throughout the film thickness (~1-2 μm). The deposited films are characterized with respect to crystalline phase, stoichiometry, and overall film quality. Further preliminary results regarding the formation of $Cu_2ZnSn_{(1-x)}(IV)_xS_4$ by means of this processing approach will be reported.

[1] H. Wang. "Progress in Thin Film Solar Cells Based on Cu_2ZnSnS_4," International Journal of Photoenergy 2011 (2011).

[2] Wang, Wei, Mark T. Winkler, *et al.* "Device Characteristics of CZTSSe Thin-Film Solar Cells with 12.6% Efficiency." Advanced Energy Materials 4, no. 7 (2014).

[3] Johnson, M., S. V. Baryshev, *et al.* "Alkali-Metal-Enhanced Grain Growth in Cu2ZnSnS4 Thin Films." Energy & Environmental Science 7, no. 6 (2014): 1931–38.

Scanning Probe Microscopy Focus Topic
Room: 212A - Session SP+AS+MI+NS+SS-FrM

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

8:20am **SP+AS+MI+NS+SS-FrM1 Direct Visualization of Magnetoelectric Domains in Hexagonal Manganites**, *Weida Wu*, Rutgers University **INVITED**
Multiferroics are materials with coexisting magnetic and ferroelectric orders, where the cross-coupling between two ferroic orders can result in strong magnetoelectriceffects [1-4]. Therefore, it is of both fundamental and technological interest to visualize cross-coupled magnetoelectric domains and domain walls in multiferroics. Recently, intriguing topological defects with six interlocked structural antiphase and ferroelectric domains merging into a vortex core were revealed in multiferroic hexagonal REMnO$_3$ (R=rare earths) [5, 6]. Many emergent phenomena, such as enhanced conduction and unusual piezoelectric response, were observed in charged ferroelectric domain walls protected by these topological defects [7-9]. More interestingly, alternating uncompensated magnetic moments were discovered at coupled structural antiphase and ferroelectric domain walls in hexagonal manganites using cryogenic magnetic force microscopy (MFM) [10], which demonstrates the cross-coupling between ferroelectric and magnetic orders. Here we present the application of a magnetoelectric force microscopy (MeFM) technique that combines MFM with *in situ* modulating high electric fields. This new microscopy technique allows us to image the magnetoelectric response of the domain patterns in hexagonal manganites directly [11, 12]. We find that this response changes sign at each structural domain wall, a result that is corroborated by symmetry analysis and phenomenological modelling , and provides compelling evidence for a lattice-mediated magnetoelectric coupling. The direct visualization of magnetoelectric domains at mesoscopic scales opens up explorations of emergent phenomena in multifunctional materials with multiple coupled orders.

References

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[3] S-W. Cheong, and M. Mostovoy, Nat. Mater. 6, 13 (2007).

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[5] T. Choi et al., Nature Materials 9, 253 (2010).

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[8] D. Meier et al., Nat. Mater. 11, 284 (2012).

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[10] Y. Geng et al., Nano Letters 12, 6055?6059 (2012).

[11] Y. Geng, and W. Wu, Rev. Sci. Instrum. 85, 053901 (2014).

[12] Y. Geng et al., Nat. Mater. 13, 163 (2014).

9:00am **SP+AS+MI+NS+SS-FrM3 Kelvin Probe Force Microscopy Studies of Magnetic Atoms on Ultrathin Insulating MgO Film**, *Taeyoung Choi*, W. Paul, S. Baumann, C.P. Lutz, A. Heinrich, IBM Almaden Research Center
The interplay of single atoms and their local environment on surfaces influences the atoms' spin excitations and dynamics, which can be utilized in progress toward atomic-scale memory and quantum information processing. We find that spin-excitation energy of Fe atoms on an insulating MgO film shifts depending on the tip-to-atom separation. This may be attributed to the electric field across the tunneling junction, as well as to local charge and structural changes around the atom. The Kelvin Probe Force Microscopy (KPFM) has been very useful tool to measure changes of local contact potential differences between a tip and a sample at the atomic level [1]. In this talk, we employ tuning fork KPFM/STM and show preliminary results on the charge character and spin excitations of Fe atoms.

This work is supported by grants from IBM.

[1] Leo Gross et al., Phys. Rev. B **90**, 155455 (2014).

9:20am **SP+AS+MI+NS+SS-FrM4 Nanoscale Schottky Barrier Height Mapping Utilizing Ballistic Electron Emission Microscopy**, C. Durcan, W. Nolting, College of Nanoscale Science and Engineering, *Vincent LaBella*, SUNY Polytechnic Institute
The Schottky barrier is the electrostatic barrier between a metal and a semiconductor that results in rectification and is found in many types of devices such as source drain contacts to sub 20-nm-node transistors. Naturally, the Schottky barrier height can fluctuate across the interface due to variations in bonding, compositional fluctuations in the materials, and the presence of defects. However measuring and mapping these electrostatic fluctuations is impossible with bulk IV or CV techniques. This presentation will demonstrate how the Schottky barrier height can be mapped to nanoscale dimensions using an STM based technique called ballistic electron emission microscopy (BEEM). The STM tip is positioned on a regularly spaced grid and BEEM spectra are acquired from which the barrier height can be extracted. A map and histogram is then generated by measuring and fitting thousands of these spectra. These maps provide detailed insight into the electrostatic fluctuations occurring at the buried interface with nanoscale resolution that cannot be accomplished with other bulk measurements.

9:40am **SP+AS+MI+NS+SS-FrM5 Electron Transport Studies of Metal Films Utilizing Ballistic Electron Emission Microscopy**, *Christopher Durcan*, SUNY College of Nanoscale Science and Engineering, V. LaBella, SUNY Polytechnic Institute
Understanding scattering of electrons in nanometer thick metal films is of fundamental and technological importance. One method to study electron scattering is with ballistic electron emission microscopy (BEEM), which is a three terminal STM based technique that measures both scattering through a metal film and the Schottky barrier height for metal-semiconductor junctions with both nanometer spatial resolution and meV energy resolution. This presentation will describe our work at understanding the relationship between the metal resistivity and the electron scattering lengths measured with BEEM by exploring metals with a range of resistivities from Ag (1.7 μΩ-cm) to Cr (12.6 μΩ-cm). In addition, nanoscale mapping of the Schottky barrier height of these metals to silicon will also be presented to understand the spatial uniformity of the transport.

10:00am **SP+AS+MI+NS+SS-FrM6 Utilizing Ballistic Electron Emission Microscopy to Study Sidewall Scattering of Electrons**, *Westly Nolting*, C. Durcan, R. Balsano, College of Nanoscale Science and Engineering, University of Albany, *V. LaBella*, College of Nanoscale Science and Engineering, SUNY Polytechnic Institute
Sidewall scattering of electrons within aggressively scaled metallic interconnects increases the resistance since the mean free path (~40 nm) is larger than the dimensions of the material. One method to study hot-electron scattering in nm-thick metallic films is Ballistic Electron Emission Microscopy (BEEM), which is an STM based technique. In this work, we perform BEEM scattering measurements on lithographically patterned fin structures with a Schottky diode interface to determine its ability to measure sidewall scattering. This is accomplished by acquiring BEEM spectra on a regularly spaced grid and fitting the results to determine both the Schottky barrier height and the slope of the spectra. The slope of the spectra is related to the scattering in the film and interface. The position of fin structures are then determined by mapping both the Schottky height and slope over a square micron to observe scattering at the interface caused by the patterned structures. The poster will discuss the fabrication of the patterned 50-nm-

pitched sidewall structures that are used for mapping the sidewall scattering. In addition, it will present the preliminary BEEM measurements on these structures.

10:20am SP+AS+MI+NS+SS-FrM7 Progress in Nanoscale Magnetic Resonance Imaging, *Daniel Rugar*, IBM Research Division **INVITED** Nuclear magnetic resonance (NMR) is the basis of powerful spectroscopic and imaging techniques, but extension to nanoscale samples has been a longstanding challenge due to the insensitivity of conventional detection methods. We are exploring the use of individual, near-surface nitrogen-vacancy (NV) centers in diamond as atomic-size magnetometers to detect proton NMR in organic material located external to the diamond. Using a combination of electron spin echoes and proton spin manipulation, the NV center senses the nanotesla field fluctuations from the protons, enabling both time-domain and spectroscopic NMR measurements on the nanometer scale. By scanning a small polymer test object past a near-surface NV center, we have recently demonstrated proton magnetic resonance imaging (MRI) with spatial resolution on the order of 10 nm.

One key issue in NV-NMR experiments is the loss of spin coherence when the NV center is located near the diamond surface. Although this loss of coherence is frequently attributed to the effect of magnetic noise emanating from unpaired spins on the diamond surface, we will show evidence that electric field noise from fluctuating surface charge may be the dominant factor.

Work performed in collaboration with M. Kim, H. J. Mamin, M. H. Sherwood, C. T. Rettner, K. Ohno, and D. D. Awschalom

11:00am SP+AS+MI+NS+SS-FrM9 Reactive Intermediates Created and Analyzed by Scanning Probe Microscopy, *Bruno Schuler*, IBM Research - Zurich, Switzerland, *N. Pavliček*, IBM Research - Zurich, *S. Collazos*, CIQUS, Universidade de Santiago de Compostela, *N. Moll, S. Fatayer*, IBM Research - Zurich, *D. Pérez, E. Guitán*, CIQUS, Universidade de Santiago de Compostela, *G. Meyer*, IBM Research - Zurich, *D. Peña*, CIQUS, Universidade de Santiago de Compostela, *L. Gross*, IBM Research - Zurich
Reactive intermediates are involved in most chemical transformations. However, their characterization is a great challenge because of their short lifetime and high reactivity.

Here we report on the creation of single radicals and diradicals on a thin insulating surface by means of atomic manipulation. Importantly, the thin insulating film facilitates the stabilization of these reactive intermediates at cryogenic temperatures. The molecules were characterized by atomic-resolution atomic force microscopy (AFM) imaging with a CO functionalized tip [1] and scanning tunneling microscopy (STM) orbital imaging [2]. We show that the molecules' reactivity is preserved even at low temperatures by performing different on-surface reactions by atomic manipulation. As an example, the generation of aryne is discussed, a very reactive intermediate caught for the first time [3].

References:

[1] L. Gross et al. Science **325**, 1110 (2009)

[2] J. Repp et al. Phys. Rev. Lett. **94**, 026803 (2005)

[3] N. Pavliček et al. On-surface generation and imaging of arynes by atomic force microscopy. (submitted)

11:20am SP+AS+MI+NS+SS-FrM10 The Negative Stiffness and Positive Damping of Squeezed Air in Dynamic Atomic Force Microscopy, *x. Yu, M. Tao*, *Nancy Burnham*, Worcester Polytechnic Institute
By oscillating a micro-sized cantilever beam at a certain frequency and observing its interaction with the sample surface, dynamic mode atomic force microscopy (AFM) has gained attention for characterizing mechanical properties of a variety of materials at the micro and nano scales. The thin air film, confined between the oscillating cantilever beam and the stationary sample surface, causes the so-called "squeeze-film effect" when the gap between the two boundaries is less than a hundred microns. Although studies have shown that the squeeze film can act as a spring and a damper in accelerometers and microelecromechanical systems [1], the influence of the squeeze-film effect on the dynamics of an AFM cantilever has not been previously explored, to the authors' knowledge. In this project, the stiffness and damping properties of the squeeze film between an oscillating AFM cantilever and a glass slide were calculated from the cantilevers' amplitude and phase responses as recorded by the AFM digital system. The smaller the cantilever-sample gap, the larger the absolute values of the stiffness and the damping of the squeeze film. Results from different cantilevers (consequently having different spring constants and resonant frequencies) indicated that the air film exhibited **negative stiffness and positive damping**, with normalized changes from free values of up to 40%.

Theoretical analysis was conducted using an equivalent-circuit model [2] along with the phasor diagram, and the derived stiffness and damping values were in excellent agreement with the experimental ones. Interestingly, a rotation angle between 20° and 30° in the fit of the data to the model reveals a phase *lead* of the squeeze-film damping before the usual air damping when the cantilever is far from a surface: the maximum squeeze-film damping occurs before the maximum velocity of the cantilever because air becomes less dense as it rushes out of the tip-sample gap. The surprising sign of the stiffness is thus explained by the phase lead. Future work includes incorporating the squeeze-film effect into more accurate measurements of a material's stiffness and damping properties using dynamic AFM.

References:

1. Starr, James B. "Squeeze-film damping in solid-state accelerometers." *Solid-State Sensor and Actuator Workshop, 1990. 4th Technical Digest., IEEE.* IEEE, 1990.

2. Veijola, Timo. "Compact models for squeezed-film dampers with inertial and rarefied gas effects." *Journal of Micromechanics and Microengineering* 14.7 (2004): 1109.

Tribology Focus Topic
Room: 230B - Session TR+AS+BI+NS-FrM

Nanoscale Wear and Biotribology
Moderator: J. David Schall, Oakland University

8:20am TR+AS+BI+NS-FrM1 2D or not 2D? The Impact of Nanoscale Roughness and Substrate Interactions on the Tribological Properties of Graphene, *James Batteas*, Texas A&M University **INVITED** Control of friction and wear is a ubiquitous challenge in numerous machined interfaced ranging from biomedical implants, to engines, to nano- and micro-scaled electromechanical systems (MEMS) devices. While lubricant additives are one approach to the development of surface coatings that can impede wear and reduce friction, in some cases, such approaches are simply not amenable and the development of ultrathin films are required. Recently, the robust mechanical properties of graphene has made it a material of interest as a means of modifying surface frictional properties. While graphene can readily adapt to surface structure on the atomic scale, when deposited on substrates with nanoscopic roughness (~ 10 – 20 nm rms as is common in many machined interfaces) a conformal coating cannot be fully formed due to competition between adhesion to substrate nanoscopic asperities and the bending strain of the graphene. This often leaves a mixture of supported and unsupported regions which respond differently to applied load and shear strain. Here we describe a combination of AFM nanomechanical and confocal Raman microspectroscopy studies of graphene on silica surfaces with controlled nanoscopic roughness to examine the how this impacts the frictional properties of graphene. Composite interfaces where graphene is supported on self-assembled alkylsilane monolayers will also be described along with the synergistic influence of such mixed interfaces on the frictional properties of the surface.

9:00am TR+AS+BI+NS-FrM3 Atomic–Scale Wear and Wear Reduction Mechanisms Elucidated by *In Situ* Approaches, *R.W. Carpick*, University of Pennsylvania, *Tevis Jacobs*, University of Pittsburgh **INVITED** As technologies shrink to nanometer length scales, tribological interactions play an increasingly dominant role. A lack of fundamental insight into the origin of friction and wear at the nanoscale hinders the advancement of such technologies. Furthermore, macroscopic tribological applications often involve contact between nanostructured materials or at nanoscale asperities, due to surface roughness. Observing and understanding the nanoscale mechanisms at play is inhibited by the hidden nature of the buried interface and the challenge of performing observations at the nanometer scale. Recent advances in *in situ* methods are enabling tribological mechanisms at previously inaccessible interfaces to be studied with unprecedented resolution and sensitivity. We will discuss the application of two *in situ* experimental methods to develop new physical insights into tribological processes. The first approach addresses contact and wear phenomena at the atomic scale by *in situ* sliding in a transmission electron microscope [1], and the second addresses the generation of tribofilms from anti-wear additives using atomic force microscopy while immersed in additive-infused oil [2].

References:

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[2] Gosvami, N.N., Bares, J. A., Mangolini, F., Konicek, A.R., Yablon D.G., and R. W. Carpick. "Mechanisms of Antiwear Tribofilm Growth Revealed In Situ by Single Asperity Sliding Contacts," Science, 348, 2015, 102-106.

9:40am **TR+AS+BI+NS-FrM5** **Influence of Polysaccharide Conformation on Friction and Adhesion**, *Rowena Crockett*, Empa, Switzerland **INVITED**
The friction behavior of the polysaccharide dextran has been investigated on surfaces coated with PLL-dextran brushes as well as randomly orientated covalently attached chains in aqueous solution. It was found that while there was a strong dependence of friction on load for the dextran brushes, the randomly orientated chains showed a more constant friction coefficient. Polysaccharides play an important role in bioadhesion, but are also used in the mining industry to assist in the separation of minerals. Despite the high adhesion associated with polysaccharides, investigations showing that they can be used to achieve low friction have also been reported. It was proposed that this transition from low friction to high adhesion is achieved as a result of hydrogen bonding. That is, as the load increases, water is forced out of the contact and the number of hydrogen bonds between the polysaccharide and surface increase, inducing a transition to high adhesion.

10:20am **TR+AS+BI+NS-FrM7 Tribological Rehydration of Cartilage: A New Insight into an Old Problem**, *David Burris*, *A.C. Moore*, University of Delaware **INVITED**
The bulk of cartilage lubricity is due to its multi-phasic structure and the pressurization of interstitial fluid during loading. Unfortunately, the same pressure gradients that support load and lubricate the contact also drive fluid from the tissue over time. This observation led McCutchen, the researcher responsible for the discovery of this unusual lubrication mechanism, to ponder how the joint prevented the loss of interstitial fluid over time. He proposed that articulation intermittently exposes the loaded zone to the bath, thus allowing the tissue to imbibe fluid. It wasn't until 2008 that Caligaris and Ateshian showed that interstitial pressure can be maintained if the contact migrates across cartilage more quickly than the diffusive speed of fluid in the tissue; because the joint involves a migrating contact, they proposed that this discovery resolved any uncertainty about how the joint maintains lubrication. However, joints spend only a fraction of the day articulating and the majority of the day exuding fluid in static compression. If the migrating contact simply prevents the loss of fluid by moving quicker than the fluid can respond, we contend that it cannot explain long-term maintenance of interstitial fluid in the joint; there must be an active uptake mechanism in which articulation drives fluid back into the cartilage surface at a rate that outpaces exudation. This paper explores the origins of this mechanism and in doing so uncovers several phenomena that cannot be explained by existing theory. Contrary to existing theory, we show that stationary contacts are able to sustain fluid pressures in a manner similar to the migrating contact. Furthermore, we demonstrate active recovery of interstitial fluid in a stationary contact without exposing the loaded zone to the bath. The results demonstrate that sliding alone, even at sub-physiological speeds, forces fluid back into the cartilage at rates that outpace exudation rates. The results suggest that interstitial or weeping lubrication is the primary lubrication mechanism in the joint and that hydrodynamic effects prevent the loss of this mechanism in the long-term.

11:00am **TR+AS+BI+NS-FrM9 Biomimetic Aspects of Lubrication with Polymer Brushes and Gels**, *C. Mathis, L. Isa, Nicholas Spencer*, ETH Zürich, Switzerland
The role of the solvent is crucial in lubrication with polymer brushes and gels. Firstly it is important in maintaining the structure of the brush or gel layer in an unloaded state. Under loading, however, a new phenomenon becomes crucial, namely the Darcy flow of the solvent through the porous system. This aspect brings in a new set of properties to consider: the viscosity of the solvent determines the rate at which the solvent is forced through the porous network, and the sliding speed determines the extent to which the solvent is expelled from beneath the contact. The very act of expulsion of solvent is actually a process that bears a portion of the load. This phenomenon is well known in cartilage, and has been dubbed "fluid load support". This presentation will illustrate the ways in which this biomimetic approach can be utilized to protect polymer brushes and gels from wear, thus increasing their attractiveness as applicable lubricating systems, and will describe the approaches that can be used to quantify the process.

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